Reports of China's Basic Research

Bingheng Lu *Editor*

Fundamental Research on Nanomanufacturing

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Reports of China's Basic Research

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Featuring science, basics, and advances, the series of *Reports of China's Basic Research* is organized by the NSFC to present the overall level and pattern of China's basic research, share innovative achievements, and illustrate excellent breakthroughs in key fields. It covers various disciplines including but not limited to, computer science, materials science, life sciences, engineering, environmental sciences, mathematics, and physics. The series will show the core contents of the final reports of the Major Programs and the Major Research Plans funded by NSFC, and will closely follow the frontiers of basic research developments in China.

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Editor

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Preface to the Series

As Lao Tzu said, “A huge tree grows from a tiny seedling; a nine-storied tower rises from a heap of earth.” Basic research is the fundamental approach to fostering innovation-driven development, and its level becomes an important yardstick for measuring the overall scientific and national strength of a country. Since the beginning of the twenty-first century, China’s overall strength in basic research has been consistently increasing. With respect to input and output, China’s input in basic research increased by 14.8 times from 5.22 billion yuan in 2001 to 82.29 billion yuan in 2016, with an average annual increase of 20.2%. In the same period, the number of China’s scientific papers included in the Science Citation Index (SCI) increased from lower than 40,000 to 324,000; China rose from the 6th to the 2nd place in global ranking in terms of the number of published papers. In regard to the quality of output, in 2016, China ranked No. 2 in the world in terms of citations in 9 disciplines, among which the materials science ranked No. 1; as of October 2017, China ranked No. 3 in the world in the numbers of both Highly Cited Papers (top 1%) and Hot Papers (top 0.1%), with the latter accounting for 25.1% of the global total. In talent cultivation, in 2006, China had 175 scientists (136 of whom from the Chinese mainland) included in Thomson Reuters’ list of Highly Cited Researchers, ranking 4th globally and 1st in Asia.

Meanwhile, we should also be keenly aware that China’s basic research is still facing great challenges. First, funding for basic research in China is still far less than that in developed countries—only about 5% of the R&D funds in China are used for basic research, a much lower percentage than 15%–20% in developed countries. Second, competence for original innovation in China is insufficient. Major original scientific achievements that have global impact are still rare. Most of the scientific research projects are just a follow-up or imitation of existing research, rather than groundbreaking research. Third, the development of disciplines is not balanced, and China’s research level in some disciplines is noticeably lower than the international level—China’s Field-Weighted Citation Impact (FWCI) in disciplines just reached 0.94 in 2016, lower than the world average of 1.0.

The Chinese government attaches great importance to basic research. In the 13th Five-Year Plan (2016–2020), China has established scientific and technological innovation as a priority in all-round innovation and has made strategic arrangements to strengthen basic research. General Secretary XI Jinping put forward a grand blueprint of making China into a world-leading power in science and technology in his speech delivered at the National Conference on Scientific and Technological Innovation in 2016, and emphasized that "we should aim for the frontiers of science and technology, strengthen basic research, and make major breakthroughs in pioneering basic research and groundbreaking and original innovations" at the 19th CPC National Congress on Oct. 18, 2017. With more than 30 years of unremitting exploration, the National Natural Science Foundation of China (NSFC), one of the main channels for supporting basic research in China, has gradually shaped a funding pattern covering research, talent, tools and convergence, and has taken action to vigorously promote basic frontier research and the growth of scientific research talent, reinforce the building of innovative research teams, deepen regional cooperation and exchanges, and push forward multidisciplinary convergence. As of 2016, nearly 70% of China's published scientific papers were funded by the NSFC, accounting for 1/9 of the total number of published papers all over the world. Facing the new strategic target of building China into a strong country in science and technology, the NSFC will conscientiously reinforce forward-looking planning and enhance the efficiency of evaluation, so as to achieve the strategic goal of making China progressively share the same level with major innovative countries in research total volume, contribution and ground-breaking researchers by 2050.

The series of *Advances in China's Basic Research* and the series of *Reports of China's Basic Research* proposed and planned by the NSFC emerge against such a background. Featuring science, basics and advances, the two series are aimed at sharing innovative achievements, diffusing performances of basic research, and leading breakthroughs in key fields. They closely follow the frontiers of basic research developments in China and publish excellent innovation achievements funded by the NSFC. The series of *Advances in China's Basic Research* mainly presents the important original achievements of the programs funded by the NSFC and demonstrates the breakthroughs and forward guidance in key research fields; the series of *Reports of China's Basic Research* shows the core contents of the final reports of Major Programs and Major Research Plans funded by the NSFC to make a systematic summarization and give a strategic outlook on the achievements in the funding priorities of the NSFC. We hope not only to comprehensively and systematically introduce backgrounds, scientific significance, discipline layouts, frontier breakthroughs of the programs, and a strategic outlook for the subsequent research, but also to summarize innovative ideas, enhance multidisciplinary convergence, foster the continuous develop of research in concerned fields, and promote original discoveries.

As Hsun Tzu remarked, "When earth piles up into a mountain, wind and rain will originate thereof. When waters accumulate into a deep pool, dragons will come to live in it." The series of *Advances in China's Basic Research* and *Reports of China's*

Basic Research are expected to become the "historical records" of China's basic research. They will provide researchers with abundant scientific research material and vitality of innovation, and will certainly play an active role in making China's basic research prosper and building China's strength in science and technology.

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Preface

Nowadays, the world sees the rapid advancement of science and technology and fierce competition for cutting-edge technologies. Only those who are the leaders of scientific and technological development and innovation can be at the forefront of the world economic tide. As an important pillar of national economic development, the manufacturing industry is the "heavy weapon of the country" to realize upgrading and development. On the one hand, for the deep space exploration at the interstellar light-year scale, such as more mature Earth observation satellites, manned spacecraft, space stations, new concept solar sails, micro-nano satellites, satellite detectors, we rely on large-scale nanoprecision manufacturing technology to provide important support for human exploration and understanding of the nature of the universe; on the other hand, for the deconstruction and reconstruction of molecular and atomic scales, such as biomolecular motors, nano-motors, nano-robots, molecular photoelectric devices, nano-circuits, nanosensors, nano- intelligent devices and systems, the construction of materials, structures, devices and systems is realized by means of manufacturing technologies based on the atomic scales, such as adding materials, reducing materials or other materials, which provides an important foundation for human beings to explore the essence of life and matter. Therefore, whether it is for large-scale nanoprecision (ultra- precision) manufacturing, it is also nanoscale manufacturing as small as atoms. The development of new methods and technologies for nanomanufacturing is of great significance to many fields such as information, materials, environment, energy, biomedicine, aerospace and national defense security. It is an important guarantee for the country's future strategic layout, the development of emerging industries, and the adjustment and upgrading of economic structure.

The development of nanomanufacturing processes and technology has enabled manufacturing objects to move from macroscope to microscope and nanoscope, which not only greatly improves the manufacturing accuracy and quality, but also greatly broadens the scale range of manufacturing technology. The application of nanotechnology to obtaining the discovery and research results of micro/nanoview will help to achieve batch and consistent manufacturing of micro- nano-products, thus enriching material products and greatly saving materials and energy. The research of nanomanufacturing will promote interdisciplinary, develop new manufacturing theories and methods, so as to enrich and deepen the research of manufacturing science. In order to enhance the source innovation capability of nanomanufacturing in China, the National Natural Science Foundation of China (NSFC) officially launched the Major Research Plan "Fundamental Research on Nanomanufacturing" in 2010. Aiming at the cutting-edge development of nanomanufacturing, oriented to address major national needs, and focusing on manufacturing methods based on physical/chemical/biological principles, we are committed to researching nanostructure growth, processing, modification, assembly and other new nanomanufacturing methods and new processes, as well as the structure and structure in the nanoscale manufacturing process. We have found the performance evolution law of structures and devices in the process of nanoscale manufacturing, so as to form the original new principles and methods of nanomanufacturing and improve the level of nanomanufacturing in China. And all those efforts are made to solve the bottleneck and "neck sticking" problem of manufacturing technology in China.

This Major Research Plan follows the overall idea of "limited goal, stable support, integrated sublimation and leapfrog development," focuses on the major strategic needs of national economy, social development and scientific frontier, and combines the top-level design guidance of experts with the free application of scientific and technical personnel to gather superior strength so as to form a project group with relatively unified objectives or directions. Through the relatively stable and certain intensity of support, it actively promotes interdisciplinary development, trains innovative talents, and realizes leapfrog development in several key areas or important directions, thereby enhancing China's fundamental research innovation capability and providing scientific support for national economic and social development.

During the implementation of the Major Research Plan of "Fundamental Research on Nanomanufacturing," 153 projects (including 4 integration projects, 24 key support projects, 121 cultivation projects and 4 strategic research projects) were funded through expert communication review and conference review. The funded projects focus on 5 directions including nanostructure manufacturing based on physical/chemical/biological principles, nanoprecision manufacturing of macrostructures, integrated manufacturing of macroscale, microsacale and nanoscale structures and devices, evaluation and measurement of nanomanufacturing precision, and equipment and platform technology of nanomanufacturing. The intersection of manufacturing science with mathematics, chemistry, information, biology and other disciplines in this Major Research Plan highlights the "manufacturing" attribute, that is, how to ensure the batch and consistency of nanomanufacturing. This Plan focuses on funding nanoscale manufacturing, nanoprecision manufacturing, cross-scale manufacturing, equipment manufacturing, device manufacturing, characterization and measurement and other fields. This book collects some research results obtained from funded projects; among them, there are quite a large number of outstanding papers by young and middle-aged scientific and technological workers in China, which shows that China's nanomanufacturing program has cultivated a strong research team with quite high research level, which is the most outstanding achievement of this Major Research Plan.

After 8 years of concerted efforts and struggle, the NSFC reviewed and approved the conclusion of the Major Research Plan “Fundamental Research on Nanomanufacturing” on December 13, 2018. Through interdisciplinary cross- disciplinary research, the participants of the plan explored new principles and methods of nanofabrication based on physical/chemical effects, revealed surface/ interface effects and scale effects in processing, forming, modification and cross-scale manufacturing on nanometer scale and with nano precision, and clarified the evolution mechanism of material structure. Meanwhile, the precise characterization and measurement method of nanomanufacturing process is established, and a number of original nanomanufacturing processes and equipment are developed, especially the chemical mechanical removal mechanism at atomic level is revealed, and a new method for realizing electronic material processing with atomic precision is created in this project; meanwhile, a new principle of nanostructure forming based on electron/charge dynamic regulation is proposed, and the manufacturing scale extends to atomic level. A series of methods and technologies for cross-scale batch manufacturing have been developed and applied in some industrial fields; a relatively perfect nanomanufacturing method and process system has been established, such as chemical mechanical polishing, electric field forceinduced nanoimprint, electron beam control hole processing, cross-scale device manufacturing, forming independent equipment and breaking international monopoly in several fields. The project achievements serve major national science/projects such as lens polishing of lithography machine, manufacturing of target ball micropore array, meter-level two-dimensional metrological grating for high-end equipment, and multi-level micro-nano structure skin on the surface of space vehicles, providing a theoretical basis for the improvement of China’s nanomanufacturing technology and equipment level at source.

In the past 8 years, from project establishment and implementation to final results conciseness and summary, thanks go to the members of the guiding expert group, the comrades of the NSFC and the young and middle-aged researchers in related fields in China for their strong support. Intending to grasp the frontier direction, focusing on research content, optimizing research objectives and strengthening the conciseness of results, each research group focuses on the established requirements of Major Research Plan and makes efforts to drill through the fundamental theory, find out the application of the results, and make the interdisciplinary work practical, leading the development direction of nanomanufacturing technology in the future, demonstrating the current research level of nanomanufacturing in China. That is how we can effectively serve the major needs of China and the main battlefield of our national economy, and pave the way for the research and development and application of downstream products in the future.

I am very glad that the Center for Science Communication and Achievement Transformation of the NSFC invited us to compile the summary report, achievement report and strategic research report of the Major Research Plan, and included them in the series of *Report on China’s Fundamental Research*. In order to reflect the important achievements and leapfrog development of this Major Research Plan, we have sorted out the highlights of the integration projects, key projects and cultivation projects of this Major Research Plan.

"The way stretches endless ahead, I shall search heaven and earth." Although the implementation of this Major Research Plan has achieved some fruitful results, this is only the beginning of developing nanomanufacturing technology with Chinese characteristics in the new period. Therefore, I hope that in the future, Chinese researchers will take deepening the theoretical research of nanomanufacturing and innovating the key technologies of nanomanufacturing as their own missions and ensure the national strategic needs as the starting point. Through deep integration with information, physics, chemistry and life, in-depth research on nanomanufacturing tools, nanomanufacturing processes of important materials, nanomanufacturing equipment and nanomeasurement methods has been launched, systematically nanomanufacturing theory has been structured, and core technologies have been conquered. That is how we develop a number of original innovative technologies, obtain a number of technological achievements with important engineering prospects in the fields of aerospace, biomedicine, information, new energy, etc., and form exchangeable exclusive core technologies, which can be used in the motherland and serve ordinary people's homes.

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Chapter 1
Project Overview

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1.1 Project Introduction

Nanomanufacturing, as a basis to support the application of nanotechnology, information technology and biotechnology, mainly researches new methods and processes of nanomanufacturing such as nanostructure growth, processing, modification and assembly, as well as the performance evolution law of structures and devices in the nanoscale manufacturing process. In the past 10 years, the National Natural Science Foundation of China (NSFC) has maintained considerable support for research in the field of nanomanufacturing. In order to further enhance the source innovation capability of nanomanufacturing in China, aim at the frontier of discipline development and meet the major strategic needs of national development, the NSFC

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officially launched the Major Research Plan "Fundamental Research on Nanomanufacturing" in 2010 [1], aiming at the fundamental scientific problems in nanoprecision manufacturing, nanoscale manufacturing and cross-scale manufacturing. By strengthening top-level design, condensing scientific objectives, promoting interdisciplinary research and cultivating innovative talents, we have scored leapfrog development in several key areas or important directions, and that is how we improve the innovation ability of fundamental research in China, and provide scientific support for national economic and social development.

This Major Research Plan follows the overall idea of "limited goal, stable support, integrated sublimation and leapfrog development", focuses on the major strategic needs of national economy, social development and scientific frontier, grasps the basic, forward-looking and cross-cutting research characteristics of this plan, and combines the top-level design guidance of experts with the free application of scientific and technical personnel to gather superior strength so as to form a project group with relatively unified objectives or directions. Over the past 8 years, with the concerted efforts of relevant researchers in China, this Major Research Plan has fully utilized the advantages of interdisciplinary cooperation in machinery, materials, physics, chemistry, life, information and mechanics, and expanded the physical connotation and technical extension of various processing principles after the manufacturing object enters the micro from the macro, which has successfully completed the initially set goal, greatly broadened the scale range of manufacturing technology, opened up new research fields, greatly improved the manufacturing accuracy and quality, and developed new manufacturing theories and methods. This Major Research Plan has played a positive role in promoting interdisciplinary research, promoting deeper and more perfect research in manufacturing science, and giving full play to the supporting role in the trend of transforming new discoveries in nanoscience into cutting-edge manufacturing technologies.

1.1.1 Overall Scientific Objectives

As a Major Research Plan in the field of engineering and materials science, the "Fundamental Research of Nanomanufacturing" aims to explore new principles and methods of nanomanufacturing based on physical/chemical effects through interdisciplinary research, and reveal surface/interface effects and scale effects in processing, forming, modification and cross-scale manufacturing with nanoscale and nanoscale precision. Meanwhile in the "Fundamental Research on Nanomanufacturing", the evolution mechanism of material structure is clarified, the accurate characterization and measurement method of nanomanufacturing process is established, and some original nanomanufacturing processes and equipment are developed, which provides a theoretical basis for realizing the consistency and batch of nanomanufacturing. Therefore, this Major Research Plan focuses on the following research directions and has made a series of research breakthroughs [2, 3].

We have made a lot of research achievements in the principle and method of sub-nanometer precision surface manufacturing. Based on the interaction mechanism between atoms/molecules of matter and energy beam, the law of atomic migration and material removal processing at the atomic scale is revealed; the new manufacturing principle, method and process route are established, which provides theoretical support and technical approach for integrated circuit (IC) manufacturing with linewidth below 14 nm.

We have done a lot of fruitful work in accurate replication manufacturing of large-area micro-nano structures. Based on the physical/chemical interaction mechanism induced by external field in micro-nano gap, the material rheology and removal law in the process of micro-nano structure generation is revealed, and new manufacturing principles, methods and process routes are established to realize efficient preparation of large-area micro-nano structures such as flexible electronics devices, new sensors and micro-optical array elements.

We have done a lot of fruitful work in the research on nanomanufacturing methodology of combining "top-down" and "bottom-up". Combining "top-down" and "bottom-up" processing methods, the new nanoscale manufacturing principle, method and process route are established to solve the manufacturability problem of nanodevices and system structures.

And a new method of ultra-fast laser micro-nano fabrication based on electronic dynamic control is explored. By optimizing the temporal and spatial distribution of ultra-fast laser pulse sequences whose pulse width is shorter than the electron relaxation time, the electronic states such as electron density, temperature, energy level distribution, spin and the like of the processed material and the corresponding instantaneous local material characteristics are adjusted, so as to realize a brand-new manufacturing method with high quality, high precision and high efficiency, and apply it to the manufacturing of key devices/structures in the fields of aerospace and information.

1.1.2 Core Scientific Issues

According to the overall scientific goal of this Major Research Plan, combined with the current situation of nanomanufacturing in China and the major strategic needs in the national economy, social development and scientific frontier, the research work plan is mainly implemented around the following three core scientific issues.

1. **New principles and methods of nanoprecision manufacturing**

Nanoprecision surface finishing is one of the core issues of nanomanu- facturing, and an important research issue of this Major Research Plan. With the decrease of IC characteristic line width and the increase of wafer size, the requirements for finishing precision are increasing day by day. The 193-nm lithography objective lens requires sub-nanometer surface precision; the 300-mm wafer planarization requires 2% in-chip uniformity; the wafer thinning process requires the thickness to be reduced to less than 50 μm to avoid warping. In order to achieve these indicators, some new methods and processes must be explored, and the key problem lies in how to realize non-damage, efficient and controllable finishing of nanoprecision surface.

This Major Research Plan has carried out research on the principle and process methods of nanoprecision surface finishing. The contents include: ion beam sub-nanometer surface controllable finishing, new principles and technologies of nano-precision surface planarization for integrated circuit manufacturing, mechanochemical nanoprecision grinding technology, and chemical–mechanical planarization theory and technology under ultra-low pressure, etc.

2. **New principles and methods of nanoscale structure fabrication**

Nanoscale processing is a means to realize the manufacture of nanostructures and devices, and it is also the cornerstone of nanotechnology. At present, there are many nanoscale processing methods such as atomic force microscope, femtosecond laser, electron beam, self-assembly, nanolithography and etching. However, such problems of these processing methods as batch, repeatability, consistency and low cost have not been well solved, and they have not transformed from processing technology to manufacturing technology, which makes it difficult for nanotechnology products to move from laboratory to industrial application. Nanoscale structure manufacturing is one of the core contents of this Major Research Plan, and its goal is to explore the theory, method, technology and application of nanoscale manufacturing on the basis of the existing principles of physics/chemistry/biology, and lay a foundation for the research and application of high-precision sensors, high-efficiency micro-energy, integrated micro-nano systems/post-Moore era electronic devices and integrated circuits.

The main research contents of nanoscale structure manufacturing include: new nanoscale manufacturing theory and method, high-precision micro-nano structure controllable manufacturing with structure self-restraint, external field induced three-dimensional manufacturing and nanostructure controllable manufacturing based on self-assembly, etc.

3. **Principle and method of efficient and multiscale fabrication of large area nanostructures**

Multiscale manufacturing is one of the research focuses of this Major Research Plan. With the increasing demand for flexible and intelligent electronic devices such as flexible displays, flexible thin-film solar cells and flexible sensors, breakthroughs in large-area nanostructure manufacturing technology are urgently required. Due to the scale effect of nano, micro and macro interconnections, it is difficult to accurately control the device performance, and it is full of challenges to realize large-area, high-efficiency, high-precision and low-cost manufacturing of nanostructures.

This Major Research Plan focuses on the bottleneck problems of multiscale manufacturing. The main contents include: multiscale manufacturing based on special effects in microelectronic processing technology, theory and method of new and effective molding manufacturing for high-scale manufacturing of large- area micro-nano structures, integrated manufacturing and application of multiscale micro-nano structures, etc.

Fig. 1.1 Project deployment

1.2 Project Layout

1.2.1 Project Deployment

During the 8 years starting from the implementation of the Major Research Plan of "Fundamental Research on Nanomanufacturing", the total funds are about 190 million yuan, developing 4 integrated projects (55 million yuan, accounting for 29.01%), 24 key projects (62.4 million yuan, accounting for 32.91%), 121 cultivation projects (62.31 million yuan, accounting for 32.87%) and 4 strategic research projects (9.8788 million yuan, accounting for 5.21%), as shown in Fig. 1.1 [4, 5]. The research content covers four research fields: nanoprecision manufacturing, nanostructure manufacturing, multiscale manufacturing and exploration of new methods of micro-nanomanufacturing, forming four project groups, namely, new principles and methods of nanoprecision manufacturing, high-efficiency manufacturing methods of large-area micro-nano structures, new principles of nanomanufacturing combining "top-down" and "bottom-up" and exploration of new principles and methods of laser micro-nanomanufacturing [5].

1.2.2 Project Integration and Sublimation

This Major Research Plan has made positive progress in all directions supported, especially in new methods such as nanoprecision surface finishing, high-efficiency manufacturing of large-area micro-nano structures, nanomanufacturing combining "top-down" and "bottom-up", and ultra-fast laser micro-nanomanufacturing based on electronic dynamic control. Combined with the objectives of this Major Research Plan, the progress made and the major demand of the country, the plan condensed and planned 4 integrated projects in the implementation process.

1. **Principle and method of sub-nanometer precision surface manufacturing**

In sub-nanometer precision surface manufacturing, the interaction mechanism between material atoms, molecules and energy beams is discovered, the law of atomic migration and material removal at the atomic scale is explored, and the manufacturing principles, methods and process routes such as precision optical device processing and IC wafer polishing are established. Combining machinery, chemistry, materials and mechanics, the molecular/atomic material removal mechanism is explored, and the principle and methods of nanoprecision surface manufacturing are established. Through the research of this integrated project, key scientific problems can be broken through, systematic process methods can be formed, equipment technical bottlenecks can be broken through, and the technology of nanoprecision manufacturing in China can be improved.

2. **Accurate replication manufacture of large area micro-nano structures**

Based on the physical/chemical interaction mechanism induced by external field in the micro-nano gap, the material rheology and removal law in the formation process of the micro-nano structure is revealed, and new manufacturing principles, methods and process routes are established to develop efficient preparation of large-area micro-nano structures such as flexible electronics devices, new sensors and micro-optical array elements. Facing several major strategic demands of China (such as precision metrological grating, special-shaped physical grating in ignition plan, ultra-high efficiency nanooptoelectronic components), the research on precision template manufacturing method, multi-field induced replication method, error transfer theory and precision traceability method is integrated to develop nanoscale accuracy and efficient replication manufacturing principle. This plan reveals the evolution law of structure and physical properties induced by external field, discovers a new principle of nanostructure replication manufacturing, and develops the error transfer control of replication forming and the traceability theory of precision measurement.

3. **Research on nanomanufacturing method combining "top-down" and "bottom-up"**

Based on the "top-down" and "bottom-up" processing methods, the new multi-scale manufacturing principle, method and process route are established to solve the manufacturability problem of nanodevices and system structures. Integrating the new principles of self-assembly and nanoscale processing in this Major Research Plan and the original methods in micro-nano composite manufacturing and making full use of the characteristics of mature integrated manufacturing technology in microelectronics industry, the integration from nanostructure to technology and function is realized and a breakthrough from nanomaterials to nanodevices and systems is achieved. Through the research of this integrated project, a series of high-sensitivity, low-power gas and biological sensors (such as environmental monitoring and anti-terrorism) that can be applied to the internet of things are developed.

4. **Exploration of a new method of ultra-fast laser micro-nanomanufacturing based on electronic dynamic control**

By optimizing the temporal and spatial distribution of ultra-fast laser pulses whose pulse width is shorter than the electron relaxation time, the electronic states such as electron density, temperature, energy level distribution, the spin of the processed material and the corresponding instantaneous local material characteristics are controlled, thus realizing a brand-new manufacturing method with high quality, high precision and high efficiency, and being used to manufacture key devices/structures in the fields of aerospace and information. Through the research on this integrated project, the mechanism of electronic dynamic control of spatiotemporal shaping femtosecond laser pulses in material processing is detected and revealed, the key parameters of ultra-fast pulse sequence are optimized, and high-efficiency and high-quality processing is realized. The research is used to manufacture key structures/devices in major national projects/information and other fields.

1.2.3 Interdisciplinary and Integration

From the very beginning of its implementation, this Major Research Plan attaches great importance to interdisciplinarity, mainly involving machinery, materials, physics, chemistry, life, information, mechanics and other fields, as shown in Fig. 1.2. In the cross-integration of electrochemistry and manufacturing science, electrochemistry and traditional mechanical grinding technology are combined to establish a low-damage and high-precision polishing technology for functional surfaces, which is applied in the field of integrated circuit manufacturing and realizes low-stress planarization of nanoprecision surfaces and high-precision optical lens processing. In the cross-integration of mechanics and manufacturing science, the original rheological forming technology of electrically driven polymer nanostructures is established by combining fluid mechanics, electrodynamics and molding replication technology, which provides an efficient and reliable manufacturing method for complex nanostructures such as multiscale and great aspect ratio structure. In the cross-integration of chemistry, microelectronics and manufacturing science, chemical growth and physical self-assembly technology are combined with traditional micro-nanomanufacturing technologies such as lithography and etching, and self-assembly technology is developed into a nanomanufacturing method that meets the manufacturing characteristics, thus realizing the manufacturing of typical nanostructure functional devices such as high-precision sensors. In the cross-integration of laser, chemistry and manufacturing science, ultra-fast laser processing technology has been developed, laser processing theories and methods such as electronic dynamic control, two-photon polymerization and multiphoton reduction have been established, and the application potential of laser manufacturing technology in the field of nanomanufacturing has been expanded. In the cross-integration of material science, information science and manufacturing science, controllable manufacturing and processing technologies for new electronic materials such as graphene and semiconductor nanowires

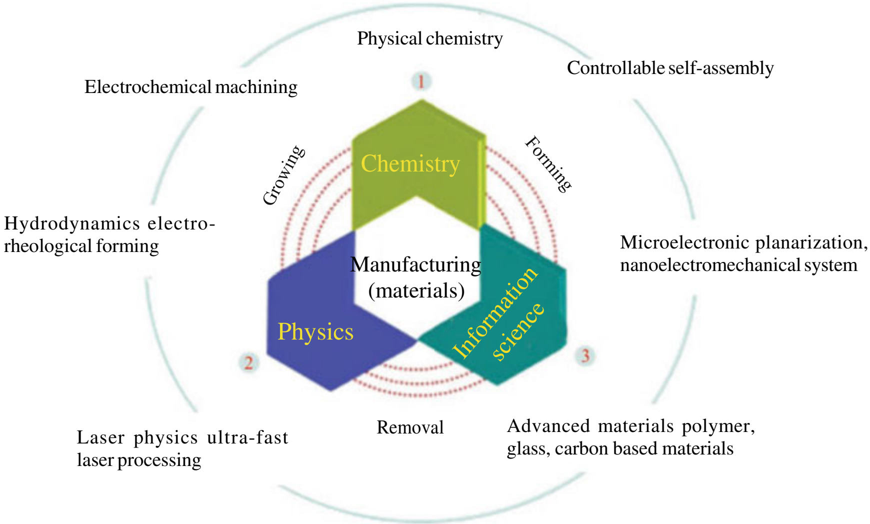

Fig. 1.2 Interdisciplinary situation

have been established, and prototype manufacturing of nano devices with excellent performance has been realized through macro, micro and nanoscale interconnection. This Major Research Plan not only expands the discipline interface, but also promotes the interdisciplinary integration. The results of the paper involve 28 disciplines such as materials science, physics, chemistry, engineering and optics, with an average interdisciplinary rate of 2.06%.

1.3 Research Significance

This Major Research Plan innovatively incorporates macro-scale nanoprecision research into nanomanufacturing research, focusing on batch, consistent and low-cost manufacturing technology. Through the breakthrough of principle innovation and cutting-edge technology, a group of interdisciplinary and excellent teams engaged in nanomanufacturing research have been trained and gathered, which has laid a solid foundation for the development of China's nanomanufacturing technology and played an important role in solving the strategic tasks of China's manufacturing and getting research results with important influence in the world.

Since its launch, this Major Research Plan has aimed at cutting-edge scientific issues and development trends in the field of nanomanufacturing, and has made great efforts to promote the cross-integration of machinery, materials, physics, chemistry, life, information, mechanics and other disciplines, achieving great innovative research results as follows [6].

Through continuous efforts, we have released the atomic-level chemical mechanical removal mechanism, established the processing method of optical full- frequency sub-nanometer precision, and formed the wafer chemical mechanical planarization equipment and lithography lens polishing equipment, which have been applied in integrated circuit production lines, breaking the foreign monopoly and providing key support for solving the "containment" problem in the chip manufacturing industry.

It is for the first time that in the world, a new principle and a new method of nanoimprint with interface charge regulation have been proposed. A series of nanoimprint equipment such as gas-electricity cooperative imprint and roll-to-roll multiscale imprint have been developed, which have been applied in major national projects, national defense and military, consumer electronics and other fields, making nanoimprint move from laboratory to engineering application.

A new principle and a new method of femtosecond laser manufacturing with electronic dynamic control have been put forward, which has realized the active control of instantaneous local electronic dynamics for the first time in the world, and laser micro-nanomanufacturing technology and equipment have been developed, which has provided support for target pellet manufacturing of major national projects.

Local selective multi-construction and mass manufacturing methods for micro structured surfaces have been developed, a relatively perfect nanomanufacturing method and process system has been established, and 17 sets/kinds of equipment have been independently developed, breaking the international monopoly in several fields and reaching the international advanced level.

In the progress of implementing of this Major Research Plan, 3,813 SCI papers were published in international journals, including 19 papers in top journals such as *Nat Nanotechnol*, *Nat Mater*, *Nat Phys*, and *Nat Energy*, and 91 highly cited papers in ESI; 935 invention patents (including 11 US/European patents) were authorized and 66 monographs were published in both Chinese and English; 6 second prizes of the National Natural Science Award, 5 second prizes of the National Technological Invention Award, 1 second prize of the National Science and Technology Progress Award, 2 Ho Leung Ho Lee Foundations, 1 National Defense Science and Technology Innovation Team Award, 21 provincial and ministerial awards, were awarded. With the support of this Major Research Plan, interdisciplinary development have been realized, and a group of outstanding scientists with international standards have been cultivated in the field of nanomanufacturing. In total 6 members of the expert steering committee or project undertakers were elected academicians of the Chinese Academy of Sciences and 2 members of the Chinese Academy of Engineering. Among the project undertakers, 4 members were selected as members of the American Society of Mechanical Engineers (ASME) and the Institute of Electrical and Electronic Engineers (IEEE), 18 members were supported by the National Science Fund for Distinguished Young Scholars, and 6 members were awarded the Science Fund for Outstanding Young Scholars [6].

The implementation of this Major Research Plan has greatly improved China's position in the international nanomanufacturing field and realized China's leap-forward development from tracking to becoming one of the world's advanced ranks.

The comparison of the development trend in the field after the completion of this Major Research Plan can be seen in Table 1.1.

Table 1.1 Comparison of development trends

Core scientific issues under the scientific goal	Domestic research plan when the plan is started	Domestic research status at the end of the plan	International research status at the end of the plan	Advantages and gaps compared with the international research situation
Nano/sub-nanometer precision surface manufacturing	Surface/subsurface damage: micron scale Surface roughness: *Ra* 50 nm Surface accuracy: root-mean-square (RMS) 3 μm	Surface/subsurface damage: 15 nm Surface roughness: *Ra* 0.1 nm Surface accuracy: RMS 0.3 μm	Surface/subsurface damage: 8 nm; Surface roughness: *Ra* 0.1 nm; Surface accuracy: RMS 0.2 μm	Advantage: a relatively complete and recognized theory and model, new methods, new processes, and new equipment Gap: there is still a need to improve the consistency of large web
Nanoscale manufacturing	Manufacturing theory is in a catch-up state; Scale: 5–10 μm	A series of theories such as the electrically driven nanoimprint, electron dynamic control of laser manufacturing are established; scale manufacturing of 10–20 nm is realized; independent equipment such as laser direct writing, nanoimprint and near-field exposure is formed	Processing scale: 7 nm	Advantage: a relatively complete and basic theory and model, new methods, new processes, and some autonomous equipment are established Gap: there still exists generation difference of 1–2 generation compared with international micro- nano processing still existing

(continued)

Table 1.1 (continued)

Core scientific issues under the scientific goal	Domestic research plan when the plan is started	Domestic research status at the end of the plan	International research status at the end of the plan	Advantages and gaps compared with the international research situation
Cross-scale micro-nano structural manufacturing	No theory, centimeter-scale microstructure, zero equipment (international: meter scale micro-nano composite structure)	The manufacturing theories such as nanoimprint and a maskless manufacture method are established; 3D etching, nano-printing and other equipment are developed; the manufacture of meter-scale web nanostructures is now available	Manufacture of meter-scale web nanostructures	Advantage: a series of key components such as sensor, flexible display, flexible electronics, autonomous equipment/process Gap: large web manufacturing accuracy and consistency

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Chapter 2
Research Situation

Bingheng Lu, Jianbin Luo, Zhongqun Tian, Dongming Guo, Han Ding, Changzhi Gu, Zhihong Li, and Ming Liu

2.1 Research Status of Nanomanufacturing

1. **Development of fundamental research on nanomanufacturing**

Nanoscience is the frontier of modern science, and nanomanufacturing is the foundation of the development of nanoscience. The research achievements of physics, chemistry and other basic disciplines, as well as the progress of information technology, have driven the development of nanomanufacturing technology. The breakthrough and emergence of innovative technologies in nanomanufacturing also serve disciplines such as related nanoscience and provide technical and equipment support in

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the process of understanding and exploring unknown natural mysteries. In the twenty-first century, nanomanufacturing has shown a strong driving force in today's scientific and technological innovation and development, and has become the commanding heights that can lead the development of science and technology in the world in the future, such as biomolecular-motors, nanomotors, nanorobots, molecular photo-electric devices, nanocircuits, nanosensors, nanointelligent devices and systems that attract extensive and in-depth attention from governments, scientific and technological circles and industry. Since the launch of the National Nanotechnology Initiative (NNI) implemented by the United States in 2001, there has been a worldwide upsurge in the research and development of nanotechnology. Nanomanufacturing technology, as the technical core supporting the development of various nanotechnologies, has been listed as a key research direction supported and developed by developed Western countries. At present, developed countries/regions including the European Union and its member states, Japan, Canada, Singapore, the ROK and other developed countries, China, India, Brazil and other newly industrialized developing countries, facing this new manufacturing field, have seized the opportunity and successively issued their nanomanufacturing development strategies and special plans, so as to grasp the initiative in future scientific and technological and economic development and ensure the continuous improvement of national core competitiveness.

In 2017, the global market output value of nanomanufactured products has exceeded 3.7 trillion US dollars. In recent years, this data has shown a rapid upward trend. According to the forecast of the National Science and Technology Council (NSTC), the global nanotechnology market will exceed 5 trillion US dollars per year after 2020. Faced with such huge business opportunities and markets, European countries such as the United Kingdom, France, and Germany invest 500 million to 1 billion euros in nanotechnology research each year, and nanomanufacturing has been listed as an important research field for national development; government departments in developed Asian countries such as Japan and the ROK have also paid great attention to the nanomanufacturing market and invested huge sums of money in research. The confidence of various countries in the increasing trend of nanomanufacturing has increased unabated, investment has gradually increased, and a series of strategic research plans have been formulated accordingly. All countries enhance the core competitiveness of science and technology through technological breakthroughs and industrial expansion of their own countries. For example, the United States, Australia, etc. have achieved breakthroughs in nanomanufacturing innovation technology through multidisciplinary integration to solve the challenges of existing technical problems; Germany, the ROK, Japan, etc. focus on the effective transformation of existing nanomanufacturing achievements.

2. **Development of nanomanufacturing technology**

As a manufacturing method based on physical/chemical/biological principles, nanomanufacturing is mainly aimed at a new manufacturing process integrating material, structure and function in the nanoscale range such as nanostructure growth, processing, modification and assembly. It is a new method for the performance evolution of nanoscale structures and devices. After manufacturing science moves towards nanometer scale, the objects of manufacturing change from the macro to the micro, creating new technical goals and judgment standards. In response to the precision and quality requirements that are different from traditional manufacturing, new manufacturing theories and methods have been developed. Nanomanufacturing technology has played a positive role in promoting the intersection of different disciplines, providing brand-new research conditions and innovative ideas for the deepening and development of scientific research such as physics and biology. In recent years, nanomanufacturing technology has successfully transformed the new discoveries and achievements of nanoscience into physical products.

Therefore, driven by the research results of disciplines such as physics and chemistry and the progress of information technology, the emerging nanomanufacturing technology has become an enabling technology. Nanomanufacturing technology not only provides a unique solution for disciplines to go deep into nanoscale fields that could not be explored in the past, but also provides unique manufacturing technology means for similar engineering disciplines.

3. **Nanomanufacturing guides the development of industry**

At present, nanomanufacturing technology has involved the manufacture of core products in many fields such as information, materials, environment, energy, biomedicine, agriculture, aerospace and national defense security, which has played an important supporting role in the future development of national strategic emerging industries and the establishment of international scientific and technological status. For example, in recent years, the European Union has increased the manufacturing and application research of graphene and other two-dimensional materials. The purpose is to strengthen the basic leading role of nanomanufacturing, open up new battlefields in the fields of biology and energy, and occupy the commanding heights of future scientific and technological development.

In the field of biomedicine, the combination of nanomanufacturing, biology and medicine is rapidly developing into the forefront and hot spot of emerging scientific research fields, which will definitely have a significant impact on the future development of biotechnology and pharmaceutical industry and the layout of international industries. The development of nanomanufacturing technology provides a brand-new development prospect and vigorous power for the biomedical field, and also promotes the development of nanobiomedical industry.

In the field of energy, the development of nanomanufacturing technology provides strong technical support for energy conservation, emission reduction and sustainable development goals. It provides a technical means for the efficient utilization and low emission of traditional energy materials, the development of new energy storage and energy conversion materials, and the improvement of solar photothermal and photoelectric conversion efficiency.

In the field of new materials, the manufacture of nanomaterials has brought an unprecedented revolution to the development of traditional materials. The unique optical, electrical, thermal and magnetic properties of nanomaterials and devices have been utilized and developed to a greater extent, which has promoted the upgrading and replacement of traditional industries.

In the field of information and communication, the development of nanomanufacturing technology has provided mankind with a solution to make up for the shortage of resources and energy with the advantages of information and software technology, and has provided an unprecedented innovative manufacturing method for high-performance, miniaturized and intelligent products.

In the report submitted to the US Congress in 2016 (GAO-14-181SP), the US Government Accountability Office (GAO) pointed out that the contribution of nanomanufacturing technology to the economy will surpass semiconductor technology and become one of the main pillars of economic development around 2025.

2.2 National Strategic Demand and Development Trend of Nanometer Manufacturing

Since the beginning of the twenty-first century, governments of various countries have realized more clearly that the strategic goal of nanomanufacturing is a long-term strategic task, and they must give sustained and stable support to promote its development. As the innovation source of the new generation technology, "Fundamental Research on Nanomanufacturing" must be strengthened, and "Fundamental Research on Nanomanufacturing" should rise to the height of national will. Europe, the United States, Japan and other countries have successively formulated government strategy reports on the development of nanomanufacturing technology. The common feature is that they all emphasize application-oriented fuction, integrate the research strength of various disciplines, and establish an integrated research platform of research, apply research and technology transfer research. The emerging technological features of nanomanufacturing provide opportunities for other countries to achieve leapfrog development in the field of science and technology. China, Brazil, India and other countries and regions have set up relevant government plans according to their respective economic and technological status, aiming at enhancing the core competitiveness of science and technology with European and American countries by promoting and accelerating the development of nanomanufacturing technology. In recent years, with the continuous support and promotion of fundamental nanomanufacturing, China has shown a strong momentum of scientific and technological development. It has made more and more innovative achievements in the field of nanomanufacturing science and technology and has played an increasingly prominent supporting role in the development of emerging industries.

1. **Demand for nanomanufacturing in development strategies of various countries**

Among the advocates of nanotechnology innovation strategy, the scientific and technological community has always adhered to understanding and controlling substances on a nanoscale, expecting to trigger a new round of technological and industrial revolution through the industry. After years of policy implementation in various countries, the original intention of nanotechnology research has been basically realized, which has fully stimulated the great enthusiasm of the government, scientific and technological circles, and industry for the sustainable development of nanotechnology.

Since 2014, a series of mission-oriented research programs have been issued one after another by the United States. The main think tank of the White House, the Advanced Research Projects Agency of the US Department of Defense, and other institutions and consulting companies have continued to release strategic plans for nanomanufacturing such as "Research Strategy for the Development of Nanomanufacturing", "Prospect for the Development of Nanomanufacturing in 2020", "Manufacturing from Atoms to Products", "Sustainable Nanomanufacturing" and "Major Challenges Caused by Nanotechnology: Future Computing", which refl the important position of nanomanufacturing technology in the development of nanotechnology [1–6]. In 2017, under the guidance of the National Science and Technology Council (NSTC), NNI revised the development goals in the field of nanotechnology and technology, and put forward the Nanotechnology Signature Initiatives and Grand Challenges (NSIs), taking the Nanomanufacturing Signature Initiatives as the primary development goal, and realizing batch-level results by supporting nanotechnology and industry [7]. Under the guidance of this programmatic document, the US Department of Defense, the US Institute of Standards and Technology, the US Natural Science Foundation of China and other departments have successively formulated their own development plans for nanomanufacturing, hoping to achieve a series of new achievements in related fields.

Faced with the great temptation of nanomanufacturing prospects, the EU is not to be outdone. In 2002, 2006 and 2007, the Sixth Framework Plan, the Seventh Framework Plan and the European Nanotechnology Development Strategy were formulated respectively, taking nanomanufacturing technology as one of the key development contents of nanotechnology. Since 2010, the EU Nanotechnology Strategic Plan began to focus on functional materials, new energy, environment, biomedicine, flexible electronics and other fields, and has successively launched "Graphene Flagship Plan" (2015), "Human Brain Plan" (2014) and other transnational cooperation projects [8–12]. Under the overall framework of the EU, EU countries have also formulated their own nanotechnology development strategies, such as Germany's "Nanotechnology Action Plan 2015" (2012) and "Nanotechnology Action Plan 2020" (2016) [13], and the "Nano Functional Materials Research Plan" (2014) initiated by the British Engineering and Natural Science Research Council [14]. Although the nanotechnology development strategies of Germany, France, Britain and other countries are obviously different from those of Belgium, Denmark, Finland and other countries, all countries start from their own scientific and technological priorities and industrial status, focus on the scientific and technological status in the future nanomanufacturing subdivision field, and support their innovation and breakthrough in nanotechnology through the development of nanomanufacturing technology.

In the Asia–Pacific region, Japan, which is leading in science and technology and economically active, has put forward several nanotechnology research and development plans in order to strengthen the development of nanotechnology. Therefore nanotechnology development has been included in Japan's "Plan for Science and Technology" and a research committee has been set up to strategically guide the development and promotion of nanotechnology. In recent years, the Japanese government has devoted itself to the systematic development of nanotechnology with the goal of problem-oriented research. The "2013 Comparative Report on Nanotechnology Research and Development in Major Countries" published by the Japan Science and Technology Promotion Agency pointed out that the development of nanotechnology in Japan in the future required long-term attention to the three key directions of bio-nano, green nano and nanoelectronics manufacturing [15]. The Summary and Analysis Report on Research and Development of Nanotechnology and Materials in Japan released by the Agency in 2015 analyzed in detail the development trend of nanotechnology in the fields of environment and energy, health and medical care, social infrastructure, information, communication and electronic products and fundamental technology in Japan. The development trend of nanotechnology has determined that transforming basic research into products is the basic idea of nanomanufacturing technology [16]. In addition, in 2018, the Nano and Materials Science and Technology Committee under the Ministry of Education, Culture, Sports, Science and Technology of Japan also issued the "Research and Development Strategy of Nano and Materials Science and Technology", which takes nano and materials technology as the key research and development field, and proposes 4 major measures to be taken to realize the material revolution: create new materials that can bring about social changes; deepen the science system and apply innovative materials to society; promote the development of laboratory research and development to high efficiency, high speed and precision; formulate specific national policies to promote the material revolution [17].

In 2014, the ROK released the "Second National Nanotechnology Roadmap (2014–2025)" [18] in accordance with the development trend of nanotechnology at home and abroad and the direction of national science and technology policy advancement. The road map proposes 21 technical directions for the development of nanodrugs, high-efficiency light-emitting diode(LED)/organic light-emitting diode(OLED), panel lighting, high-performance nanofibers, ultra-light nanocomposite structural materials, nano-analysis and measurement equipment, nanothin film materials, nanosensors, nanoenergy conversion devices, nanosemiconductor devices, etc., and formulates a detailed development road map. The ROK will increase its investment in nanomanufacturing technology on a large scale, and its proportion will be expanded from less than 5 to 10%. The goal is to expand to more than twice the existing investment scale by 2020, that is, to 800 billion won (about 750 million US dollars).

The Australian Academy of Sciences released its report "Australia's National Nanotechnology Research Strategy" in 2012 [19], and it is hoped that nanotechnology can be used to solve major challenging problems, and it is proposed to realize nanodriven economic development. It is necessary to link the research and development opportunities of nanotechnology with the major challenging problems of the country, make use of nanomanufacturing technology to give full play to the capabilities of large-scale and multidisciplinary collaborative research, and find out solutions to these major problems.

In 2014, the government of the Russian Federation approved the report "Prediction of Science and Technology Development in the Russian Federation to 2030" [20], which identified key areas affecting the long-term development of Russia's economy, society and science, the market prospects of Russia's innovative technologies and products, and research and development priorities in various fields. The report pointed out that the priority areas of Russia's scientific and technological development in the future are information and communication technology, biotechnology, medicine and health, new materials and nanotechnology, rational utilization of natural resources, transportation and space systems, energy efficiency improvement and energy conservation, and emphasized the need to give full play to nanotechnology breakthroughs in various fields, combined with the national conditions of the country and the world's outstanding achievements in the field of nanomanufacturing, which will promote the efficient and rapid development of Russia in various fields in the next 15 years.

2. **The demand of China's development strategy for nanomanufacturing**

Facing the great development prospect of nanotechnology, China closely follows the United States in the strategic layout of nanotechnology. In 2000, the National Nanotechnology Steering and Coordination Committee was established, and the National Nanotechnology Development Outline (2001–2010) was issued, which made a top-level design for China's nanotechnology work. In 2006, the State Council issued the Outline of the National Medium- and Long-Term Science and Technology Development Plan (2006–2020), and "nanotechnology" is considered as one of the fields that are expected to achieve leap-forward development in China. The Chinese government and relevant institutions have provided continuous financial support for nanotechnology. Since 2006, the Ministry of Science and Technology has organized and implemented the "Nano Research" major scientific research plan, after the reform of science and technology plan management. In 2016, the Ministry of Science and Technology officially launched the implementation of the national key research and development plan. As one of the first batch of key projects, "nanotechnology" will continue to promote the application research of nanotechnology in key industries in China. In April 2013, the Chinese Academy of Sciences launched the "Focus on Transformative Nano Industry Manufacturing Technology" (hereinafter referred to as the "Nano Pilot Project") to promote the development of research on nanotechnology in the fields of nanomaterials, nanocatalysis and nanoenergy. In 2010, the National Natural Science Foundation of China officially launched the Major Research Plan "Fundamental Research on Nanomanufacturing", from a manufacturing point of view, to explore the theory and key methods/technologies of new principles, new methods and new processes of nanomanufacturing. Echoing other nanotechnology programs in China, the research level of nanotechnology manufacturing in China has been improved, a professional team engaged in nanotechnology manufacturing has been trained, a number of research teams with world-leading level have been built, and a number of internationally influential leaders have emerged.

The supporting effect of nanomanufacturing on China's strategic demand is mainly reflected in the following five aspects.

Chip manufacturing field. Chip manufacturing restricts the "neck-stuck" technology in the overall development of China's science and technology, and has a far-reaching impact on China's national defense, cutting-edge science, advanced manufacturing, high-end equipment and other fields. Wafer planarization equipment and lithography machine equipment are typical representatives of "neck sticking" technology in chip manufacturing in China. The key lies in: how to achieve full frequency band profile accuracy better than $\lambda/500$ (i.e., 1–2 nm) for a lithography machine lens with a diameter of 300 mm; at present, the difficulty of the high-end 7 nm lithography machine, which is completely banned from China in the world, lies in how to realize that the motion accuracy of the exposure platform is better than 2 nm and the wafer polishing reaches $Ra < 0.2$ nm. Therefore, to break through the "neck-stuck" technology of chip manufacturing, it is urgent to develop China's nanomanufacturing technology and equipment.

Space observation field. The large telescope system for deep space observation needs to realize the profile accuracy better than 1 μm and the surface roughness better than 1 nm on the optical mirror surface with meter width; the manufacturing accuracy and guidance accuracy of cruise missiles are the main factors restricting the hit accuracy. The manufacturing error of the missile needs to be accurately controlled (if the error increases by 1 μm, the missile will deviate from the target by hundreds of meters). Therefore, nanomanufacturing, which is mainly characterized by nanoprecision batch and consistent manufacturing, will provide important support for this field.

National strategic areas. In the processing of target pellets in major national projects, high depth-diameter ratio inflatable through holes with diameters ranging from several microns to more than ten microns are processed on spherical shells with a diameter of less than 2 mm. Concentric countersunk holes used for inflatable intubations require extremely high micropore quality (such as heat-affected zone/microcrack/recast layer/hole shape). Therefore, nanomanufacturing characterized by nanoprecision, nanoscale and cross-scale manufacturing will support the needs of national strategic manufacturing and ensure the improvement of national security and national defense level.

Biomedical field. China is implementing the Healthy China Development Strategy. As an important step of the Healthy China Development Strategy, vigorously promoting precision medicine is the key. Taking tumors as an example, at present, the research on cancer genomics is accelerating all over the world. To achieve accurate diagnosis and treatment of tumors requires the intersection of multiple disciplines, including not only gene sequencing technology, but also human proteome and metabolome technology, even the molecular imaging, molecular diagnosis, endoscopic minimally invasive technology, targeted drugs, big data analysis tools, etc.

Because it involves monitoring, diagnosis and treatment at the cellular or molecular level, the development of nanomanufacturing technology in China will greatly promote the rapid development of precision medicine in China.

High-end nanoprecision scientific instruments. At present, almost all nanoprecision scientific instruments are imported in China, and 100% of high-end instruments in some fields are imported. China's annual import of high-end nanoprecision scientific instruments is more than 10 billion US dollars, increasing at a rate of 30% every year. At present, almost all of China's nanoprecision scientific instruments are imported, and 100% of high-end instruments in some fields are imported. China's annual import of high-end nanoprecision scientific instruments cost more than 10 billion US dollars, increasing by 30% every year. Nanoprecision scientific instruments have become a major constraint for China to build a powerful country in science and technology.

2.3 Development Trend of Nanomanufacturing in China

2.3.1 Development Trend of Research on Nanomanufacturing in China

In the field of nanomanufacturing, China has become an important contributor to the progress of nano science and technology in the world today. It is a major nation in the research and development of nano science and technology in the world. Some fundamental research has leaped to the international leading level. At present, China's nanomanufacturing presents the following development trend.

China's manufacturing level has expanded from macro manufacturing (mm/sub-mm manufacturing precision) to micro-nanomanufacturing (micron/sub-micron manufacturing precision, reaching nano precision in some fields). Manufacturing tools have expanded from traditional tools to high-energy beams, and new manufacturing processes, such as laser processing, mechanochemical polishing, self-assembly, have made significant progress.

Chinese manufacturing has opened the era of nanoprecision. The manufacturing accuracy of nanoprecision surfaces such as chips and lithographic objective lenses reaches *Ra* 0.05 nm, reaching the world's leading level; original manufacturing methods such as the third generation of nanoimprint are pioneering engineering applications.

"Fundamental Research on Nanomanufacturing" in China has promoted the research in related fields. Eighteen manufacturing technologies programs funded by this Major Research Plan have entered major national research programs such as "the National 02 Project", "04 Project", "0902 Project" and "the Instrument Project", giving birth to a series of key research and development programs of the Ministry of Science and Technology.

Gradually, we possess the independent research and development capability of nanomanufacturing equipment, and China voices have began to appear in the formulation of nanomanufacturing standards. The self-developed wafer polishing process equipment has entered the international mainstream IC manufacturing production line; the self-developed nanoimprint series equipment has been applied to mass manufacturing of products such as flexible electronics; the self-developed femtosecond laser processing equipment has been applied to the ignition engineering and other key projects in China; five standards for nanomanufacturing/characterization have been formed, including one international standard.

A nanomanufacturing research team with interdisciplinary, full coverage of nanomanufacturing directions and a prominent international position has been formed, and a large number of high-level nanomanufacturing talents have been trained.

1. **The development trend of academic research**

With the support of various aspects and channels, China's fundamental research on nanomanufacturing has developed rapidly. The overall research level has entered the world's advanced ranks, and the research results in some directions are at the forefront of the world. In terms of fundamental research, the number of SCI papers published in the field of nanomanufacturing in China has entered the forefront of the world, as shown in Fig. 2.1. It can be seen from the figure that since the implementation of this Major Research Plan in 2010, the number of papers published in related fields in China has increased significantly, and the overall number slightly exceeds that of the United States. In particular, in 2017, the number of papers published in international academic journals of nanomanufacturing reached 9,654, ranking first in the world, and the top 1% of highly cited papers ranked first in the world.

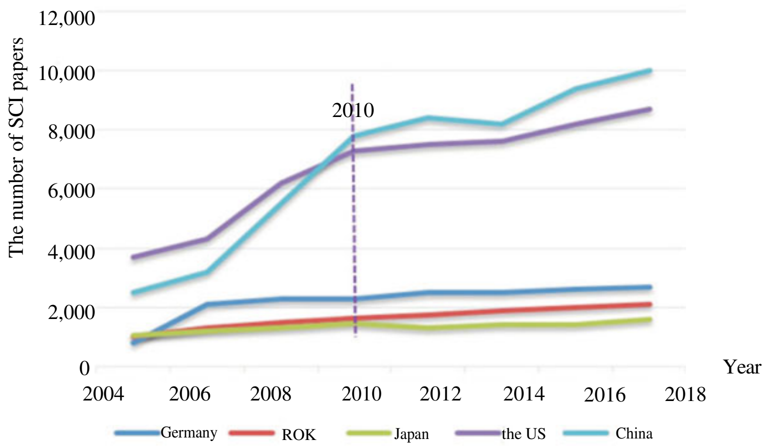

Fig. 2.1 Publication of research papers in the field of nanomanufacturing in China supported by this Major Research Plan

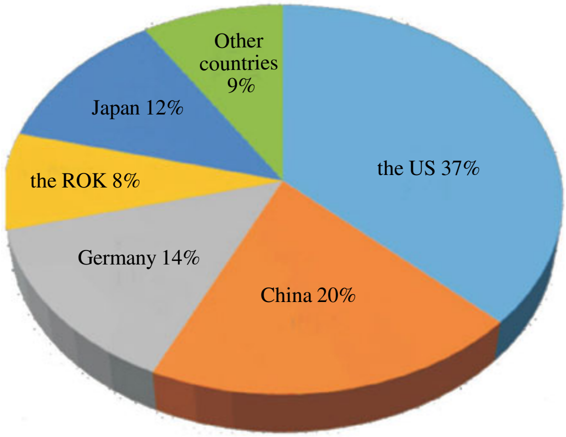

Fig. 2.2 Contribution of fundamental research in the field of nanomanufacturing in China to fundamental research in the field of nanomanufacturing in the world under the support of this Major Research Plan (*Source* GAO Highlights of a Forum in Emergence and Implications of Nanomanufacturing, 2016)

The research results are mainly published in journals related to nanomanufacturing in the fields of physics, chemistry, materials, optics and manufacturing. Among them, *J Mater Chem* of material chemistry, *Appl Phys Lett* of physics and *Opt Lett* of optics are the journals that publish the most papers. In terms of high-level papers, research papers are mainly published in *Nat Mater*, *Nat Phys*, *J Am Chem Soc*, *Adv Mater*, *Nano Lett and Phys Rev Lett* and other important international journals; high-level journals with specially invited review papers include *Chem Soc Rev*, *Energy & Environ Sci*, *Nano Today*, *Mater Today*, and so on.

2. **The status of China's "Fundamental Research on Nanomanufacturing" in the World**

China has strong international competitiveness in fundamental research and applied research on nanomanufacturing. By the end of 2016, China's contribution to "Fundamental Research of Nanomanufacturing" ranks second only to the United States, as shown in Fig. 2.2. Due to the influence of fundamental equipment, process technology, scientific research funds, industry foundation and other factors, there is still a gap between China's nanotechnology research and the world's top level. China's nanomanufacturing processing maturity is not high, and nanomanufacturing needs to be improved in industrial applications.

2.3.2 Development Trend of Key Technologies of Nano-manufacturing in China

1. **Nanomanufacturing technology and its development trend in China**

Nanomanufacturing is an inevitable trend of nanotechnology and technology development. Aiming at the major needs of integrated circuit manufacturing, thermonuclear fusion, new energy and ultraprecision manufacturing, China has selected nano precision manufacturing, nanoscale manufacturing, cross-scale manufacturing and nanomanufacturing equipment, which is related to the future development of nanotechnology in China, taking typical key fundamental research fields as breakthrough points. In the field of fundamental research on nanomanufacturing, a number of original nanomanufacturing processes and equipment principles have been explored in the fundamental research field of nanomanufacturing. It promotes the cross-integration of manufacturing science with materials, physics, chemistry, optics and information. A group of outstanding talents engaged in fundamental research of nanomanufacturing has been trained, and a collaborative innovation research team of nanomanufacturing has been formed based on the joint laboratory of "Fundamental Research on Nanomanufacturing", which has effectively improved the level of fundamental research in related fields of nanomanufacturing in China and promoted the initial application of nano-scientific and technological achievements. A number of important progress has been made in nanoprecision manufacturing, nanoscale manufacturing and cross-scale manufacturing. Influential papers have been published in relevant top academic journals, which have also provided strong support for major national strategic needs such as major projects in integrated circuit manufacturing and major scientific projects.

2. **Development trend of intellectual property rights in technology research**

In terms of applied research, the number of domestic patents applied for or authorized in China has increased significantly. According to statistics, the number of patents related to nanomanufacturing reached nearly 6,300 from 2015 to 2018, about 1.5 times that of the United States, ranking first in the world. The development trend of patents funded by this Major Research Plan is shown in Fig. 2.3. This reflects that China's nanotechnology research and development has reached the world's advanced level. China's applied research has attracted great attention from the international community, and some achievements of applied research have been introduced many times by famous international media.

In terms of base construction, China has successively built national nano scientific research bases such as "National Nanoscience Center" and "National Engineering Research Center for Nanotechnology and Applications". In addition, about 40 regional or industrial nano research centers with different characteristics have been established one after another. In particular, universities or scientific research institutions and enterprises have jointly established some research centers aiming at application.

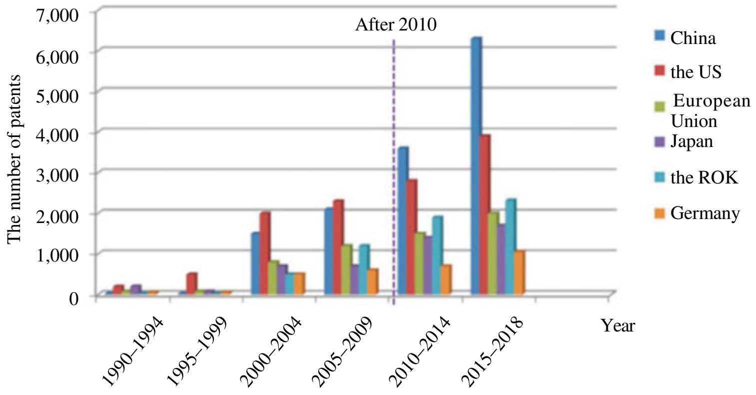

Fig. 2.3 Patent development trend funded by this Major Research Plan

2.3.3 Promotion of the Project to Nanomanufacturing in China

During the implementation of this Major Research Plan, it has always aimed at the forefront of international nanomanufacturing development, developed original new principles and methods of nanomanufacturing, and devoted itself to solving the bottleneck problem and "neck sticking" technology of nanomanufacturing in China. After 8 years of continuous support, several key scientific and technical problems related to precision improvement and batch manufacturing in the nanomanufacturing process have been solved, and the theoretical system and technical foundation of nanomanufacturing process and equipment have been initially established, providing the theoretical basis and technical equipment support for the consistency and batch of nanomanufacturing.

In the aspect of nanoprecision manufacturing, the principle of layered removal of atomic-level materials on nanoprecision surfaces are proposed and the theory of sub-nanometer surface precision control is available, which realizes the ultimate smooth surface polishing at the atomic scale, and systematically solves the common problem of surface manufacturing accuracy from nanoprecision to sub-nanometer and it has been applied to national strategic fields such as chip manufacturing and high-intensity laser mirror manufacturing, achieving wafer flattening and equipment autonomy in the chip manufacturing process.

In nanoscale manufacturing, the principle of nanoimprint fabrication with interface charge regulation is proposed, the principle of three-dimensional manufacturing induced by external fields, and the principle of high-precision controllable manufacturing of nanostructures with the self-constraint structure are explored, which solves the bottleneck of multiscale special-shaped nanostructure manufacturing technology. It has been applied to the fields of anti-surface icing of unmanned aerial vehicles, reversible adhesion films in space and the like, and effectively supports the development of related national defense and military fields in China. The principle and method have been applied to large-size capacitive touch screens, flat panel displays (ultra-thin light guide plates) and other fields, moving from laboratories to industrial applications, forming upstream and downstream innovation chains, and forming and giving birth to nanomanufacturing related industries in China.

In cross-scale manufacturing, a new principle of ultra-fast laser space–time shaping micro-nano machining is proposed, the precision transfer theory and the large-format consistent manufacturing theory in the manufacturing of large-format micro-nano structures have been established. The results have been applied to major national science/projects such as lens group assembly of 193 nm lithography machine, the ground test of spacecraft segment separation, and posture monitoring of off-axis parabolic mirrors in major national projects to support the smooth implementation of the national development strategy.

In terms of nanomanufacturing equipment, China has made great progress and gratifying achievements in nanomanufacturing equipment. From the import of the whole machine at the beginning of the project to the current independent equipment development, some core devices have been independently manufactured and 17 sets of independent equipment have been developed.

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Chapter 3
Nano/Sub-nanometer Precision Manufacturing

Bingheng Lu, Jianbin Luo, Zhongqun Tian, Dongming Guo, Han Ding, Changzhi Gu, Zhihong Li, and Ming Liu

Nanoprecision surface manufacturing has been widely used in many high-tech fields such as very large scale integrated circuit (VLSI) manufacturing and high-precision optical manufacturing, which provides strong support for the development of national defense, national economy, science and technology. Taking integrated circuit (IC) as an example, high-precision wafer processing and high-precision lithography objective lenses processing are two crucial technologies in IC manufacturing. For wafer surface manufacturing, the process with feature dimensions less than 14 nm requires that the wafer surface roughness *Ra* with a diameter of 300 mm reaches 0.1 nm, and the material thickness deviation should be controlled to the scale of 30 nm, i.e. 1/10 billion of the diameter, and the surface/subsurface has no damages and

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defects such as cracks, residual stresses and scratches; for the lithography objective lens, the lithography process with a feature dimension of 14 nm uses extreme ultraviolet (EUV) light with a wavelength of 13.5 nm, and its optical parts of the lithography system require full-frequency error control: the low-frequency surface error (the spatial period is 1 mm to the full aperture of the optical parts) must reach 0.25 nm RMS, the intermediate frequency roughness error (the period is 1 μm–1 mm) must be about 0.2 nm RMS, and the high-frequency roughness error (the period is less than 1 μm) must be less than 0.1 nm RMS. In other fields, such as substrate surface manufacturing in LED manufacturing and mirror manufacturing of high-energy lasers, their surface requires sub-nanometer roughness (*Ra* less than 0.2 nm) and nanometer surface precision (RMS less than λ/50). Therefore, a smooth surface with high flatness, extremely low surface roughness and few defects is a common requirement in the fields of microelectronics, optoelectronics and optical manufacturing. Especially, the requirements for surface precision and surface roughness are close to the physical limits, and breakthroughs in principles, technologies and methods of nanomanufacturing are urgently needed.

When traditional manufacturing represented by micron precision turns to nano/sub-nano precision manufacturing, the relevant theoretical basis will be dominated by molecular physics, quantum mechanics and surface/interface science. Basic research on key scientific issues is promoted, for example, the formation mechanism and control method of surface/sub-surface damage, the migration law of atoms/molecules in sub-nanometer precision surface manufacturing and its influence mechanism on micro-morphology, and the generation mechanism and control method of uniform convergence of macro and micro multiscale sub-nanometer precision, which is of great significance to reveal the scientific laws of nanoview and even atomic scale and promote the development of nanomanufacturing science.

3.1 Theoretical Model and Method of Atomic Layer Material Removal

In order to explore the removal mechanism of monatomic layer, the Tsinghua University Nanomanufacturing Research Team adopted the molecular dynamics method based on ReaxFF (reactive force field) to simulate the interaction process between silicon oxide particles and silicon materials in water environment during polishing, revealing the removal mechanism of silicon atoms and atomically layered materials [1–5], as shown in Fig. 3.1a and b. By tracking the bonding and bond breaking processes between atoms in the process of interface slip, it is found that there are mainly two removal paths for silicon atoms on the silicon substrate: the first one is caused by bond breaking of Si–O–Si chemical bonds on the substrate due to stretching, as shown in Fig. 3.1c; the second one is the Si–Si bond of the substrate, which is broken due to stretching, as shown in Fig. 3.1d. The research results lay a

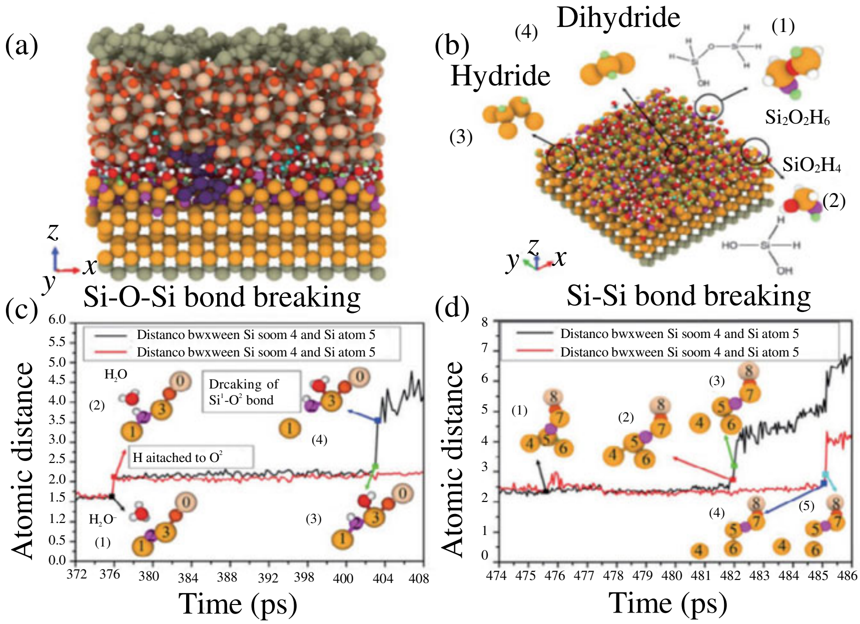

Fig. 3.1 Removal mechanism of silicon atoms and atomic layer materials (**a** Molecular dynamics model of ReaxFF [reactive force field]; **b** Surface reaction product; **c** Silicon atom removal path 1: Si–O–Si bond breaking; **d** Silicon atom removal path 2: Si–Si bond breaking)

theoretical foundation for accurate control of material removal in surface finishing [6].

It is very important to realize ultra-precision manufacturing with atomic precision in the process of nanoprocessing to develop the unique functions of nanoelectronic devices. Theoretically, the processing limit of semiconductor wafer materials is monatomic layer removal. In the past, traditional processing methods, such as diamond cutting and lithography technology developed later, could not reach the processing limit. Although atomic layer etching technology or focused ion beam assisted lithography technology can achieve atomic precision processing, it will bring problems such as surface chemical pollution or processed surface defects.

Southwest Jiaotong University cooperated with Tsinghua University Nanomanufacturing Team. Through quantitative experimental research, the layered removal law of monocrystalline silicon atomic-level materials was proved, and the energy threshold of atomic migration on the surface of monocrystalline silicon was quantified. Based on which, for the first time, extreme precision processing was realized on the surface of monocrystalline silicon materials without layered cleavage surface based on scanning probe technology, i.e. controllable removal of monolayer silicon atoms, as shown in Fig. 3.2a and b [1, 7]. This method without characteristics of chemical corrosion does not need mask, and could be directly operated by tribochemical reaction in common humid environment. Different from the wear, fracture and plastic deformation of materials in traditional machining, the tribochemical removal of atomic-level materials of monocrystalline silicon was mainly attributed to the stripping of matrix silicon atoms under the atomic bonding between sliding interfaces. Therefore, the subsurface crystal structure of the atomic layered material after removal remained intact, and there were no defects such as slip or lattice distortion, as shown in the Fig. 3.2c and d [8, 9]. In this study, direct evidence of atomic layered removal of monocrystalline silicon materials is given through high-resolution transmission electron microscopy observation, and the tribochemical stripping mechanism of silicon atoms is revealed by combining molecular dynamics simulation. The layered removal of wafer material originates from the stripping of silicon atoms on the substrate surface under the atomic bonding of sliding interface. In the process of layered removal of wafer materials, mechanical action reduces the energy barrier of Si–Si bond fracture, so the reaction rate and contact pressure of atoms between contact interfaces under friction induction satisfy the atomic removal model, namely Arrhenius equation [1].

The research on controllable removal of single-layer atoms in wafer materials based on tribochemistry has attracted international attention. The news platform of the American Association for the Advancement of Science and its journal *Science*

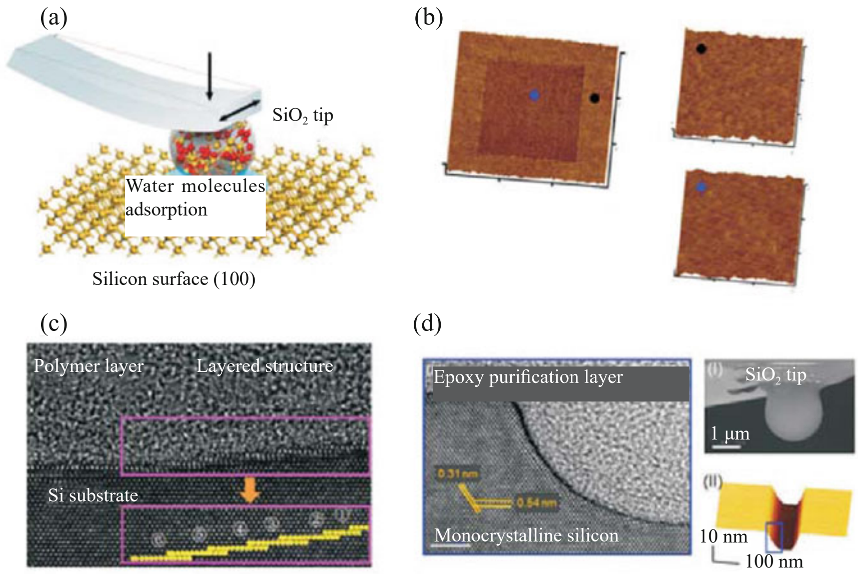

Fig. 3.2 Atomic layered removal of monocrystalline silicon (**a** A schematic diagram; **b** An AFM topography of a single primary lay removed on that surface of the monocrystalline silicon [100]; **c** TEM characterization result of layered removal of monocrystalline silicon material; **d** Tribochemical removal without damage)

made a special report on the topic “a simple method etches patterns at the atomic scale”, which was reprinted and reported by the American Chemistry Society, the German journal *MRS Bulletin* and the American Society of Tribologists and Lubrication Engineers in their official websites. Professor Nicholas Spencer (academician of Swedish Academy of Engineering), editor-in-chief of *Tribol Lett*, an internationally renowned journal, and Professor Wilfred Tysoe, former chief editor, jointly wrote an article on the topic of “tribochemical regulation of atomic topology” and evaluated the method as “precise control of deep etching of monatomic layer on the wafer surface, which can have a significant impact on other scientific fields”.

Based on the above research on atomic layer material removal mechanism, aiming at the problem that how to reduce defects, reduce the thickness of damaged layer and improve the thinning efficiency in wafer thinning, the ultra-precision machining technology research team of Dalian University of Technology, propose a high-speed scratch test method for single diamond particle nanocutting depth; develope a high-speed scratch device for single diamond particle nanocutting depth and a single diamond tool with nanocurvature radius; realize the high-speed scratch (>30 m/s) for nanocutting depth on the surface of monocrystalline silicon, and obtain ultra-long scratches (length-depth ratio $>10^5$) with continuously changing depth from 0–1 μm, as shown in Fig. 3.3; reveal the brittle-ductile transition of monocrystalline silicon and the evolution law of surface/subsurface damage in the grinding process, propose the judgment method of monocrystalline silicon ductile domain machining, establish the subsurface lesion depth model of single abrasive particle ductile domain cutting monocrystalline silicon, and determine the critical machining conditions for effective removal of monocrystalline silicon and ductile domain removal [10–14]; by analyzing the relationship between single diamond abrasive particle cutting and grinding and wheel grinding, as well as the relative motion among the grinding wheel, the abrasive particles and the workpiece in the grinding process, the relationships between the cutting depth of abrasive particles in the grinding process of wheel and the process parameters and the characteristic parameters of the grinding wheel are determined, the cutting depth model of abrasive particles of diamond grinding wheel and the prediction model of surface damage depth of silicon wafer grinding are established, and the selection method of grinding wheel characteristic parameters and grinding process parameters under the constraints of machining efficiency and surface lesion depth is proposed [15–19]. It is found that at the initial position of debris generation, the subsurface only contains an amorphous layer of 30–50 nm, determining the theoretical limit lesion depth of ultra-precision grinding of monocrystalline silicon with diamond grinding wheel, and developing two new low damage grinding wheels and ultra-precision grinding machines for monocrystalline silicon wafers. The damage depth of monocrystalline silicon grinding is less than 15 nm (ceria soft abrasive grinding wheel, material removal rate 1 μm/min) and 48 nm (ceria diamond composite grinding wheel, material removal rate 10 μm/min) is realized, and the surface/subsurface quality and material removal rate have reached the advanced level of similar products in the world [20–22].

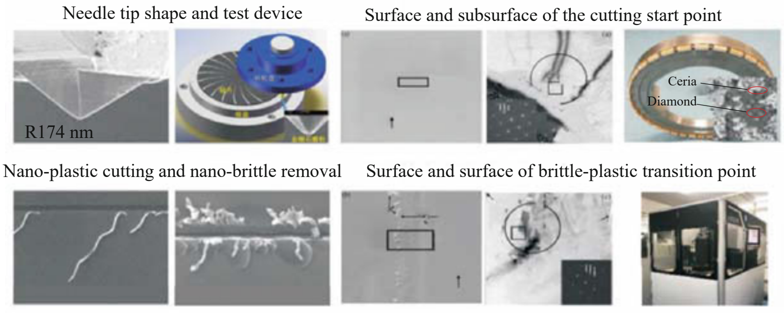

Fig. 3.3 High-speed scratching test method of single diamond nanocutting depth and developed new grinding wheel and silicon wafer ultra-precision grinder

The nanomanufacturing research team at Tsinghua University has achieved atomic scale extreme smooth surface polishing through chemical mechanical polishing technology. For hard and brittle materials such as sapphire and SiC, that the surface can be polished until atomic step morphology begins to appear, with step heights of 0.22 nm and 0.25 nm respectively, as shown in Fig. 3.4. After theoretical calculation, the step height is consistent with the atomic layer thickness simulated by theory, which shows that the surface roughness after polishing is close to the physical limit. For silicon substrate materials, an ultra-smooth surface of *Ra* 0.05 nm was obtained by optimizing the particle size of abrasive particles [23], and the technological principle of wafer-level deep sub-nanometer roughness surface manufacturing was popularized and established, and a processing technological method to realize large-size surface consistency and deep sub-nanometer surface roughness was established, which was applied to the fi of regenerated wafer manufacturing.

3.2 Important Engineering Application of Nanometer Precision Manufacturing

The ultra-precision machining team of the National University of Defense Technology has studied the sub-nanometer surface precision control theory, formed a method for converging the sub-nanometer precision error in the full frequency band, and realized that the full frequency band error of the lithographic objective lens is better than 0.3 nm [24, 25]. The influence law of tool characteristics [26, 27] and micro-area material characteristics [28, 29] on sub-nanometer precision surface generation is studied, and the nonlinear model of removal function and residence time compensation algorithm [30, 31] are established, as shown in Fig. 3.5a, b and c. This reveals the symbiotic mechanism of atomic/molecular material removal, flow and addition during ion sputtering, and realizes sub-nanometer surface precision machining and ultra-smooth surface machining [32, 33]. This is applied to

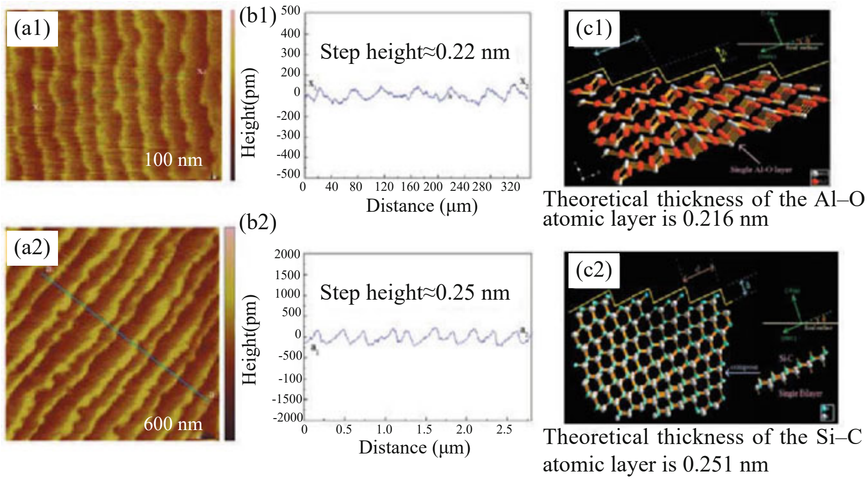

Fig. 3.4 Polishing step topography of ultra-smooth surface (**a1**–**c1** Sapphire substrate; **a2**–**c2** SiC substrate)

the self-developed process equipment, realizing the full frequency band error of low frequency 0.27 nm RMS, intermediate frequency 0.124 nm RMS, and high frequency 0.088 nm RMS, as shown in Fig. 3.5d, and solving the problem of processing the lens element of the lithography. Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences has developed a complete set of sub-nanometer precision ion beam polishing and smoothing polishing equipment, as shown in Fig. 3.6a and b, which is applied to the processing of the lithography objective lens of the 193 nm lithographic exposure system to successfully process into a sub-nanometer precision lithographic objective lens with the low frequency better than 0.5 nm RMS, the intermediate frequency better than 1.3 nm RMS and a high frequency better than 0.2 nm RMS. It is also applied to the development of the first set of NA0.75-ArF lithography projection objective lens in 2017, and the lithographic resolution better than 85 nm was obtained through the verification test of the whole machine exposure process, breaking through the core technical bottleneck restricting the development of high-end lithography in China, as shown in Fig. 3.6c.

For immersion lithography technology below 45 nm, the team of Zhejiang University has studied the key fluid behaviors and control methods that affect its exposure resolution and yield, and has made a series of innovative achievements in immersion fluid interface behaviors and their control, gas–liquid two-phase recovery flow and its modulation, immersion flow field distribution pattern detection and pollutant control, as shown in Fig. 3.7. On this basis, the immersion system, one of the four core components of the immersion lithography machine, was developed, the ultra-clean immersion liquid was prepared, which was controlled to fill between the final objective lens and the silicon wafer to play the role of a flowing disposable

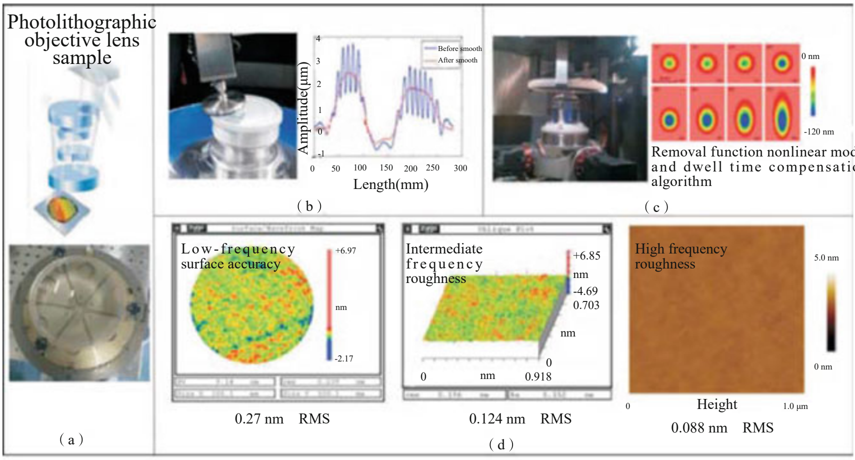

Fig. 3.5 Full-band sub-nanometer precision combination process of lithography objective lens (**a** A photolithographic objective lens sample; **b** Smooth polishing; **c** Ion beam modification; **d** Full-band surface error result)

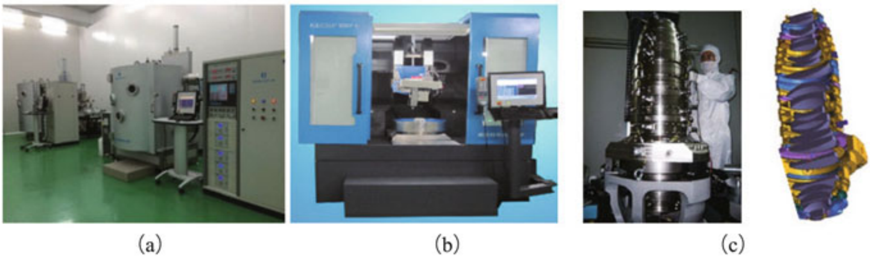

Fig. 3.6 Complete set of sub-nanometer precision processing equipment (**a** Sub-nanometer precision ion beam polishing complete set of equipment; **b** Smooth polishing complete set of equipment; **c** NA0.75-ArF lithography projection objective lens after processing and alignment)

liquid lens, thus effectively improving the numerical aperture and exposure resolution of the lithography machine. At present, the key performance indexes of the immersion liquid system prototype have been broken through so that the scanning speed reaches 600 mm/s, bubbles above 50 nm are effectively removed, and the total organic carbon of the immersion liquid is controlled below 1 ppb. Product development and competence construction of 28 nm immersion system is being carried out by this achievement with the support of "the National 02 Project" (the project of manufacturing technology and complete sets of technology for very large scale integrated circuits).

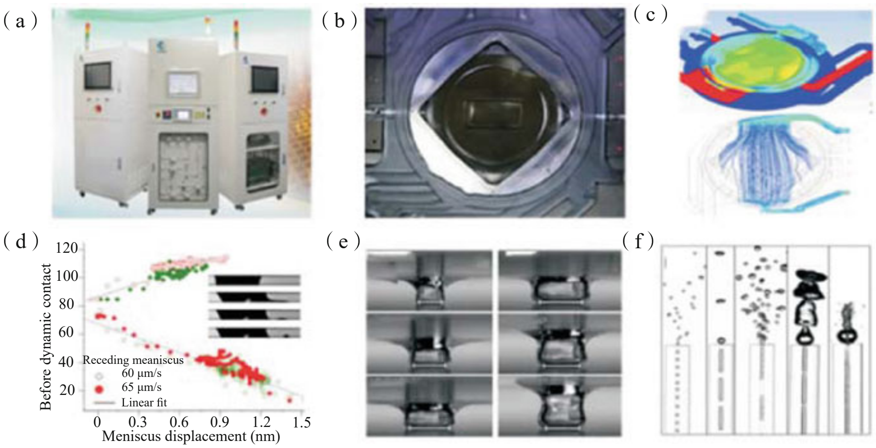

Fig. 3.7 Development of immersion system of lithography machine (**a** Immersion liquid treatment and delivery control system; **b** An immersion control unit; **c** Immersion flow field control; **d** Control of residual liquid membrane on the surface; **e** Air knife seal interface stability control; **f** Vibration control of gas–liquid recovery of immersion head)

3.3 Process Equipment for Nanometer Precision Manufacturing

In order to reverse the situation that China's nanoprecision manufacturing equipment has been subject to others for a long time, with the support of this Major Research Plan, around the theme of "nanoprecision manufacturing", a number of related research projects have been laid out in advance through deployment and cultivation, key support, integration and other forms, and a series of related technologies and equipment reserves represented by chemical mechanical polishing (CMP) equipment have been obtained. The Tsinghua University Nanomanufacturing Research Team has developed CMP equipment based on the surface sub-nanometer precision manufacturing theory and applied it to large integrated circuit production lines. After overcoming many key technologies such as multi-zone pressure control, endpoint detection, wafer transmission and post-cleaning [34–36], the first 12-inch "dry in and dry out" CMP equipment in China was developed. Through the transformation of scientific research achievements, commercial models such as Universal-300 series have been successfully launched, and they have successively entered Semiconductor Manufacturing International Corporation (SMIC), Intel, Yangtze Memory and other advanced integrated circuit production lines at home and abroad, as shown in Fig. 3.8a and b. By the second quarter of 2019, more than ten 12-inch CMP equipment had been sold cumulatively, and the mass production of wafers exceeded 800,000, with a value exceeding 400 million US dollars. Through the verification of various front and back key CMP processes such as STI, W, Cu, TSV, 3D NAND, Si, it can meet the

Fig. 3.8 Application of CMP equipment (**a**–**b** CMP equipment is applied to SMIC integrated circuit production line; **c** CMP equipment of Tsinghua University Research Group selected in "National 12th Five-Year Science and Technology Innovation Achievement Exhibition")

process requirements of 28–90 nm technology nodes, break the foreign monopoly, and effectively solve the problem that polishing equipment is subject to other people in chip manufacturing.

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Chapter 4
Consistent Manufacturing of Macro, Micro and Nano Cross-Scale Structures

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Nanotechnology is widely used in many fields such as information, optoelectronics, materials, environment, energy, biology, medicine and national defense security. Nanostructure is the functional carrier of almost all nano devices/products/systems, and its forming principle and method are one of the research focuses of nanomanufacturing. Taking a planar lens as an example, a lens with a thickness of only 1 μm can focus all kinds of light waves of any polarization state at one point, and its imaging performance is equivalent to that of a first-class complex lens system. The functional carrier of planar lens is its nanostructure, which is mainly characterized by "super pixel" structure with characteristic scale below tens of nanometers; nanostructured materials are functional materials, such as photoelectric materials like TiO_2; the scale of device or system level can reach more than tens of millimeters, ensuring

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large format consistency and morphology accuracy. Thus, the development of nanostructure manufacturing, not only does it stay in the nanoscale structure geometry forming of sacrificial materials (i.e., process auxiliary materials in the processing process, such as photoresist), but lies in various specific functional materials (i.e., the final working medium of the device or system), such as optical polymers, metals, low-dimensional nanocomposites, and semiconductors. Nanostructures with desired physical/chemical properties can be formed directly or through the shortest process chain within the area range of the device or system level scale. As one of the core processes of nanomanufacturing, "nanostructure imprint forming" technology needs to be efficient, economical, consistent and universal.

4.1 Principle and Method of Electric Field Driven Nano-imprint

Nanoimprint manufactures nanostructures using the concept of mold replication in the field of mechanical manufacturing. It is a typical technology for manufacturing large-format nanoscale structures. It has the advantages of low cost, high efficiency and high resolution, and has broad application prospects in microelectronics, optoelectronics, and characteristic structures and components. For conventional nanoimprint techniques, such as hot embossing, ultraviolet embossing, the filling of the mold plate cavity is realized by means of mechanical load and fluid pressure. As the size of the structure reduces, the ratio of the surface area to the volume of the structure cavity increases significantly, the external load required to overcome the wall resistance during the filling process rises sharply, and large imprint force will cause many problems, such as structural deformation of equipment system and mold, graphic structure defects, precision distortion, which will bring serious challenges to the high-precision manufacturing of nanostructures. It has been listed as the core bottleneck restricting the industrial application of nanoimprint by the International Device and System Technology Roadmap. In order to break through the technical bottleneck of nanoimprint, the research team of Xi'an Jiaotong University puts forward the principle and method of electric field-driven nanoimprint, which realize the filling efficiency of electric field regulation at liquid–solid interface, micro-shape control of multi-physical field cooperative control, and forming control of micro-nano structure electric field drive, thus breaks through the technical bottleneck of nanoimprint in principle.

4.1.1 Near-Zero Pressure Filling Principle of Electric Field Regulation at Liquid–Solid Interface

Wettability is the key factor affecting filling performance. Imprinting templates are typically characterized by low surface energy, with the purpose of reducing the release adhesion between the nanostructure and the template. However, this low surface energy characteristic often makes the filling material in a non-wetting state on the template surface, and the resulting surface tension additional pressure, liquid–solid interface resistance and other surface interface effects hinder rheological filling. The research team of Xi'an Jiaotong University proposed to reduce the interfacial tension coefficient of liquid–solid and improve the filling capacity by using the electric field regulation (i.e., electrowetting effect) of the wetting characteristics of solid–liquid interface. However, when the voltage increases to a certain extent, the change of wetting contact angle no longer follows Young-Lippmann theory, and presents a saturated state of contact angle, which seriously restricts the electric field regulation of interface wettability. Academia has speculated the internal mechanism of contact angle saturation from thermodynamics, electromagnetism and other perspectives, and put forward various hypotheses of contact angle saturation mechanism, but so far there is no direct evidence, and there is even less way to break through contact angle saturation [1].

The research team adopted the "frozen electron microscope" experimental method to solidify and freeze the liquid–solid interface into a solid–solid interface to eliminate the influence of liquid flow on the characteristics of the liquid–solid interface and study the original surface characteristics of the wetting interface through direct separation of the solid–solid interface as shown in Fig. 4.1a. With this experimental method, direct evidence of charge injection is found at the wetting interface, and it is found that the confined charge is the internal mechanism leading to contact angle saturation, that is, the confined charge prevents the contact angle from continuously decreasing with the voltage by shielding the external electric field, forming the saturation phenomenon of electrowetting. By adjusting the interface confined charge, an electric field modulation method in the super-wetting state is proposed, which reverses the shielding effect of confined charge into electric field superposition enhancement effect through transient switching of electric field polarity, breaking through the limitation of contact angle saturation, as shown in Fig. 4.1b. Relevant theories and methods are published in *Adv Mater* [2] in the form of cover papers. It is considered that electrowetting technology is widely used in the industrial field, but the traditional contact angle saturation limits its performance. The research team proposed a new method to break through the contact angle saturation limit by interface charge.

Based on the super-wetting characteristics of fluid under electric field, the research team has established an electric field-driven micro-nano structure cavity filling method. The method obtains a concave gas–liquid interface [2] in the template cavity through the super-soaking effect of fluid climbing along the wall surface at the gas/liquid/solid three-phase intersection boundary, reversing the wall surface

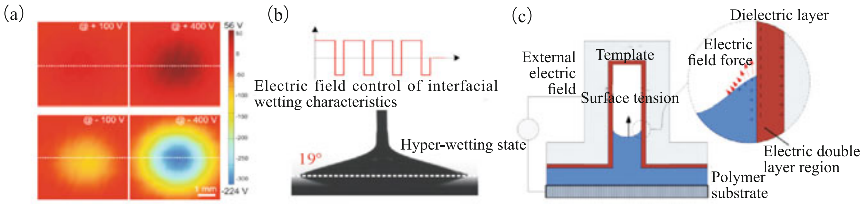

Fig. 4.1 Theory and method of "near zero pressure filling" for electric field regulation at solid–liquid interface (**a** Interfacial charge distribution during electrowetting; **b** Electric field regulation of interface wetting characteristics; **c** Schematic illustration of electric field driven filling)

action and the surface tension of the gas–liquid interface into filling power, as shown in Fig. 4.1c. The filling resistance of conventional nanoimprint mainly comes from solid–liquid interface resistance and gas–liquid interface surface tension, and its resistance increases significantly with the decrease of scale. Therefore, the reversal of the above-mentioned surface-interface interaction actually changes the size effect that restricts filling into the size effect that is beneficial to filling, thus solving the problem of nanostructured cavity filling from the principle and method. The team further clarified the dependence of the electrical characteristic parameters (thickness, dielectric constant, etc.) of the dielectric layer on the surface of the conductive template and the characteristic parameters (viscosity, dielectric layer constant) of the filling material on the amplitude, frequency, waveform, duty cycle of the working voltage. The process parameter system of electric field driven nanoimprint is enriched, and the manufacturing of nanoscale structures (minimum linewidth 15 nm), high aspect ratio structures (aspect ratio larger than 10) and cross-scale structures are realized.

Compared with the conventional nanoimprint methods in the world, the electric field-driven nanoimprint method starts with the electric field regulation mechanism of interface wetting characteristics. It completely abandons the traditional idea that the conventional imprint filling process depends on external load, eliminating the influence of mechanical load on the forming process, and providing a theoretical basis for near zero pressure manufacturing of high precision structures, high aspect ratio structures and brittle substrate surface structures [3]. The principle and method are considered by international scholars as discovering the charge confinement mechanism of the liquid–solid interface, breaking through the contact angle saturation limit of electrowetting, effectively accelerating the filling of the cavity by fluid, and the manufacturing capability of its high aspect ratio structure breaking through the performance limitation of planar devices [4–7]. The theory and method of filling synergy controlled by electric field at liquid–solid interface have solved the basic problems in nanostructure imprint manufacturing, such as high fidelity complex, functional material completion filling, brittle structure surface near zero pressure imprint forming, effectively promoting nanoimprint from laboratory to engineering application.

4.1.2 Micro-shape-Control Method for Multi-physical Field Cooperative Control

The dielectrophoresis characteristics of fluids make it possible to manufacture complex micro-nano structures. Under ideal conditions, the corresponding structure can be obtained by controlling the electric field distribution on the fluid surface. However, unlike the ideal state, there is usually microscopic disturbance on the surface of thin film fluid, which seriously affects the morphology evolution of thin film fluid under electric field and increases the difficulty of rheological control. How to restrain and eliminate the influence of microscopic disturbance on structural evolution behavior is the premise and key to realize shape-controlled manufacturing.

The research team of Xi'an Jiaotong University discovered the evolution mechanism of each disturbance component of thin film fluid under uniform electric field, observed the electric field enhancement phenomenon of specific disturbance wavelength, and clarified the inherent law of single wavelength enhancement of thin film disturbance; the team also found the regulation mechanism of the spatial structure electric field on the microscopic disturbance of the thin film fluid, clarified the competitive relationship between the average component and modulation component of the space electric field on the flow of thin film fluid, and established the space electric field strength-weak modulation criterion for the evolution of micro-nano structure morphology, which realized the comprehensive suppression of each component of micro-disturbance and eliminated the influence of micro-disturbance on the rheological forming process [8], as shown in Fig. 4.2a and b. The discovery of the mechanism of enhancing and suppressing fluid disturbance by electric field lays a theoretical foundation for electrorheological forming of complex structures.

Based on the control law of electric field on thin film fluid and the constraint characteristics of template, the team established a manufacturing method of special-shaped micro-nano structure controlled by template, electric field and their cooperation. On the basis of completion filling of complex structures, the concept of lost

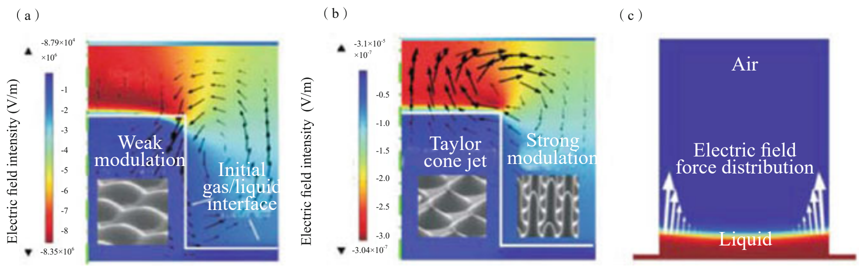

Fig. 4.2 Micro-shape-control mechanism of multi-physical field cooperative control (**a** Weak modulation mechanism of space electric field on capillary disturbance; **b** Strong modulation mechanism of space electric field on capillary perturbation; **c** Control mechanism of gas–liquid interface morphology in microcavity)

foam injection molding is introduced into the imprint shape control manufacturing field of complex structures, and a scalable manufacturing method that can accurately define the morphology of complex micro-nano structures is established [9]; the microstructured conductive template is used to enhance the modulation component of the spatial electric field, suppress the influence of thermal disturbance wave on the liquid film rheological forming process, and realize accurate and batch shape control manufacturing of various complex special-shaped micro-nano structures [10, 11]; the inhomogeneity of the force acting on the gas–liquid interface in the micro-nano cavity by the electric field is used to accurately control the curvature of the gas–liquid interface [12], as shown in Fig. 4.2c.

Compared with the conventional nanoimprint methods in the world, the micro-shape control mechanism of multi-physical field cooperative control proposed by the team, based on the mechanism of electric field on fluid rheological behavior, a control method system of template, electric field and their cooperative control of micro-nano structure micro-morphology was constructed, which broke through the problem of single structure morphology in conventional imprint technology, provided an innovative way for scalable manufacturing of special-shaped micro-nano structure, and expanded the forming capability of nanoimprint. This is considered by international peers to have the ability to realize a variety of innovative structure manufacturing and it is an innovative method that can effectively control the shape and size of structures, solving the challenge of high-precision three-dimensional structure manufacturing, and scalable manufacturing is the core of this method [13–16].

4.1.3 Forming Control Mechanism Driven by Electric Field of Micro-nano Structure

It is a very challenging problem in manufacturing technology to control the crystal structure, molecular orientation and other material properties while forming the structure, and it is also the ultimate goal pursued by manufacturing disciplines. In 2009, *Nat Mater* reported a work of preparing ferroelectric nanostructures with orientated molecular chains by using imprint filling shear rheological effect, opening an attempt to manufacture functional nanostructures by nanoimprint forming control [17]. However, conventional nanoimprinting is difficult to meet the actual requirements of forming and controlling manufacturing of special functional structures. The shear rheological effect is weak when large-size structures are filled, and secondary treatment is required to meet the requirements of material properties; multi-step process increases the complexity of manufacturing. Reducing the structure size can enhance the shear effect, but small-sized structures are not only difficult to fill, but also limit the selectivity of device design. Therefore, it is an important challenge for nanoimprint to realize the shape-controlled manufacturing of micro-nano structures in a large size range.

In order to break through the basic theoretical problems of nanostructure forming controlled manufacturing, the research team of Xi'an Jiaotong University systematically studied the evolution law of functional materials in the process of electric drive filling, revealed the mechanism of the applied electric field on the molecular orientation of functional materials in the rheological process [18], and found the preferred orientation characteristics of the internal components of functional materials under the coupling effect of template constraint and electric field polarization [3, 19]; using template constraint and electric field polarization effect, a forming-controlled imprint method of functional structure was established, and the unity of structure forming and crystal orientation was realized [3, 18, 19]. This method breaks through the limitation of the traditional imprinting process on the structure size and lays a theoretical foundation for the direct imprinting manufacturing of special functional structures, as shown in Fig. 4.3a.

The research team of Xi'an Jiaotong University adopts the electric driven forming control method, in-situ enhancement of β crystal phase orientation in polymer piezoelectric material structure is realized, the problem of in-situ forming control manufacturing of high-performance piezoelectric devices is solved, and the sensitivity of flexible sensors is improved by nearly one order of magnitude, as shown in Fig. 4.3b. The prepared arrayed sensors can quickly detect dynamic force trajectories and display stress state distribution in real time, as shown in Fig. 4.3c and d. The electrowetting properties of fluid also make it possible to encapsulate special functional structures in situ, and while the functional structure is manufactured with shape control and property control, the reliable connection between the piezoelectric

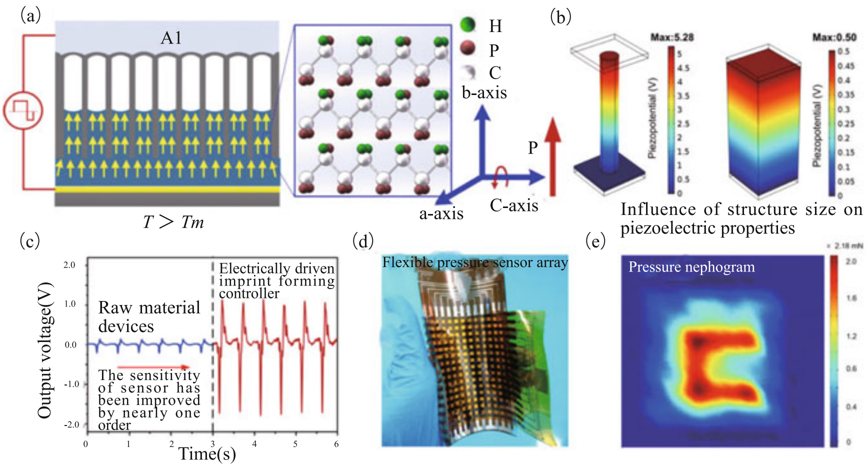

Fig. 4.3 Principle and method of forming controllability driven by electric field of micro-nano structure (**a** An electrically driven nanoimprint forming control schematic diagram; **b** Electrically driven nanoimprint improves sensitivity of the sensor by an order of magnitude; **c** Arrayed flexible pressure sensor objects; **d** Arrayed sensor pressure nephogram; **e** In-situ manufacture of curved surface structure functional integration force/thermal sensing unit)

microstructure and the functional electrode is realized in situ by the electrowetting effect, solving the steady problems such as unstable electrical connection between the sensing structure and the electrode, easy wear and the like in the packaging process of the piezoelectric sensor, and providing a new way for the manufacture of high-performance flexible sensing electronics [18]. Related work was selected as the cover papers of *Small, Nanoscale* and *J Mater Chem C*, and the hot papers of *British Chemical Society*, and was introduced by Wiley Publishing House as a video summary, which was considered as an amazing experimental result. Electric field-driven nanoimprint method has attracted extensive attention from experts at home and abroad. It is considered as an innovative way to manufacture functional devices. It has in-situ control capability and significantly improves device performance [20–22]. The principle and method of forming controllability driven by electric field of micro-nano structure solve the problem of forming controllability manufacturing of micro-nano functional structure, and provide theoretical support for in-situ manufacturing of high-performance sensors and three-dimensional curved surface sensing circuits.

Focusing on the principle and method of electric field regulation in nanoimprint process, the research team of Xi'an Jiaotong University started from the surface-interface regulation mechanism of rheological filling process, found the influence mechanism of solid–liquid interface charge on the wetting characteristics and filling behavior of fluid, and expounded the microstructure morphology control method constrained by multiple physical fields, and revealed the in-situ preferred orientation law of functional material molecular chains in the process of electric field driven forming. Finally, an electric field-driven nanoimprint method system with three dimensions of near zero pressure filling, micro-shape control and structural formation is formed, the theoretical model and method of the third generation nanoimprint are established, which solves the three major problems that restrict the filling, shape control and formation of nanoimprint, pushes nanoimprint to a new height of precise manufacturing, shape control manufacturing and formation manufacturing of nanostructures, and provides principle and method guarantee for nanoimprint to truly move towards engineering application.

4.2 Principles and Methods of Electrochemical Nano-imprinting of Semiconductor Materials

Nanoimprint lithography can replicate high-precision micro-nano structures in a large area. Because of its advantages of ultra-high resolution, high throughput and low cost, it is a potential industrialization technology. However, conventional nanoimprint lithography is mainly suitable for the imprint forming of thermoplastic and light-curing materials. Generally, subsequent pattern transfer is required to realize the nanostructure of semiconductor wafer materials in integrated circuits, micro-electro-mechanical system (MEMS), photovoltaic, optoelectronic and other industries. The pattern transfer process involves wet and dry etching, etc., with high cost and complex process. In order to achieve direct imprinting of semiconductor materials, the research team of Xiamen University combines the principle of local electrochemical corrosion induced by contact potential with the working mode of nanoimprint, and proposes an electrochemical nanoimprint lithography (ECNL) based on the principle of contact potential-induced semiconductor local etching. Through the removal of electrochemical etching, three-dimensional micro-nano structures can be directly processed on the surface of semiconductor wafers without using thermoplastic or light-curing media. At the same time, it has the advantages of high precision, high efficiency, and batch manufacturing. In order to improve the processing accuracy, processing efficiency and material application range of ECNL, the physical external field cooperative modulation technology has been further developed, and a new nanoimprint micro-nanomanufacturing method has been formed, which is of great significance for the functionalization, device-based and batch manufacturing applications of semiconductor materials.

4.2.1 Principle and Method of Electrochemical Corrosion Induced by Contact Potential

Conventional nanoimprint lithography involves the process of transferring nano patterns to semiconductor materials for etching, in which reactive ion etching and other processes are easy to cause surface and subsurface damage of etched structures [23]. Laser-assisted nanoimprint lithography can directly prepare micro-nano structures on the surface of Si wafers by rapidly melting the surface of Si wafers with high-power pulsed laser and using quartz template for high-pressure forming, but only shallow grain structures can be obtained, and they are not suitable for brittle and flexible materials [24]. Electrochemical stamping technology of quasi-solid and solid electrolytes can also realize direct forming of semiconductor structures, but it is limited by gel or superionic conductor electrolyte materials and their applicable metal workpiece materials, and there are technical problems to be solved urgently in processing accuracy, efficiency and controllability [25, 26]. It has always been a very challenging problem to develop a batch manufacturing technology of large-format 3D micro-nano structures directly on the surface of semiconductor functional materials under normal temperature and pressure without light curing, thermoplastic medium and any auxiliary process.

For this reason, the research team of Xiamen University proposed an electrochemical nanoimprint method for semiconductor materials [27, 28]. According to the basic principle of solid physics, when the thermodynamic equilibrium state is reached, the Fermi energy levels of two-phase electrons in arbitrary contact are equal; however, due to the difference of electron work function between the two phases, electron transfer will occur at the interface, thus establishing contact electric field and contact potential at the interface between the two phases. As shown in Fig. 4.4, the polymethyl methacrylate (PMMA) three-dimensional micro-nano structure template with metal Pt nanofilm deposited on the surface is pressed on the surface of the semiconductor n-GaAs workpiece [Fig. 4.4a], and a certain pressure (0.5 atm) is maintained to form effective contact [Fig. 4.4b]. Due to the difference in electron work function between the two, electrons on the n-GaAs side will be transferred to the metal Pt side [Fig. 4.4d and e]. The electron accumulation on the Pt side of the interface will increase the barrier of electron migration on the n-GaAs side until the Fermi energy levels of the two phases are equal and finally reach thermodynamic equilibrium. At this time, a contact electric field is formed at the interface between the metal Pt and the n-GaAs, and a contact potential is established, wherein the interface Pt side is positively charged, and the n-GaAs side is negatively charged. In the H_2SO_4 and $KMnO_4$ solutions, MnO_4 will transfer electrons on the Pt side to undergo a cathodic reduction reaction, thereby promoting the electron on the n-GaAs side to continue to transfer to the Pt side, and the anodic dissolution reaction [29] will occur on the n-GaAs side due to hole accumulation, and then completing the entire corrosion galvanic reaction: Pt cathode; n-GaAs anode.

As the etching reaction progresses, once Pt and n-GaAs lose effective contact, the etching reaction stops immediately. Therefore, the contact potential-induced n-GaAs etching reaction strictly and spontaneously proceeds along the Pt/n-GaAs/electrolyte solution three-phase interface, only effective contact needs to be formed, and no external energy injection is needed. The machining accuracy depends on the rate of n-GaAs etching reaction and the diffusion coefficient of holes on the n-GaAs surface [$\delta = (D/k)^{1/2}$, D: the diffusion coefficient of holes, k: etching rate], and theoretically does not exceed the Debye length of the space charge layer [27].

Since the occurrence of the reaction requires an effective contact force, the research team of Xi'an Jiaotong University and the research team of Xiamen

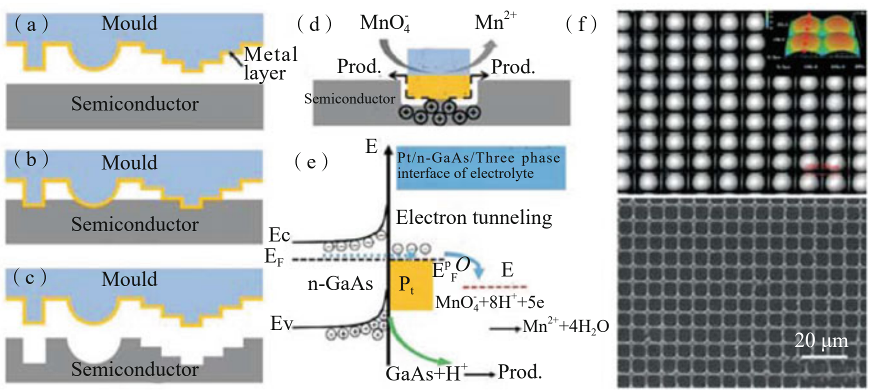

Fig. 4.4 Schematic diagram of electrochemical nanoimprinting lithography (ECNL) principle (**a**)–(**e**) and direct imprinting of semiconductor three-dimensional structure (**f**)

University jointly put forward the working mode of nanoimprinting, verifying the application of contact potential-induced semiconductor local etching principle in micro-nano processing of semiconductor crystals. Using MnO_4 as electron acceptor, three-dimensional micro-nano structures are processed on the surfaces of semiconductor wafers such as n-GaAs, p-GaAs, p-GaP and n-Si [Fig. 4.4f], thus proposing and developing electrochemical nanoimprint lithography [30, 31]. Relevant work is published in journals such as *Chem Sci*, *Nanoscale* and *Electrochem Commun*, and research papers are selected into the flagship journal *Chem Sci* 2017 Chinese New Year Special Edition of Royal Society of Chemistry; selected into *Chem Sci 2019 HOT Article Collection*, the flagship journal of Royal Society of Chemistry. Many international research teams have conducted follow-up research on the direct imprinting technology of semiconductor materials, which has attracted wide attention and recognition from international peers.

4.2.2 Principle and Method of Cooperative Modulation of Electric Field, Light Field and Force Field for Electrochemical Imprinting

The key scientific problem of electrochemical micro-nanomanufacturing is to restrict the electrochemical reaction within the micro-nano scale, and its technical problem is to realize the mass transfer and potential distribution in the large-format and ultra-thin electrolyte layer. In recent years, around the key scientific problem of confined etching, the research team of Xiamen University has developed a series of physical external field modulation technologies based on force, light and electricity, which can more accurately control the electrochemical reaction rate and spatial resolution, improve the processing accuracy and efficiency of electrochemical nanoimprint lithography, broaden the range of its applicable materials, and gradually improve this new nanoimprint micro-nanomanufacturing method.

Light field accelerated electrochemical nanoimprint is based on the photoelectric effect principle of semiconductor, that is, when the semiconductor wafer is irradiated by light field, the valence band electrons are stimulated to transition to the conduction band, generating holes and electrons on the valence band and the conduction band respectively, enhancing the contact electric field between the semiconductor and the Pt metallized template electrode, and improving the contact potential of Pt/semiconductor interface, thus accelerating the electrochemical etching rate of semiconductor. As shown in Fig. 4.5, when Pt is in contact with n-GaAs, a light field is introduced to irradiate the back surface of n-GaAs, and when the injected light energy is greater than the band gap Eg of GaAs, n-GaAs absorbs photons to generate electron–hole pairs, thus improving the contact potential of the

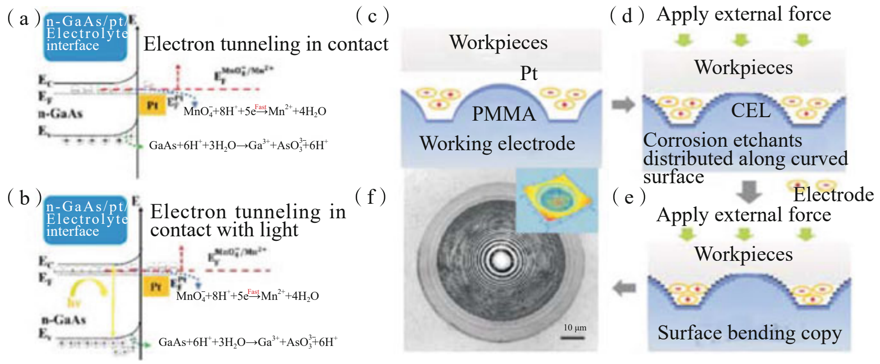

Fig. 4.5 Three-phase interface energy levels when platinum imprint template and n-type gallium arsenide are contacted under **a** Dark state and **b** Illumination conditions; **c–e** Schematic of electrochemical buckling micromachining process; **f** A multi-stage coaxial nano-ring structure obtained by processing

metal/semiconductor interface, increasing the polarization of the Pt/solution interface and the n-GaAs/solution interface and accelerating the corrosion rate of n-GaAs [32]. Under illumination, the electrochemical imprinting efficiency of n-GaAs three-dimensional microstructure is increased by more than 2 times.

The research team of Xiamen University further explained the force field regulated buckling effect in electrochemical nanoimprint lithography. Due to the difference of elastic modulus between Pt metallized nanofilm and PMMA micro-nano structure template, stress instability occurs under the action of force field, resulting in various ordered buckling patterns. By constraint etching, micro-nano multilevel structures produced by buckling effect can be copied to the surface of semiconductor wafer. As shown in Fig. 4.5c, firstly, a 100 nm thick Pt conductive layer is sputtered on the surface of PMMA convex hemispherical template by magnetron sputtering to form a double-layer structure with difference in elastic modulus, and then a constant contact force is applied between the template electrode and the workpiece. At this time, the top of the double-layer structure on the template electrode is subjected to compressive stress, and the stress is transmitted from the top to the elastic substrate along the convex hemisphere. When the compressive stress exceeds the critical buckling stress of the structure, according to the principle of minimum energy, the internal stress is released on the surface of the template by buckling fold, and a coaxial nano-ring fold pattern is formed on the convex hemisphere [Fig. 4.5d]. After that, an optimized constrained etching solution system is added and a certain potential is applied to the template electrode to generate etchant. The fold pattern generated on the template surface can be copied to the workpiece surface with high fidelity through the constrained etchant layer technology [Fig. 4.5e]. With the continuous etching and the continuous feeding of template electrodes, multi-stage coaxial nano-rings distributed on the concave hemisphere surface are finally obtained on the workpiece surface [Fig. 4.5f]. The method is electrochemical buckling processing. Through the electrochemical buckling processing method, micro-nano multilevel structures with characteristic sizes less than 50 nm can be processed on the semiconductor surface [33].

4.3 Imprinting Manufacturing Equipment for Large-Format Nanoscale Structures

Nanostructures are the functional carriers of optoelectronic devices. Large-scale manufacturing of micro-nano structures with specific materials, sizes, morphology and periodic distribution is the key to promote the development of micro-nano electronic devices. Nanoimprint has the advantages of low cost and high precision, which provides good technical support for the manufacture of large-format nanoscale structures. However, different micro-nano structure manufacture puts forward different manufacturing requirements for nanoimprint lithography, such as multiscale structure manufacture, macro-volume fabrication, and non-flat substrate manufacture. For this reason, the research teams of Xi'an Jiaotong University and Suzhou University put forward the principle of gas-electricity cooperative control nanoimprint lithography, developed general manufacturing equipment, and solved the problem of nanopatterning of wafer-level non-flat substrate surface/brittle substrate surface; at the same time, a roll-to-roll continuous roller imprint equipment for nanostructure macro-scale manufacturing has been developed to realize large-scale manufacturing of ultra-long and ultra-precision metering gratings, ultra-thin light guide plates and flexible transparent conductive films. The imprint manufacturing equipment with large-format nanoscale structure has promoted nanoimprint from laboratory to engineering application.

4.3.1 Roll-to-Roll Continuous Roll Imprint Equipment

Nanoimprint technology has attracted wide attention from academia and industry because of its high efficiency, large area, high resolution and low cost, and has been applied to integrated circuits, optoelectronic devices, energy storage and other fields. In order to meet the requirements of continuous imprinting and high yield in industrial production, researchers prepare nanostructures on rollers, so that imprinting and demoulding are continuously alternated, and continuous imprinting of graphical structures is realized, that is, roll-to-roll roller imprinting technology. Because the template is in linear contact with the substrate during imprinting, this method avoids the problems of nanostructure deformation and non-uniformity caused by factors such as uneven stress. Compared with planar nanoimprint lithography, the method has the advantages of continuous preparation, simple structure, low cost, high yield, good reliability and the like, and has realized technology iteration and industrial upgrading in nanomanufacturing fields such as large-format metering gratings, ultra-thin light guide plates, transparent conductive films and the like. However, roll-to-roll imprinting has always been a challenging subject in the transfer and replication of complex micro-nano structures across scales, the transfer of nanostructures on warped substrates, and the high-fidelity transfer of nanostructures with high aspect ratio.

The research team of Xi'an Jiaotong University and the research team of Suzhou University have developed key equipment for multiscale roll-to-roll nanoimprint, realizing manufacturing with fidelity and efficiency of multiscale structural features [34]. The cross-scale micro-nano structure on the metal mold is copied to metal, glass, polymer and other substrates with high fidelity, realizing the fast roll-to-roll micro-nano structure transfer with multiscale structure features of the line width of 100 μm–100 nm, the fidelity reaching 95%, with the continuous imprint of 24,000 m/plate, the width of 1,200 mm, and the working speed of 60 m/min. Seamless twin-roll compensation nanoimprint can be realized through tension, constant temperature, pressure, coating (0.5–1 μm), deformation servo, etc., as shown in Fig. 4.6. This scheme is a new micro-nano imprint mode, which solves the technical problem that traditional roll-to-roll imprint is difficult to manufacture multiscale complex micro-nano structures.

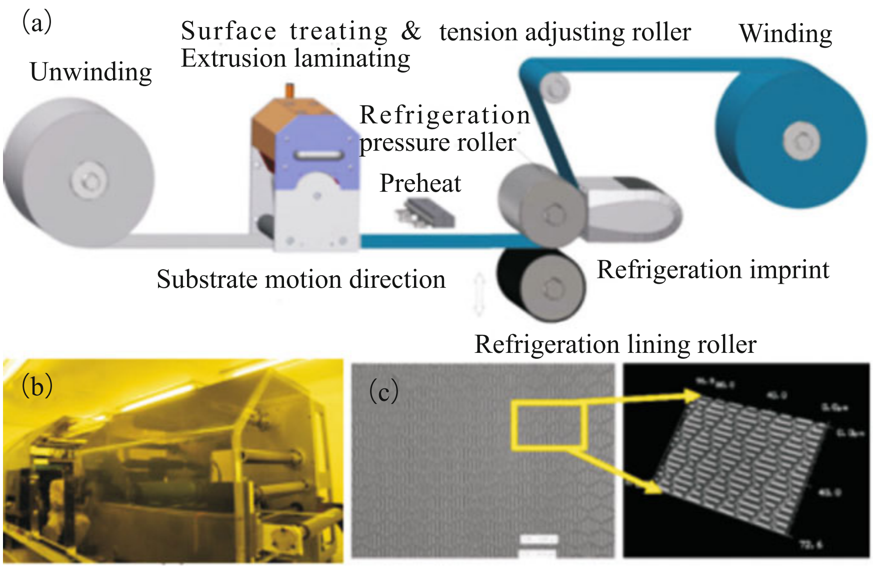

Fig. 4.6 Key equipment for multiscale roll-to-roll nanoimprint (**a** Multi-scale roll-to-roll nanoimprint principles; **b** Imprint equipment physical objects; **c** Large-area antibacterial/drag-reducing film imitating shark skin)

The roll-to-roll continuous roller imprint equipment technology developed by the research team of Suzhou University has been successfully applied in the fields of large format grating, display lighting and so on, and has produced important social and economic benefits. With this team, a double-sided nanoimprint production line was established, which realized the manufacture of ultra-thin light guide devices, replaced the traditional injection molded light guide plate, saved energy by 2.2 million kW·h/year, and reduced carbon dioxide emissions by about 2.2 million kg per year. The ultra-thin light guide plate with high light efficiency (600 mm × 1,200 mm) has gradually replaced the printed light guide plate, reducing the amount of ink used by 7,500 kg per year, avoiding the use of ketone-containing harmful substances and becoming a disruptive alternative technology in the industry.

4.3.2 Wafer-Level Gas-Electricity Cooperative Nanoimprint Equipment

Although nanoimprint technology has the advantages of high resolution and low manufacturing cost, which has been highly expected by academia and industry, nanoimprint faces many technical challenges in fabricating nanostructures on the surface of uneven and brittle wafer-level semiconductor substrates. First of all, with the expansion of wafer size, the conformal contact difficulty between the mold and the warped/non-flat substrate gradually increases, which easily leads to bubble limitation. For example, the peak and valley value of the surface shape of a 4-inch LED epitaxial wafer exceeds 150 μm, and the conformal contact between the mold and the substrate is extremely difficult. Secondly, thinness, brittleness and fragility are the common properties of most types of semiconductor wafer substrates. Mechanical force loading process is easy to damage wafer substrates/templates. How to avoid template/substrate damage caused by mechanical pressure is another difficult problem in nanoimprint application to semiconductor substrate imprint. Finally, nanoimprint, as a lithographic technique, the thickness uniformity of the underlying residual film of the imprint structure directly affects the uniformity of subsequent pattern transfer. However, the warpage/unevenness of the substrate and the nonuniformity of local imprint stress are easy to cause the nonuniformity of the residual film thickness. How to maximize the uniformity of the residual film thickness of the imprint structure is another challenge for nanoimprinting on the surface of non-flat substrates.

In order to solve the problem of patterning the whole nanoimprint lithography of brittle and non-flat wafer substrates, the research team of Xi'an Jiaotong University has proposed the principle and equipment of gas-electricity cooperative control nanoimprint [35], as shown in Fig. 4.7a, in which "gas" refers to the partition control of flexible mold through the switching of vacuum and positive pressure states of air grooves distributed in parallel on the air valve plate; "electricity" refers to that introduction of an applied electric field between the flexible transparent conductive mold and the substrate to drive the contact process between the mold and the substrate. The gas-electricity cooperative control nanoimprint system comprises two core contents, namely, a flexible transparent conductive mold and an air valve plate, wherein the flexible transparent conductive mold is fixed on the air valve plate through vacuum adsorption, parallel to the surface of the wafer substrate and retains a certain gap; then, starting from one side, the air tank is gradually switched from vacuum to positive pressure state, the mold is released, and the mold gradually forms contact with the surface of the wafer substrate under the action of electric field, and the contact area is continuously expanded; the flexible transparent conductive mold is completely spread on the whole wafer surface, and the micro-nano structure cavity on the mold surface is completely filled with liquid imprint glue under the action of electric field; keep the electric field, and the imprint glue is irradiated and cured by ultraviolet light; finally, the electric field is cut off, the air tank is gradually cut back to the vacuum state from one side, and the flexible mold is uncovered from the wafer surface to complete demoulding.

The sub-region step-by-step control strategy ensures the contact uniformity between the flexible mold and the substrate, avoids the bubble defect caused by the local convexity and concavity of the substrate during the contact line closing process, and realizes the complete contact between the flexible mold and the wafer substrate surface. Because the force driving the flexible transparent conductive mold to spread on the surface of the wafer is mainly composed of two parts, it can be modulated by the applied electric field [36, 37], so compared with the traditional mechanical load or natural capillary driving force, the electroinduced driving force

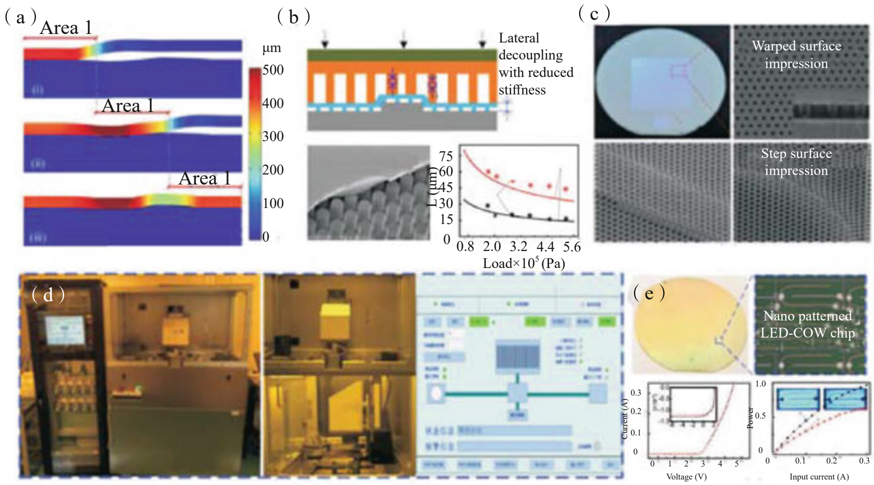

Fig. 4.7 Principle, equipment and application of gas-electricity cooperative nanoimprint lithography (**a** Finite metacomputing of conformal contact on non-flat surfaces; **b** The adaptability of the discrete support template to the surface of the step substrate; **c** Photonic crystal nanostructure imprint on a wafer-level non-flat substrate surface; **d** Gas-electricity cooperative nanoimprint equipment; **e** Imprint of photonic crystal structure on that surface of the LED chip)

can be flexibly adjusted through the adjustment of the applied electric field parameters, which can provide driving force for the bonding of the flexible mold on the wafer surface. More importantly, electroinduced liquid bridge force or electrostatic attraction force is a form of surface force, which avoids the mechanical pressure load in the imprint process and fundamentally avoids the stress failure of wafer. At the same time, after the flexible transparent conductive mold is completely in contact with the wafer, the electrostatic attraction sensitive to the distance between the polar plates continues to regulate the contact state between the two, further driving the liquid imprinting glue to continue rheology until the micro-morphology of the imprinting glue surface conformal to the morphology of the wafer substrate under the constraint of the flexible mold.

Based on the principle of gas-electricity cooperative control of nanoimprint, Xi'an Jiaotong University has developed surface nanoimprint lithography manufacturing equipment for 4-inch brittle non-flat substrates, as shown in Fig. 4.7b, and designed a flexible transparent conductive mold based on ITO and silver nanowire grid composite electrode [38]. The accuracy of gas-electricity cooperative nanostructure imprinting is better than 100 nm, the manufacturing efficiency of nanostructures on the surface of a 4-inch substrate exceeds 40 sheets/hour, and the adaptable substrate warpage exceeds 200 μm. The nanopatterning of photonic crystals on the surface of LED warped epitaxial substrate is realized by using gas-electricity cooperative control of nanoimprint lithography equipment, and the non-uniformity deviation of the thickness of the bottom film left by the nanopore structure in different regions is less than $\pm 1\%$ of the overall thickness of the adhesive layer. Combined with discrete support mold, as shown in Fig. 4.7c; nanopatterning of the surface of the raised substrate containing contaminated particles and even micro-steps is realized, as shown in Fig. 4.7d; on this basis, an LED chip brightness enhancement process with good compatibility with the LED chip industry process is further developed, which increases the luminous efficiency of the industrial chip by 41.6% compared with that before graphing, as shown in Fig. 4.7e.

4.4 Engineering Applications of Functionalized Large Area Nanostructures

Based on the research of new principles, new methods and new equipment for the manufacture of functionalized large-area nanostructures, focusing on the demand for functional nanostructures such as basic components in the field of high-end manufacturing, key equipment and forward-looking technologies in the field of national defense, and high-end product development in the field of people's livelihood, the research team of Xi'an Jiaotong University and the research team of Suzhou University has formed prototypes and products with independent intellectual property rights in large-format precision metrological gratings and their sensors, space reversible adhesion films, and large-format high-end displays, and part of the mass manufacturing has been realized, which has made beneficial exploration for principle innovation, technological breakthrough and industrial promotion in the field of nanomanufacturing in China, and has provided technical support for the development of original technology of nanomanufacturing in China.

4.4.1 Ultra-Long Metrological Grating and Its Engineering Application

Precision reflection grating has become a key displacement sensing component in ultra-precision measurement, aerospace, high-end manufacturing equipment and other fields because of its advantages of high precision, good environmental adaptability and compact structure. For example, facing the field of intelligent manufacturing, the aperture requirement of optical aspheric elements for satellite optical systems and large astronomical telescopes has reached 3 m, and the processing accuracy is required to reach nanometer level. Facing the semiconductor field, the size requirements of IC manufacturing are getting larger and larger, while the IC linewidth is getting smaller and smaller. For the next generation of 7 nm linewidth process, precision grating positioning with nanometer level accuracy and picometer level resolution is the key to ensure high quality lithography [39, 40]. In order to meet the above requirements, nanoprecision manufacturing method of grating structure, large-area consistent manufacturing process and large gap tolerance reading technology are the three key core technologies of precision reflection grating manufacturing. Limited by the technical blockade and equipment monopoly of precision reflection grating lithography manufacturing, China's two-dimensional grating, linear displacement grating with precision better than 1 μm/m and circular grating with precision better than 1" are completely dependent on imports, which is a "neck sticking" problem in the development of high-end equipment.

The research team of Xi'an Jiaotong University has carried out research on continuous rolling and imprinting manufacturing of precision grating and high-performance reading technology, has explored the influence of three-dimensional profile accuracy of nanostructures on grating measurement system, and has established the rolling printing manufacturing process of high-precision reflection grating and the technical system of interference scanning reading: a manufacturing method of an imprint template based on a time reference mapping length and a release and mold-preserving imprinting process of a precision reflection grating are invented, which realizes the traceability of grating structure accuracy to time, solves the difficult problem of nanoprecision grating imprinting and replication process, and the periodic accuracy of grating structure reaches 0.2 nm (German PTB Metrology Report); the roll-to-roll continuous imprinting manufacturing process and equipment of the precision reflection grating are invented, the problem of nanoprecision consistency manufacturing of the large format of the grating structure is solved, and the cross-scale and continuous manufacturing of 180 m ultra-long grating, meter-scale two-dimensional grating and meter-scale circular grating is realized; the structured phase grating interference imaging reading technology is invented, which solves the problem of large gap tolerance reading of precision reflection grating. The measurement accuracy of linear displacement grating is better than 0.2 μm/m, the measurement accuracy of meter-scale format two-dimensional grating is better than 0.4 μm, the measurement accuracy of circular grating is better than 0.1", the reading gap tolerance is (2.4 ± 0.3) mm, and the index is in an international leading position; the invention solves the three bottleneck problems of nanoprecision imprinting, large-area consistent manufacturing and large-gap tolerance reading of the grating structure, and forms a precision reflection grating product with independent intellectual property rights [41–48], as shown in Fig. 4.8a–b.

The developed precision linear displacement grating is applied to major national engineering requirements. The ultra-long precision reflection grating is applied to the ultra-large range space segment separation ground measurement platform, which meets the requirements of high speed (5 m/s) and high precision (5 μm/m) measurement within 55 m range; customized ultra-long grating has been applied to the 40,000-ton large aviation die forging hydraulic press of Xi'an Triangle Defense Co., Ltd. to realize accurate displacement measurement under high temperature, large vibration, strong impact, dust and other application environments during forging of aerospace titanium alloy integral structural parts; ultra-precision linear displacement grating has

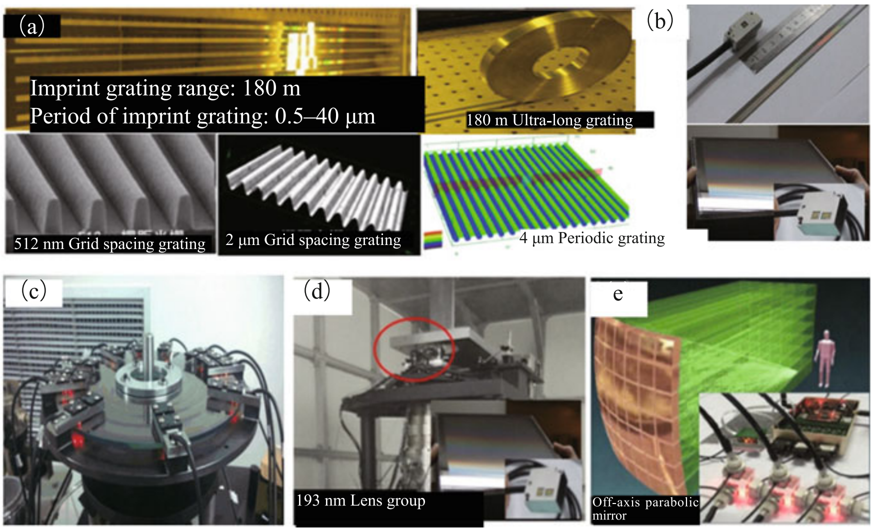

Fig. 4.8 Precision reflective grating and its application (**a** Precision reflective gratings; **b** Reading systems; **c** Application of precision circular grating in angle reference device of China Institute of Metrology; **d** Precision two-dimensional grate is applied to the assembly of the lens group of the 02 special 193 nm lithography machine; **e** Application of multi-degree-of-freedom grate to pose monitoring of off-axis parabolic len in major scientific projects)

been applied to Shenzhen Zhongtu Instrument Co., Ltd. and other enterprises. The ultra-precision circular grating measurement system is applied to the "National Plane Angle Reference" series of devices, as shown in Fig. 4.8c, which meets the construction requirements of the "National Plane Angle Reference" for ultra-precision angle measurement and lays a foundation for the establishment of a new generation of full circle continuous angle measurement system in China. The meter-scale format two-dimensional grating has been applied to the assembly of the lens group of the national 02 special 193 nm lithography machine, achieving 0.5 nm resolution and 5 nm accuracy, reducing the environmental thermal stability error, and promoting the development process of the lithography machine in China, as shown in Fig. 4.8d. The multi-degree-of-freedom stereo grating measurement system has been applied to the pose monitoring of off-axis parabolic mirrors in a major national scientific project, as shown in Fig. 4.8e, which solves the problems of off-site assembly, on-site debugging and pose locking of optical components of large optical systems. The research and development and application of a series of precision reflective grating products have broken the foreign technology monopoly and product embargo, supported the independent and controllable development needs of key measuring components in major engineering fields and core equipment in China, and promoted the product innovation and core competitiveness of application enterprises.

4.4.2 Special-Shaped Micro-nano Structure and Its Engineering Application

Special-shaped micro-nano structures have unique optical and mechanical properties and play an important role in various engineering applications. In the field of micro-nano optics, microlens array, as a typical micro-nano special-shaped structure, not only has the basic functions of traditional lenses such as focusing and imaging, but also has the characteristics of small unit size and high integration. It can realize the functions that traditional optical elements cannot complete and can form many new optical systems. In the field of bionic adhesion, mushroom- like dry adhesion structure, as a typical micro-nano special-shaped structure, has the advantages of strong adhesion, high stability, strong adaptability to materials and morphology, etc. It is listed as the only solution of "space reversible adhesion material" by National Aeronautcs and Space Adiminstration in America (NASA) Technology Roadmaps 2015–2035, supporting space operation missions such as on-orbit maintenance and orbital debris grabbing, and is expected to enter practical application at two NASA mission nodes in 2027 and 2033 [49]. The special performance and superior performance of micro-nano special-shaped structures depend on the accurate control of complex structure morphology. Therefore, how to realize large-area consistent and accurate manufacturing of micro-nano special-shaped structures is the key technical bottleneck from theoretical research to engineering application.

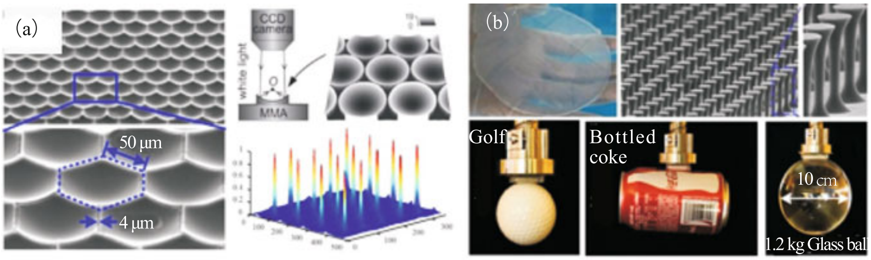

Fig. 4.9 Micro-shape control of micro-nano special-shaped structure and its engineering application (**a** A microlens array; **b** Bionic dry adhesion structure)

The research team of Xi'an Jiaotong University proposed a multi-physical field system control micro-shape control method based on space electric field control and template constraint. The large-area microlens array and dry adhesion bionic structure are formed and manufactured by using the electric field control on the rheological behavior of liquid polymer and the constraint of template geometric characteristics, as shown in Fig. 4.9. For the first time in the world, the method realizes large-area and high-efficiency manufacturing of high-performance aspheric microlens arrays (filling rate 98.8%, surface finish 0.2 nm, parabolic topography, 4 inch area), and solves the technical challenges of topography control, curvature control, precision control and efficiency control of aspheric microlens arrays [10, 12]; the bionic manufacturing of the gecko bionic mushroom microstructure array is realized, and the gecko bionic mushroom microstructure array can show high-strength adhesion characteristics on target objects such as smooth surfaces and uneven surfaces, and the adhesion strength is as high as 12 N/cm^2, which exceeds the adhesion performance of natural gecko organisms [36, 50, 51].

The bionic dry adhesive structure prepared by multi-physical field cooperative control micro-shape control method has been applied to the model development task of a research institute, which solves a series of problems such as batch manufacturing of special-shaped structures and adhesion performance control, and provides innovative manufacturing method support for major projects such as space on-orbit maintenance and assembly. In addition, the research team cooperated with Hefei Xinyihua, BOE Display and other equipment and electronic manufacturing enterprises to develop an intelligent pickup and handling system for flat panel display and lithium ion battery packaging.

4.4.3 Ultra-thin Light Guide Plate and Its Engineering Application

As the core device of liquid crystal display (LCD), the performance of light guide plate determines the quality of LCD. Since LCD has replaced cathode ray tube and

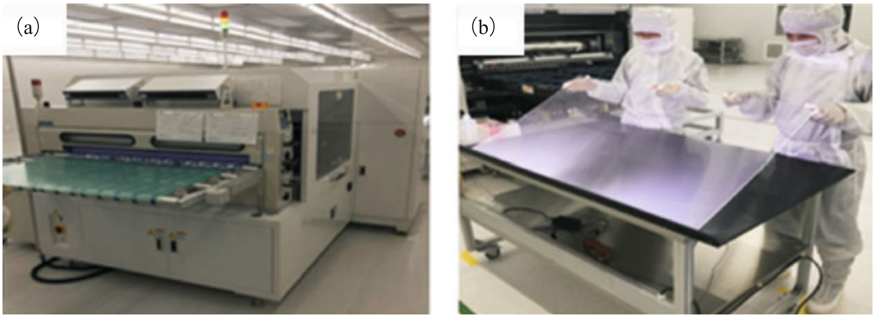

Fig. 4.10 Ultra-thin light guide plate and its engineering application (**a** Imprinting equipment for ultra-thin light guide plates; **b** 55-inch light guide plate products)

other displays, people have been looking for how to make display devices thinner and lighter, and put forward the requirement of ultra-thin backlight module. The thickness of the light guide plate made by the traditional injection molding process is relatively high, and the width is generally less than 20 inches, which has limited contribution to the overall ultra-thinning. In addition, the processing cycle of injection mold is generally 2–3 weeks, and it takes more than 1 month to complete the optical verification of one cycle, which is long in cycle and high in cost. In order to meet the needs of the rapid development of LCD and the rapid upgrading of electronic products, it is urgent to carry out overall innovation in the design, mold processing, batch production capacity and other aspects of ultra-thin light guide plate, so as to produce ultra-thin light guide plate products with simple process, low cost and large format.

The research team of Suzhou University has developed the manufacturing technology of flexible microstructure mold, genetic algorithm for optimizing light guide dot data and software development. The realized one-dimensional and two-dimensional microstructure manufacturing with 20–100 μm feature size and 3–5 μm depth has been successfully applied to 15–65 inch ultra-thin light guide plate mold. Ultra-high-speed manufacturing of microstructure mold was realized by laser high-speed scanning lithography. Using the technology of "roll-to-roll nanoimprint + sheet-to-sheet nanoimprint", the batch and green manufacturing of 5–65 inch light guide devices is realized, as shown in Fig. 4.10.

4.4.4 Flexible Transparent Conductive Film and Its Engineering Application

Transparent conducting electrodes (TCEs) are the core components of the next generation flexible electronic devices because of their flexibility, transparency and good conductivity. They can be widely used in touch sensors, display devices, organic photodiodes and other fields. Metal-based TCEs have high transparency, flexibility and conductivity, and low production cost. Its manufacturing methods mainly include nanoimprint, microsphere lithography, grain boundary lithography and so on. However, the preparation process is cumbersome and time-consuming, which often involves metal etching, template fabrication, vacuum thermal evaporation and other processes. In addition, the metal mesh of TCEs fabricated based on this scheme is attached to the surface of flexible substrate, which is a non-planar structure, and the fluctuation degree often reaches micron order. When preparing organic optoelectronic devices, it is difficult for ultra-thin organic layers (tens of nanometers) to form continuous structures on micron-sized undulating electrodes, which is prone to short circuits. In addition, the adhesion between metal and substrate is difficult to guarantee, and it is easy to fall off, which makes it difficult to meet the requirements of highly flexible optoelectronic devices. Therefore, it is urgent to develop the preparation method of transparent electrode with simple process, low cost and expandability, so as to realize TCEs with adjustable light transmittance and square resistance and good mechanical properties.

The research team of Suzhou University has invented the composite manufacturing process of "nanoimprint + additive filling" with functional structure, and realized the innovative manufacturing of micro-metal grid transparent conductive film (electrode), embedded electronic devices and flexible sensors. The method introduces a buried metal wire grid flexible transparent electrode structure, designs and realizes the integrated requirements of "flexibility-transparency- high conductivity-high mechanical properties" from the perspectives of structural design, micro-nano processing, material filling/growth, etc., and develops high-performance metal-based TCEs suitable for flexible photoelectric systems; the flexible transparent self-supporting (substrate-free) metal wire grid electrode is realized, which can bear stretching, folding and arbitrary deformation. Academic papers reflecting the research results related to the composite manufacturing process of "nanoimprint + filling and adding materials" are published in top energy journals *Energ Environ Sci* in the form of Back Inside Cover and are selected as hot articles in the magazine in 2017.

On the basis of the manufacturing process of "nanoimprint + filling and adding materials", the research team of Xi'an Jiaotong University has invented an electric field-driven large-format scraping filling method, which solves the problem of "not filling deep, not filling well and not filling quickly" faced by direct scraping filling of functional materials (such as silver nano ink materials), and has provided technical support for large-scale manufacturing of high-quality flexible transparent conductive films, as shown in Fig. 4.11. The academic paper [36, 52, 53], which expounded the principle of large-format scraping and filling driven by electric field, was selected into ACS Editors' Choice, became the most downloaded paper in *ACS Appl Mater Interfaces* in 2014, and was selected into the selected papers of Royal Physics Society in 2011.

The transparent capacitive touch screen prepared by the technology of "nanoimprint + filling and adding materials" has entered industrial application, realizing the green manufacturing of large-size transparent electrodes and flexible circuits without etching, and overturning the traditional idea that flexible circuits need etching process. For example, the transmittance of 0.1–50 European square is achieved 88% of the technical parameters, while when the transmittance of ITO in the industry is 88%, the square resistance is above 200 European square. Among them, 8–70-inch nano silver microgrid transparent capacitive touch screens have been applied in batches and have been applied to banks, games, computer terminals, giant screen touch and other fields. The products have been sold to the terminal markets of the United States, Japan and Germany, as shown in Fig. 4.12.

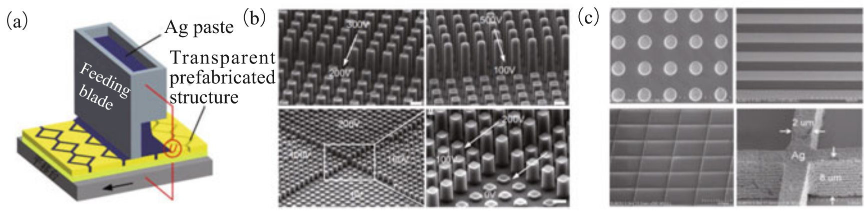

Fig. 4.11 Electric field driven scrape filling (**a** The principle of electric field driven scraping filling; **b** Influence of voltage on filling depth and control ability; **c** Electric field driven scrape filling of silver nano ink)

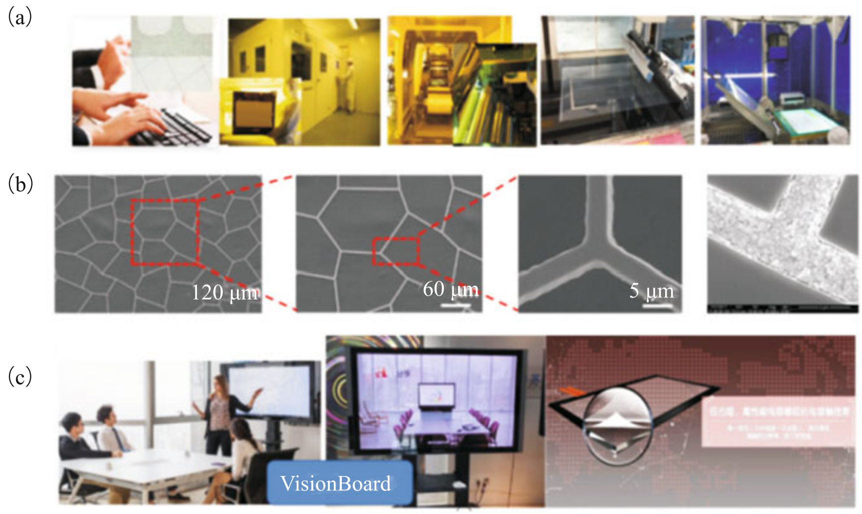

Fig. 4.12 Flexible transparent conductive film and engineering application (**a** "Nanoimprint + filling and adding materials" manufacturing equipment; **b** Typical micro-nano structures manufactured; **c** Large-size transparent conductive film and its industrial application)

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Chapter 5
Cross-Scale Integrated Manufacturing of Nanostructures and Devices

Bingheng Lu, Jianbin Luo, Zhongqun Tian, Dongming Guo, Han Ding, Changzhi Gu, Zhihong Li, and Ming Liu

On the basis of nanoprecision manufacturing and nanostructure manufacturing, the integration of nano/sub-nano precision and micro-nano multiscale structures and cross-scale manufacturing are the only way for nanomanufacturing to move towards industrial application and serve major national engineering applications. Taking the manufacture of biochemical sensor as an example, its sensing process includes two interfaces: the reaction interface at the level of biochemical molecules (the first interface) and the conversion interface between information and energy of sensing output electrical signals (the second interface). Among them, the first interface is to transmit information on the molecular structure scale, which determines the sensitivity and selectivity of the sensor. Generally, the sensor is a molecular-level ordered nano-sensitive structure; usually, the manufacturing technology of "bottom-up" is

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adopted to ensure the advantages of high sensitivity and high specificity to biochemical molecules; however, due to the limitation of growth mechanism, it is unable to achieve long-range, high sensitivity and high specificity large area, high consistency and repeatability of batch manufacturing; the second interface is to convert physical effects into measurable electrical signals, usually using the "top-down" manufacturing method. The first interface must be integrated with the second interface to form a complete biochemical sensor, otherwise the biochemical sensitive effect cannot become a signal that can be directly detected. Therefore, it is necessary to realize compatible nano-micro (macro) cross-scale integrated manufacturing between nanomanufacturing and microstructure.

To solve the bottleneck of consistency and batch manufacturing across scales, it is necessary to start with the physical and chemical intrinsic properties of material structure and external energy regulation. On the one hand, self-constrained nanostructures are formed by studying the anisotropy of growth or etching caused by structural specificity such as bond energy, periodic potential, edge hanging bonds and defects of materials, thus realizing highly controllable batch processing of nanostructures; on the other hand, the localization energy is changed by applying different external fields (such as light field, temperature gradient field and electric field), and the regulation mechanism of removal, retention and reconstruction of nanostructures on demand is studied. The on-demand construction of nanostructures on the sensor surface and a high degree of structural controllability are realized through multi-field regulation.

The research team, composed of Peking University, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, and Institute of Physics, Chinese Academy of Sciences, has carried out integrated research on the basis of self-assembly, nano scale processing and micro-nano composite manufacturing in the early stage, aiming at the major demand of monitoring and ensuring public safety for micro biochemical sensors. By combining the "top-down" and "bottom-up" processing methods, the compatibility problem of the integrated manufacturing method of nano and micro structures can be solved, the self-constrained nano processing principle based on the structural heterogeneity of materials, the physicochemical principle of cross scale on-demand controllable manufacturing of nanostructures, and the multi field control mechanism, the method of local selective multiple construction and nano batch manufacturing of micro structure surface were established, which broke through the core technology of integrated batch manufacturing of high-performance on-site biochemical sensors across micro and nano scales, and formed the verification prototype of trace rapid nano biochemical sensors, which was applied in food safety detection and public security anti-terrorism sensor system for principle verification.

5.1 High Precision Controllable Manufacturing of Self-Constrained Nanomachining

The Research Team of Shanghai Institute of Microsystems and Information Technology, Chinese Academy of Sciences, based on the principle of self-constrained nanomachining, proposed the wafer-level controllable manufacturing of silicon nanowire arrays using (111) SOI materials. Using the distribution characteristics of {111} crystal plane family on (111) silicon wafer, thin-walled single-crystal silicon structures with a width of several hundred nanometers were prepared by anisotropic etching of single-crystal silicon. Then, the thin-walled specific area is transformed into single crystal silicon nanowire structure by self-limiting oxidation technology, and the controllability of silicon nanowire array wafer level preparation is further improved by using SOI materials, as shown in Fig. 5.1. The length of the prepared samples is 5–40 μm. Suspended single crystal silicon nanowire array devices with a width of 25–100 nm have a yield of over 90%. This achievement is much better than the reported silicon nanowire array structure, which effectively promotes the further application of silicon nanowire array. The mass-produced TNT sensor can reach ppt level in gaseous environment, which is equivalent to the highest level reported in the literature. This research work has been cited for more than 260 times by 27 review articles (including 2 *Chem Rev* (IF: 52.61) and 2 *Chem SOC Rev* (IF: 40.18) and 9 monographs, and has been highly praised by international authoritative scholar and Professor Charles M. Liber of Harvard University in *Chem Rev*.

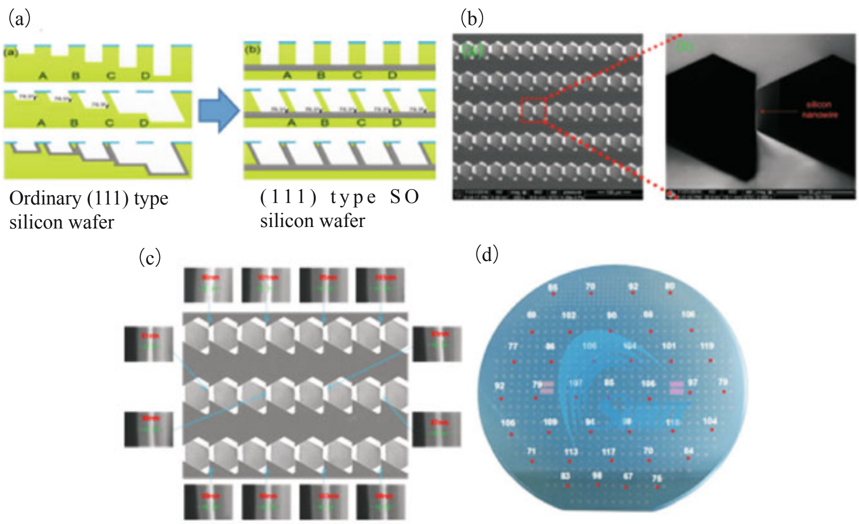

Fig. 5.1 Manufacturing of wafer-level silicon nanowire arrays using (111) SOI materials (a) Schematic diagram of processing flow; (b)–(c) Microscopic view; (d) Local amplification

The project team also realized the manufacture of N-type and P-type silicon nanowire integrated chips, and verified the complementary detection of PSA. Starting from the key etching process, nanowire refinement and process consistency, the method of integrated manufacturing of n-type and p-type silicon nanowire devices on the same chip is studied. Using anisotropic etching self-stop and nano-thickness etching self-limitation, the reliable manufacturing of the two types of silicon nanowires is realized, and the surface of the silicon nanowires is smooth and the size is uniform, with a minimum of 20 nm. Using N-type and P-type silicon nanowire arrays integrated on the same chip, complementary control detection of PSA can be carried out. By comparing the results of the two types of devices, false positive signals can be avoided, the influence of external interference can be eliminated, and the reliability of detection can be ensured. The device itself can carry out self-comparison, which is an innovative new sensing strategy, as shown in Fig. 5.2 [1].

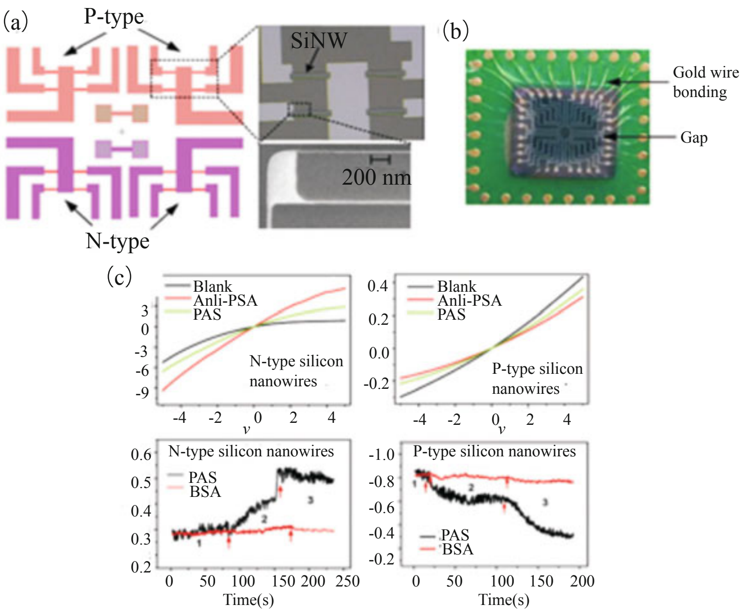

Fig. 5.2 Integrally fabricated N-type and P-type silicon nanowires and their complementary control detection of PSA

5.2 Manufacturing of Three-Dimensional Micro-Nano Structure Induced by External Field

The nanomanufacturing team of the Institute of Physics of the Chinese Academy of Sciences realized the wafer-level cross-scale manufacturing of three-dimensional micro-nano structures with a characteristic scale of 200 nm and a change in structural spatial orientation (folding and bending of 0 to 180°) through external field induction. This method can also realize the external field-induced processing of the sub-10 nm metal gap points to the array. A folding processing method of three-dimensional metal nanostructures based on focused ion beam irradiation is developed, which can shear and fold two-dimensional metal thin film materials in the plane. Through graphic design, plane shearing and multiple orderly folding, large-area controllable processing with adjustable size, period and geometric morphology of metal nanostructure units [2–4] are realized. The method has the advantage of material universality and is suitable for folding processing of three-dimensional micro-nano structures of other media and oxide films [5, 6]. The research team folded the two-dimensional metal structural unit through folding processing to form a three-dimensional structure of dielectric film/metal structural unit composite, which greatly expanded the material combination function of the folded structure and also expanded its application space in the field of optical regulation, as shown in Fig. 5.3. In addition to folding processing, a three-dimensional nanostructure bending processing method based on thin-film strain induction is explored. This technology mainly uses a large-area strain of thin films under ion beam irradiation to cause bending. The bending processing scale is as small as several hundred nanometers, and the processing efficiency is higher. Based on the above combined machining method of bending and folding, the team has realized a three-dimensional assembly processing method with greater spatial freedom on the micro-nano scale, which can construct more complex three-dimensional shapes and realize multi-level three-dimensional structures that cannot be completed by a single processing method. These structures have important application potential in the fields of bionics, biology, energy, MEMS/NEMS and micro-nano photonics [7–9]. Due to the progress of three-dimensional folding processing in micro-nano scale and controllable processing of sub-10 nm metal gap array and their application research, the research team was invited to work in Adv Mater (2019, 31, 1802211) and Small respectively (2019, 15, 180, 4177) to write a summary article.

5.3 On-Demand Regional Architecture of Functional Nanostructures

Self-assembly, which combines physical and chemical energy to regulate, is the key to achieve high selectivity and specificity of biochemical sensors, and it is also an

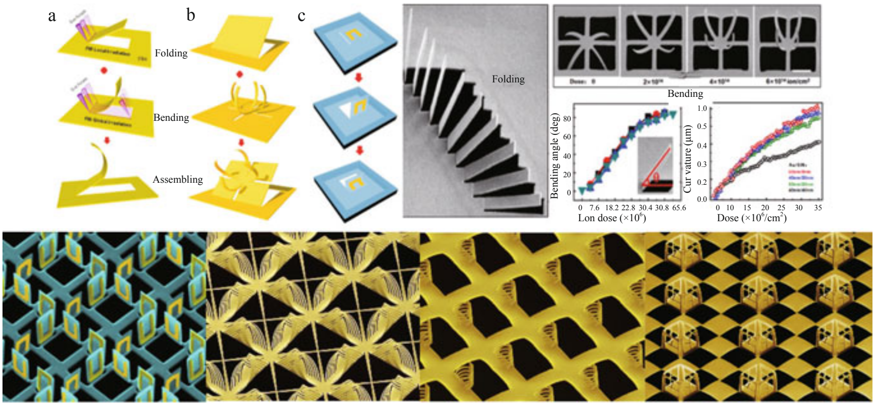

Fig. 5.3 Schematic and structural photos of three-dimensional assembly (folding/bending) processing method based on nanofilm

effective method to realize on-demand region construction of functional nanostructures. Nanostructure patterning and wafer-level integrated manufacturing are realized by mask lithography, which ensures the selectivity and consistency of biochemical sensors, and the nonuniformity of self-assembled monolayer is less than 5%. The nanomanufacturing team of Shanghai Institute of Microsystems and Information Technology, Chinese Academy of Sciences proposed the "generalized lithography" multi-molecular self-assembly technology. The "generalized lithography" multi-molecular self-assembly technology is a wafer-level manufacturing method combining "top-down" and "bottom-up", as shown in Fig. 5.4. "Top-down" refers to deep ultraviolet lithography of monomolecular films through hard masks and patterning of self-assembled monomolecular films through macro-scale tools and materials; "bottom-up" refers to the functional modification of different regions in the chip through multiple self-assembly of a large number of nanoscale molecules. The main steps are as follows: firstly, a single molecule film is deposited; deep ultraviolet exposure is completed through a hard mask, another single molecule film is grown after the first single molecule film is removed in the exposure area; the process can be repeated for many times; the wafer-level operation is carried out; the manufacturing efficiency of the chip is greatly improved. Using this technology, hydrophilic surfaces are constructed in sensitive areas of microcantilever beams, and oleophobic and hydrophobic surfaces are constructed in other areas, thus improving the fixing method of sensitive materials from manual coating method of devices one by one to wafer-level mass spin coating fixing method, and realizing high consistency batch preparation of microcantilever biochemical sensors [10–12].

The team used "generalized lithography" technology to construct hydrophobic and oleophobic surfaces and amine-based functionalized surfaces in different regions of the microchannel, and then selectively positioned and cast mesoporous material precursor solution in the region to be grown, thus realizing a micro-nano cross-scale chip manufacturing method integrating multiple nanotubes in the microchannel.

Using the variable temperature weighing method based on the resonant micro-cantilever sensor, it was found that the SiO_2 mesoporous nanomaterials can be chemisorbed with organophosphorus, so that a new solid-phase microextraction principle prototype was developed with the chip as the core. The prototype was successfully used to enrich the aqueous solution containing trace dichlorvos, chlorpyrifos and paraoxon, and the trace pesticide molecules were further extracted into ethanol miscible with water. GC-MS analysis results confirmed that the extraction recovery rate reached 80% [13], as shown in Fig. 5.5.

The research team of Shanghai Institute of Microsystems and Information Technology, Chinese Academy of Sciences also prepared micro-nano composite micro-chromatographic columns by using nanomaterial micro-region construction technology. For chromatographic columns, how to improve their separation ability is a key problem, and nanomesoporous silicon materials are ideal materials as stationary phases or stationary phase carriers because of their high specific surface area and

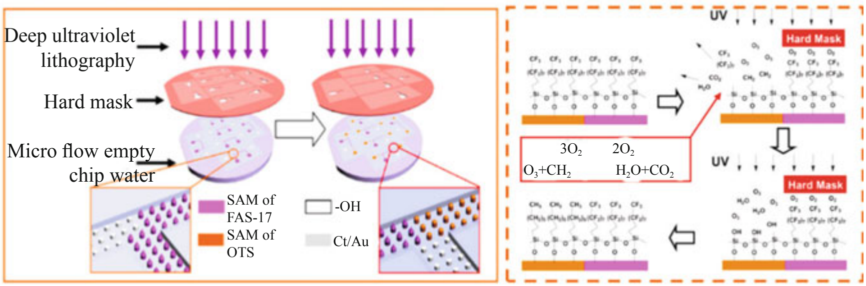

Fig. 5.4 Schematic diagram of "generalized lithography" technology principle

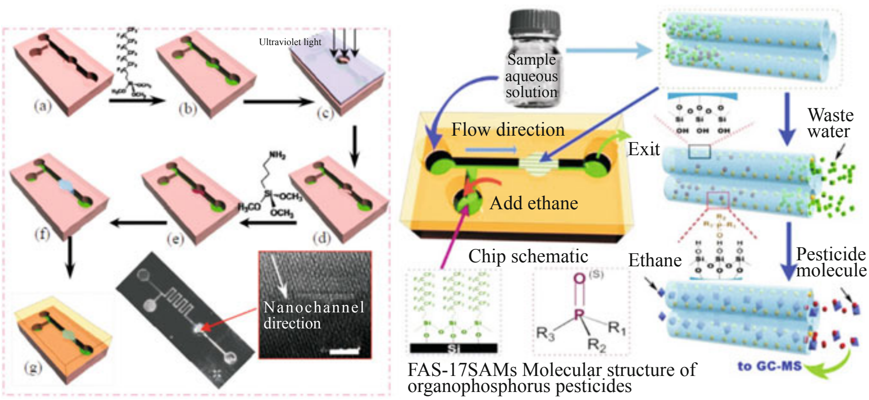

Fig. 5.5 (left) Schematic manufacturing steps of micro-nano fluidic cross-scale integrated chip; (right) Schematic illustration of that principle of enrichment and extraction of organophosphorus pesticide residue molecule using the chip

stable physical and chemical properties. Based on the silicon substrate, the team first used the "top-down" method to prepare a micro-channel containing a micro-column array, and then used the "bottom-up" method to construct a layer of nanomesoporous silicon in a silicon-based micro-chromatographic column, successfully realizing the controllable manufacturing of a three-dimensional micro-nano composite silicon-based structure so as to acquire the capability of large-scale batch manufacturing at the wafer level. Tests show that the nano mesoporous silicon constructed on the surface of the micro-chromatographic column has a specific surface area of 650 m^2/g and pore size of about 2 nm, which has a strong separation ability for light hydrocarbons. Using a 2 nm micro-chromatographic column can obtain a separation degree greater than 1 for methane ethane that is difficult to separate, as shown in Fig. 5.6 [14, 15].

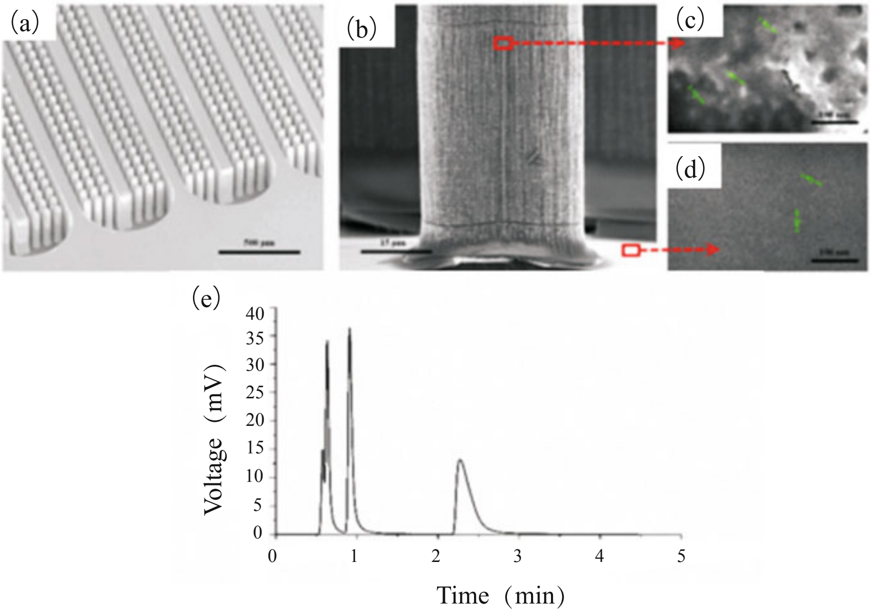

Fig. 5.6 (a) Silicon microcolumn microchromatographic column; (b) A microcolumn in a silicon microchromatographic column; (c) Mesoporous silicon on that surface of the microcolumn; (d) Mesoporous silicon at the bottom of the channel; (e) Separation effect of C1–C4 on silicon microcolumn

5.4 Controlled Machining Method of Two-Dimensional Material Nanostructures

The nanomanufacturing team of the Institute of Physics of the Chinese Academy of Sciences uses the high precision and flexibility of AFM in nanoscale manipulation to oxidize graphene at a specific position by applying a biasing voltage to the AFM needle tip, introduce periodic defects, and process the anti-point network structure of graphene. After the defects are introduced into the sample, the defects are amplified by hydrogen plasma anisotropic etching technology to form graphene inverse point network nanostructures with hexagonal hole arrays [16–18]. Since the etching of graphene by hydrogen plasma only occurs at the defects and edges of graphene, it will only enlarge the holes obtained by the AFM tip and will not cause new defects or holes. At the same time, due to the anisotropy of etching, the final nanostructure is a superlattice porous graphene nanostructure with a zigzag edge. The period of superlattice porous graphene nanostructures and the width of nanoribbons are controllable. By controlling the etching time, nanoribbons with a predetermined width can be obtained to realize a nanopore array pattern with a period less than 200 nm, as shown in Fig. 5.7. The processing method of the AFM tip is simple, which will not introduce additional pollution, and because there is only one step of gluing exposure in the whole device processing process, the surface pollution in device manufacturing is reduced. The auxiliary tip array processing technology can be used for device integration and is helpful for the mass production of graphene nanostructured devices.

The team pioneered the anisotropic etching of hydrogen plasma and the "top-down" processing method on silicon oxide substrate, and obtained various graphene

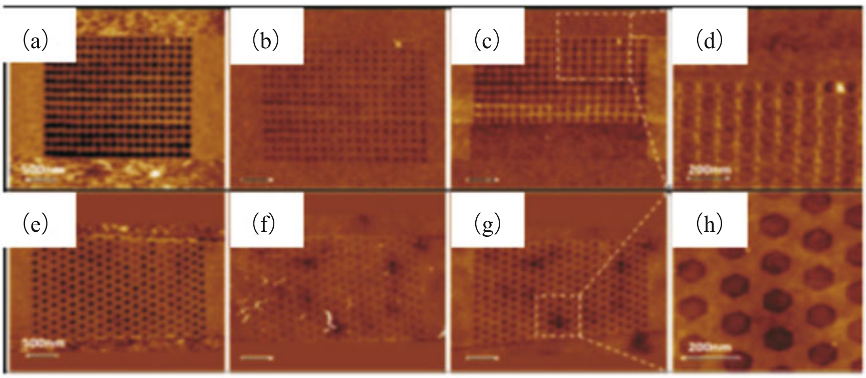

Fig. 5.7 AFM image of graphene anti-dot network. (a)–(c) Anti-dot network structure of square lattice with the period of 100 nm; (e)–(h) AFM image of anti-dot network structure of hexagonal lattice with the period of 200 nm; (a), (e) An image after completion of oxidation in contact mode; (b), (f) Image in tap mode; (c), (g) An image after hydrogen plasma etching; (d), (h) Corresponds to the enlarged image in the dashed box

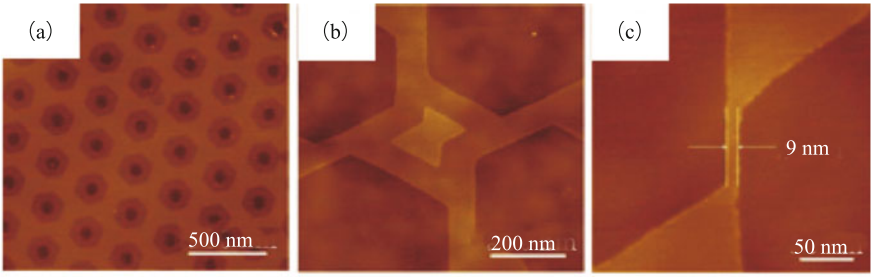

Fig. 5.8 Controlled processing of graphene nanostructures on hexagonal boron nitride substrates (a) Images on a 500 nm scale; (b) Image at 200 nm scale; (c) Image at 50 nm scale

nanostructures with double layers and above layers with zigzag atomic level flat boundary. Furthermore, the anisotropic etching of single-layer graphene was studied. A single-layer graphene nanostructure with zigzag atomic level flat boundary was obtained on hexagonal boron nitride, and controllable processing of graphene nanoribbons with extremely small sizes below 5 nm was realized, as shown in Fig. 5.8 [19–21]. Furthermore, by applying different gate voltages *in situ*, the etching mechanism of hydrogen plasma is studied, and it is confirmed that hydrogen plasma plays a major role and active hydrogen atoms play an auxiliary role in anisotropic etching. It is also found that due to the different etching rates under positive and negative gate pressures, graphene fine nanostructures can be processed in batches efficiently by adjusting gate pressures. This anisotropic etching of graphene-based on hydrogen plasma provides a new way to manipulate graphene.

5.5 Important Engineering Applications of Cross-Scale Manufacturing

The nanomanufacturing team of Peking University has proposed an innovative three-dimensional ice micro-printing technology, which can realize cross-scale manufacturing and integration of microfluidic, biochemical reactants, nanomaterials and MEMS devices by taking the advantages of low temperature, good compatibility with biomaterials, easy formation of three-dimensional structures and no pollution [22–24]. Three-dimensional ice micro-printing technology utilizes the phase transition process from water to ice, because liquid water has good fluidity and can form very tiny droplets, while solid ice has good strength, this process of forming three-dimensional ice microstructure through the phase transition of tiny water droplets is a typical “top-down” process, which also has the common advantages and characteristics of “bottom-up” method. Based on this technology, a microcapsule biochemical detection array device was developed, and a series of microcapsule detection devices were successfully prepared and tested: a pre-encapsulated microcapsule array chip for detection of nitrite and glucose, a pre-encapsulated chip for detection of *Salmonella* pathogen DNA based on LAMP constant temperature amplification, a divalent copper ion detection chip based on specificity/sensitivity quantitative detection of functional nucleic acids, and a ready-to-use water metal ion detection array chip capable of simultaneously detecting hydrogen ions, lead ions, hexavalent chromium ions, fluorine ions, nitrite ions, nickel ions, copper ions, iron ions and the like. The research team further improved the diversity of pre-encapsulated substances, improving the microencapsulation process and developing the protection process of the reaction solution. The test results show that the device has the advantages of portability, simple operation, anti-pollution and suitability for large-scale low-cost preparation, as shown in Fig. 5.9.

Aiming at the application objectives of food safety inspection and public safety anti-terrorism, the research team of Shanghai Institute of Microsystems and Information Technology, Chinese Academy of Sciences has developed a biochemical nanosensor with a biochemical detection sensitivity of 10 am by adopting a micro-nano cross-scale structure and self-assembled nanomaterials, realizing label-free rapid and sensitive detection on miRNA, protein, antigen and antibody. The developed pesticide residue detection sensor and rapid detection instrument based on resonant cantilever have passed the field test in Changsha Food Safety Detection Center of Hunan Province, and have been popularized and applied, and have been well received by users, as shown in Fig. 5.10.

The pesticide residue detection sensor and rapid detection instrument based on micro-nano composite resonant cantilever have also passed the application verification of food and drug inspection agencies; TNT detection has reached ppt level and has been applied to hazardous chemicals detection in Shanghai subway and airport; using nanomaterial micro-region construction technology, micro-nano composite micro chromatographic columns were prepared, it has been applied to the fixed product development of on-site portable meteorological chromatograph of Shanghai Yidian Group Analytical Instrument Co., Ltd., a backbone enterprise in China, the detection resolution of the traditional gas chromatograph of Shanghai Yidian Group has been improved from the level of 100 ppm to the level of ppm, and the main performance indicators have reached the level of Agilent's similar portable products (GC-490), as shown in the Fig. 5.11.

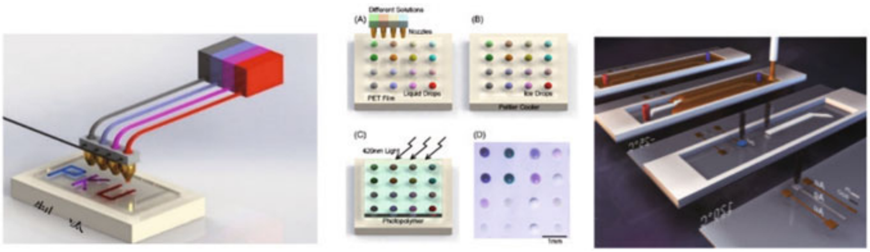

Fig. 5.9 Three-dimensional ice micro-printing technology and microcapsule biochemical detection array for food safety monitoring

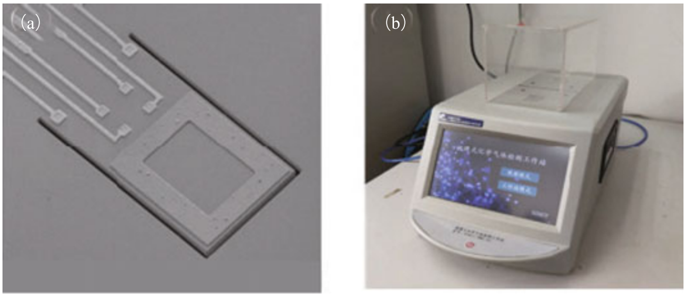

Fig. 5.10 (a) Microcantilever beam prepared; (b) Portable chemical gas detection workstations for the detection of acephate

	Agilent	μGC-60
Volume	28 cm×15 cm×55 cm	16 cm×13 cm×45 cm
Weight	≈ 5.2 kg	≤ 4 kg
Power consumption	130 W	120 W
Detection limit	10 ppm	5-20 ppm
Price	400,000 RMB	150,000 RMB (expected)

Fig. 5.11 Comparison of performance between micro gas chromatograph constructed across the micro-nano integrated micro chromatographic column and agilent products

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Chapter 6
New Methods of Laser Micro-Nanomanufacturing

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Laser manufacturing is a manufacturing method that uses the interaction between laser and matter to make it undergo heating, melting, vaporization, evaporation, sublimation, coulomb explosion, electrostatic stripping and other processes, thus realizing the forming and forming of parts/components. The laser manufacturing industry has developed rapidly in the past ten years, especially with the development of aviation, aerospace, high-end chips, new energy, transportation and other fields in China, the demand for laser manufacturing of high-performance components has become more and more urgent. Ultra-fast laser micro-nanomanufacturing is one of the frontiers of laser manufacturing, with the characteristics ultra- fast (<100 fs), super strong (>1, 14 W/cm^2), it has unique advantages in the manufacture of difficult-to-machine materials and three-dimensional complex curved surface

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micro-nano structures. With the continuous development of ultra- fast laser technology, it is expected to become one of the main means of high-end manufacturing in the future, which can provide key manufacturing support for the development of new energy, aerospace, national defense and other fields, and has important strategic significance for promoting China to become a manufacturing power. Ultra-fast laser processing faces the following common challenges in the manufacture of core components in the above fields: the processing materials are diverse and difficult to process, the processing surface is a three-dimensional complex curved surface, the size limit is continuously pushed to new extremes, and the quality requirements are continuously pushed to new extremes. These challenges put forward new requirements for ultra-fast laser manufacturing. It is necessary to understand, observe and control the energy absorption, transfer and corresponding phase transition mechanism in ultra-fast laser processing from the electronic level, and explore the change law and control mechanism of nanoscale electronic dynamic characteristics in the interaction between nonlinear and non-equilibrium ultra-fast laser and materials.

6.1 New Principle and Method of Ultra-Fast Laser Space-Time Shaping Micro-Nano Machining

In the process of ultra-fast laser manufacturing, the absorption of laser energy by materials is mostly completed by electrons as carriers. The pulse width of ultra-fast laser is one thousandth to one hundredth of the heat conduction time (10^{-12}–10^{-10} s) between electron and lattice. Therefore, during femtosecond pulse irradiation, the lattice motion can be ignored, and only the change of electronic state under ultra-fast light field needs to be considered. Although the irradiation time of femtosecond laser pulse to materials is very short (femtosecond order of magnitude), all subsequent processing processes (second order of magnitude) are determined by the interaction between femtosecond laser and electrons, so the local instantaneous electronic state must be regulated [1]. In the past, the observation and regulation of basic manufacturing research were limited to atomic, molecular and above levels. The core scientific problem is whether local instantaneous electronic dynamics can be regulated. The rapid development of ultra-fast laser technology provides feasibility for solving this scientific problem. In the past two decades, ultra-fast laser technology has won 3 Nobel Prizes, resulting in a total of 5 Nobel Prize winners. For example, Professor Ahmed H. Zewail, winner of the Nobel Prize in Chemistry in 1999, has made the world's fastest camera with femtosecond laser as a tool, has observed the process of electron relaxation changes in chemical reactions, and is expected to make breakthroughs in new principles/methods of manufacturing [2].

Inspired by Professor Zewail's work, the research team of Beijing Institute of Technology proposed a new principle of electronic dynamic control processing [1]: by designing the temporal and spatial distribution of ultra-fast laser to adjust the

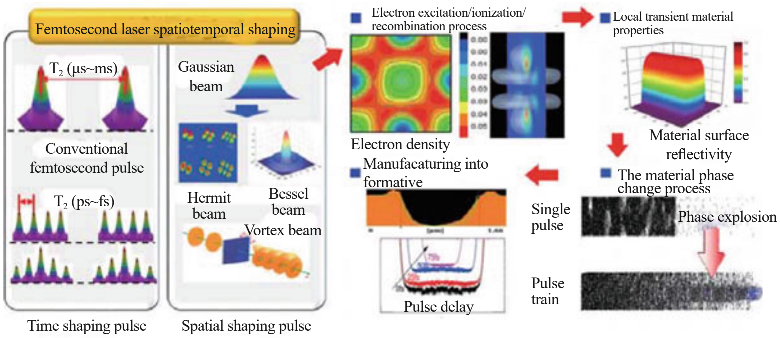

Fig. 6.1 New principle/method of femtosecond laser spatio-temporal shaping

interaction process between laser and electron, active regulation of local instantaneous electronic dynamics (density/temperature/excited state distribution, etc.) is realized, thus regulating the local instantaneous characteristics of materials (reflectivity/refractive index/conductivity, etc.), further regulating the phase transformation, forming and forming processes of materials, and realizing a brand- new target manufacturing method to improve processing quality, efficiency, accuracy and consistency, as shown in Fig. 6.1.

The interaction mechanism between ultra-fast laser and materials is studied by using plasma quantum model, improved two-temperature model, molecular dynamics model and first-principles calculation. It is predicted that the electron excitation/ionization/recombination process, local instantaneous material characteristics, material phase transition process and final forming and forming process can be controlled by ultra-fast laser spatio-temporal shaping [1, 3–5]. The ablation shape and surface texture structure of femtosecond laser were predicted for the first time, and the stable machining depth region with nanometer super diffraction limit was successfully predicted [6–9].

Based on the new principle of electronic dynamic control machining, for femtosecond laser shaping in the time domain, spatial domain, for the first time, the active control of local instantaneous electron dynamics in manufacturing has been realized, greatly improving the processing quality, precision, efficiency, depth-diameter ratio and other limit manufacturing capabilities [1, 10, 11]: femtosecond pulse sequence is proposed to control the free electron density and photon absorption efficiency, control the modification degree of material structure, and increase the etching efficiency by 37 times, as shown in Fig. 6.2 (a); a new super diffraction limit processing method for spatial shaping to control local instantaneous electron dynamics is proposed. The processed nanowires have good stability, are easy to pattern, and the linewidth can reach 1/14 of the wavelength, as shown in Fig. 6.2 (b); through time and space shaping, optimization and adjustment of ionized electron density distribution, the limit of the depth-diameter ratio of microhole processing is increased by 100 times (1000:1, 1.5 μm), and the efficiency is increased by 56 times,

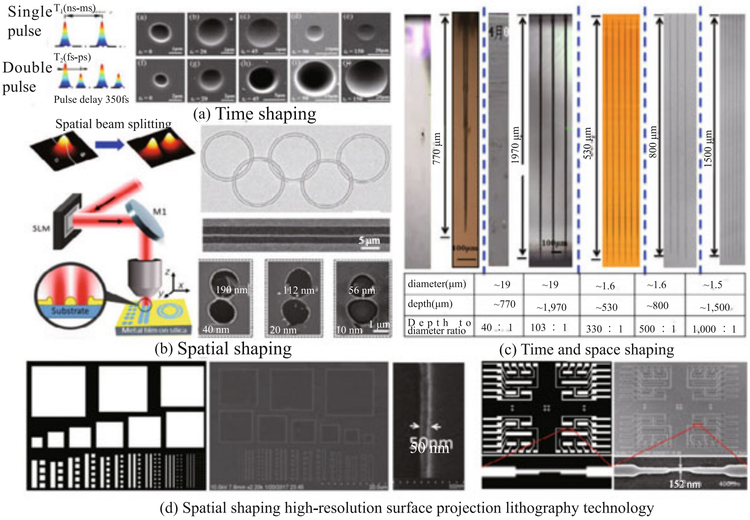

Fig. 6.2 A new method of ultra-fast laser space–time shaping micro-nano machining (**a** Time shaping to improve etching efficiency; **b** Space shape to improve machining accuracy; **c** Space–time shape to improve that depth-diameter ratio limit of micropores; **d** Large-area, high-precision, cross-scale micro-nano process)

as shown in Fig. 6.2 (c); based on the new laser space-time shaping micro-nano machining method, combined with DMD technology, large-area, high-precision, cross-scale micro-nanomanufacturing is realized, and the linewidth resolution is 50 nm, and the linewidth is realized Span 152–140 mm, as shown in Fig. 6.2 (d).

The new method of ultra-fast laser electronic dynamic control processing has attracted extensive international attention, and the related research work has been greatly positively evaluated by more than 70 academicians/scholars (including Nobel Prize winners) from various countries in *Science*, *Nature* and other journals. For example, OSA/SPIE Fellow and Professor P. Herman of the University of Toronto, Canada, cited the new manufacturing method in six places in his specially invited review paper, and listed the proposed new manufacturing method as “the best reported femtosecond laser results (one of the best reported femtosecond laser results)”. Professor Koji Sugioka of OSA/SPIE Institute of Physical Chemistry, Japan, greatly evaluated the new method in nanophotonics, saying that the new method successfully processed 3D micro-nano structures that were “previously inaccessible”. *Laser Focus World* published the topic “Shaping Femtosecond Laser to Change Electronic Dynamics and Improve Ultrafast Laser Processing Quality” to comment on this new method: “Stunning results have been obtained.” The research team was invited to be in *Light: Sci & Appl* of the *Nature* published a 26-page special topic review entitled “New Electronic Dynamic Control Micro-nano Processing Method for Femtosecond Laser Space-time Shaping: Theory, Method, Observation and Application”, summarizing the main scientific research progress of the new method in the past 10 years, and taking it as the only highlight on the front page of the journal website for more than one month. The news platform of the American Association for the Advancement of Science and its journal *Science*, titled "Femtosecond Laser Manufacturing: Realizing Dynamic Control of Electrons", made a special report on the new method, and said that the new method "may bring revolutionary contribution to high-end manufacturing, material processing and chemical reaction control", which was reprinted by more than 10 international mainstream scientific and technological media such as Phys.org.

6.2 Multi-Time Scale Observation of Ultra-Fast Laser Micro-Nanomanufacturing Process

Ultra-fast laser processing is a non-equilibrium, nonlinear and ultra-fast process, which involves many physical and chemical processes, such as laser propagation and material ionization, material phase transition, plasma eruption and radiation, shock wave formation and propagation, and microstructure formation [12]. The characteristic time of the above physical and chemical processes ranges from femtoseconds to milliseconds or even seconds, but they influence each other. Based on this, the research group of Beijing Institute of Technology proposed and established a real-time observation system spanning the multi-time scale of "femtosecond-picosecond-nanosecond-millisecond" (Fig. 6.3), spanning 12 time orders of magnitude, femtosecond laser pump detection, laser-induced breakdown spectroscopy, time-resolved plasma imaging, industrial continuous imaging and other technologies [13] are comprehensively used to capture the process of laser processing of high aspect ratio microholes in real-time by charge-coupled device (CCD) camera on the second time scale; on the nanosecond scale, the eruption process of plasma has been observed by femtosecond laser double pulse induced breakdown spectroscopy system on the picosecond time scale, the generation and evolution of laser-induced plasma/shock wave have been observed by pump-probe microscopy system on the femtosecond time scale, the dynamic propagation process of the femtosecond laser pulse and the ionization process of materials have been observed. Using a multiscale observation system, the regulation mechanism of femtosecond laser spatio-temporal shaping on electron heating, ionization and recombination in manufacturing and its influence on microstructure shaping and formation are revealed. For the first time, panoramic observation (from constant speed to 3.5 trillion times slower) of mass and energy transmission process with electrons as the main energy carrier in the manufacturing process has been realized, providing observation evidence for new manufacturing technologies and promoting the development of ultra-fast technology.

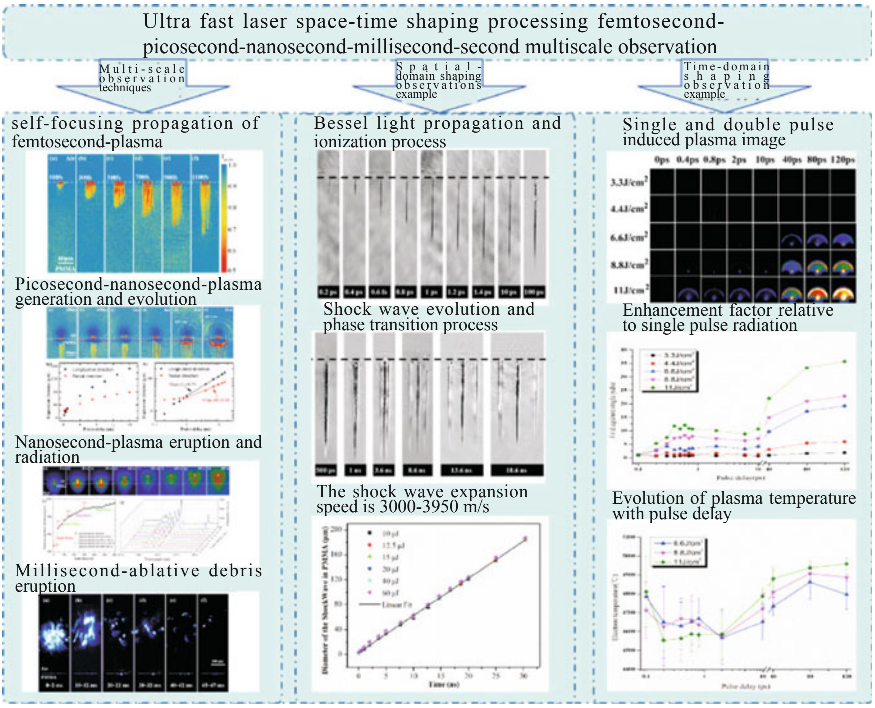

Fig. 6.3 Real-time observation of ultra-fast laser spatio-temporal shaping processing femtosecond-picosecond-nanosecond-millisecond multi-time scale

6.3 Important Engineering Applications of Laser Micro-Nanomanufacturing

Based on the new method of electronic dynamic control processing, laser micro-nanomanufacturing realizes the active control of local instantaneous electronic dynamics in manufacturing for the first time, thereby greatly improving the processing quality, precision, efficiency, depth-to-diameter ratio and other extreme manufacturing capabilities. The application of this new method successfully has solved the technical problems of many important projects and provided strong support for the country's major strategic needs.

6.3.1 Machining and Testing of Target Ball Micro-Hole

As a common structure, micropores are widely used in various fields. However, as the application requirements of major national strategic needs continue to rise, the depth-to-diameter ratio, aperture, shape complexity, and quality requirements of

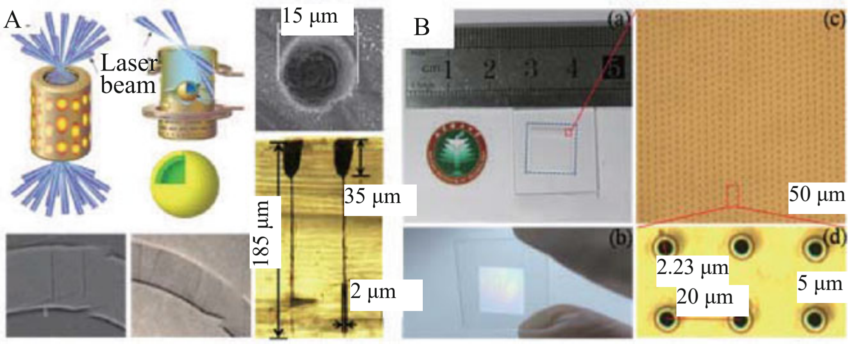

Fig. 6.4 Target ball micro-hole processing for a major national project (**a** Target ball micro-hole processing; **b** Single-pulse ultra-fast laser bessel beam flying drilling method to achieve high-efficiency, high-quality, and high-consistency micro- hole array processing)

micropores are constantly pushing to new extremes. The micro-nanomanufacturing team of Beijing Institute of Technology uses a new method of ultra-fast laser space-time shaping micro-nano processing to address the technical challenges of micro-hole processing in the core structure of a major national project (such as large depth-to-diameter ratio, minimization of recast layers/sputters, hole quality requirements are high; residues in the cavity are minimized; processing efficiency needs to be improved), the spatial distribution of the ultra-fast laser light field is changed through spatial shaping, the instantaneous local electron density distribution and its phase transition process are controlled, and the plasma is optimized and adjusted. The eruption process has overcome the large depth- to-diameter ratio (1000:1, diameter 1.5 µm), high consistency (250,000 holes/cm^2), high quality (no microcracks/recast layer), and high efficiency (100 holes in a single beam/sec), minimization of residues and other problems in the preparation of micropores (Fig. 6.4), and has been selected as the only processing technology for the micropores of the national major projects [14].

In response to the test of the inner and outer diameter and thickness parameters of the target ball in the major national engineering, the Beijing Institute of Technology research team proposed a laser radial polarization differential confocal longitudinal field tomography detection method [15, 16] (Fig. 6.5), using the difference moving confocal technology to improve the axial resolution of the confocal imaging detection technology; using radially polarized tight focus technology and pupil filter technology to significantly compress the focus spot; improving the lateral resolution of the confocal imaging detection system. Reuse image restoration technology further improve the lateral resolving power, and then improve the spatial resolving power of the system. This method, combined with image edge processing technology, can achieve 2 nm axial and 80 nm lateral resolution structural testing, and can be used for nanometer-precision metrological testing and calibration of large-scale and large convex-concave standard samples.

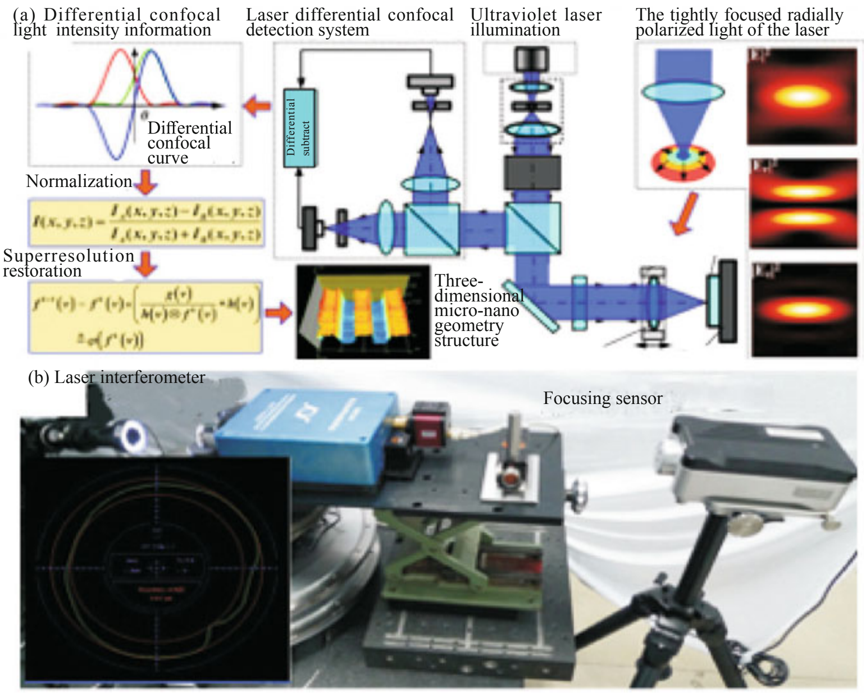

Fig. 6.5 Principle and device of laser radial polarization differential confocal longitudinal field tomography detection method

6.3.2 *Manufacturing of New Optical Fiber Sensors*

The research team of Beijing Institute of Technology has aimed at the manufacturing problems of 3D micro-nano structures of optical fiber devices and has adopted a new method of femtosecond laser manufacturing to process the invented series of temperature, pressure, vibration and concentration on optical fibers such as pure quartz with high quality and high precision. Sensors [17–19] (Fig. 6.6), as well as signal demodulators and measuring instruments, solve the common bottleneck challenges that severely restrict the development of my country's cutting-edge defense equipment: testing in small areas, high temperature, high pressure, and strong electromagnetic environments. Professor Cusano, editor-in-chief of *Opt Laser Technol*, has commented that the sensitivity of the new sensor is "the highest record currently", and it has been successfully applied to a hypersonic aircraft high temperature strain test, a stealth fighter pressure test, a missile/rocket fuze bridge wire ignition temperature, a gun bore temperature/testing of key physical quantities of major equipment in the fi of defense, such as deformation, provides important support for the development/production of my country's cutting-edge technical equipment.

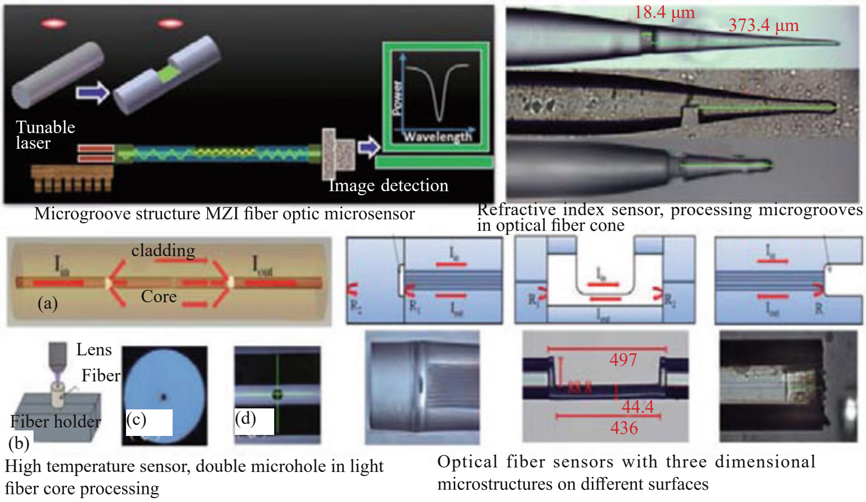

Fig. 6.6 Laser processing series of three-dimensional micro-structure optical fiber micro sensor

Focusing on the two key issues of improving manufacturing accuracy and speed, the research team of Central South University has used femtosecond laser manufacturing technology to achieve nanolevel precision processing of optical fiber micro/nano devices and the manufacturing of new device structures in order to solve the problem of micro-nano structure manufacturing of optical fiber devices. China's independent manufacturing of high-precision, high-performance optical fiber devices provides a theoretical foundation and technical reserves [20, 21].

The research team has clarified the femtosecond laser processing and forming mechanism of the fiber micro/nano structure, and has carried out the analysis of the processing mechanism of transparent media materials. By designing the beam control system and processing system, using bessel to shape the beam, the ablation processing radius in the target quartz glass can be achieved. The adjustable ring structure and micro-channel, realize micro-hole processing with a depth-to- diameter ratio of about 500:1, and realize rapid processing of micro-hole structure and long-period fiber grating on the optical fiber, and the micro-hole structure fiber has high refraction rate sensing characteristics; a high-precision and fast fiber micro-nano structure manufacturing method based on multi-beam simultaneous irradiation and femtosecond laser nonlinear effects is proposed, and the long-period fiber is written by the femtosecond laser point-by-point method and line scanning method respectively. The influence of different parameters (grating period, grating length, duty cycle, scan times, etc.) on the transmission spectrum of the LPFG under the point-by-point method is analyzad. The temperature characteristics of long-period fiber gratings are theoretically analyzed, and temperature control experiments are carried out on the long-period fiber gratings written by line scan. The experimental

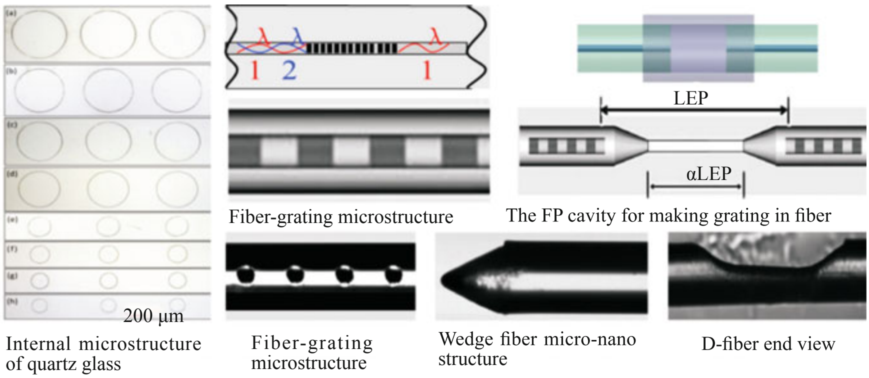

Fig. 6.7 Side view of five-ring micro-nanoscale structure and optical fiber micro-hole

results show that it is suitable for wavelength control in the low temperature range and has high temperature sensitivity in the high temperature range. Part of the result is shown in Fig. 6.7.

6.3.3 Optical Device Manufacturing

Optical device manufacturing has become a difficult problem in the manufacturing field due to its difficult material processing and high precision requirements. For example, infrared guidance window anti-reflection is a key technology for high-speed missiles. The integrated micro-nano structure does not require coating, which not only ensures reliability, but also effectively realizes anti-reflection, which is a key manufacturing bottleneck for the speed increase of high-speed missiles. The anti-reflection of infrared guidance windows has common challenges: difficult to process materials (zinc sulfide, sapphire, diamond, etc.), large area (hundreds of square centimeters), high uniformity, three-dimensional surface micro-nano structure, difficult to pass photolithography, imprinting, and reaction ion etching and other processing. The research team of Central South University and the research team of Jilin University have used ultra-fast laser direct writing to process large-area, highly consistent inverted pyramid-shaped microstructures and hole arrays (period 2 μm, diameter 1 μm, height 1 μm) on the surface of sapphire material; the transmittance reaches 92%~95%; in the incident range of 0~70°, the surface maintains high transmittance [Fig. 6.8 (a)]; at the same time, the new method of ultra-fast laser pulse shaping electronic dynamic control processing is applied , processing large area (φ100 mm) hole array infrared antireflection microstructure (period 3.6 μm, diameter 3.3 μm, depth 0.8 μm) on the surface of zinc sulfide, with a transmittance exceeding 85% [Fig. 6.8(b)] [22].

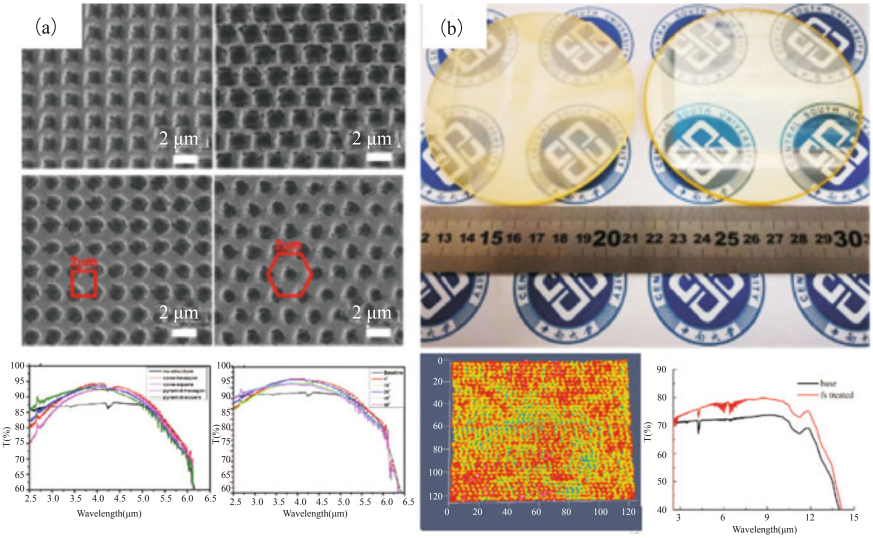

Fig. 6.8 Manufacturing of anti-reflection structures for difficult-to-process materials (**a** Sapphire material; **b** Zinc sulfide material)

The aspheric microlen is also an important optical device, which has important applications in aviation, aerospace and other fields. However, due to its three- dimensional complex and difficult-to-machine curved surface and high precision requirements, it has become a major problem in the manufacture of optical devices. The research team of Jilin University has proposed a new method for processing curved micro-lenses and arrays using femtosecond laser micro-nano processing technology in response to the manufacturing problems of aspherical micro-optical components, laying a theoretical foundation for high-precision, repeatable and high-efficiency laser micro-nano processing with technical support. It provides a new idea for the manufacture of aspheric micro-optical components that are urgently needed in the fields of aviation, aerospace and laser technology. This technology provides novel solutions for basic research and common micro-optics problems faced by frontier fields of national defense applications such as organic electroluminescence, solar cells, high-performance optical fiber sensing, micro- flow and optical flow detection, and filmless anti-reflection infrared guidance [23–26]. Based on the above-mentioned new methods and new technologies, a series of high-performance micro-optical elements represented by shaping microlenses, such as zone plates, aspheric refractive lenses, refractive hybrids, and tunable lenses, have been realized (Fig. 6.9). In addition, in response to the difficult problem of semiconductor diode laser beam shaping, femtosecond laser processing is used to fabricate integrated aspheric microlenses for vertical cavity surface-emitting lasers, which reduces the output laser divergence

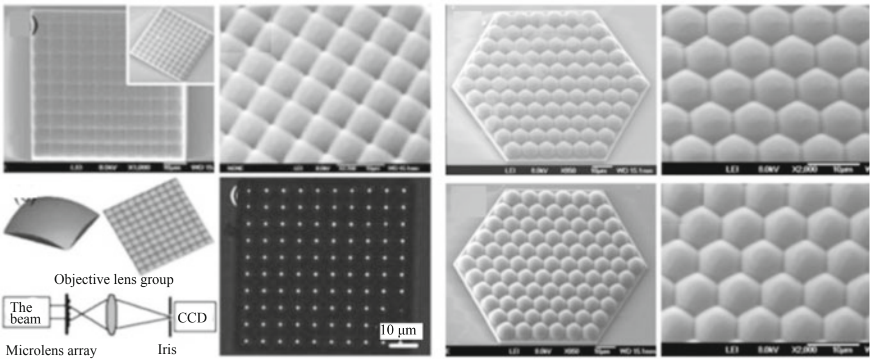

Fig. 6.9 Femtosecond laser processing of high numerical aperture hexagonal close-packed microlens array

angle from 18.16° to 0.86°. For edge- emitting semiconductor diode lasers, asymmetric multi-order zone plates and non- aligned hyperboloid lenses are prepared, achieving ideal shaping effects from 60° on the fast axis and 9° on the slow axis to 6.9 mrad and 32.3 mrad. The efficiency of optical fiber coupling is higher than 80%.

6.3.4 Preparation of New Materials

The new method of ultra-fast laser processing not only has an important application in the manufacture of traditional materials, but also shows significant advantages in the preparation of new materials. The Beijing Institute of Technology research team has established a laser-assisted preparation method system for graphene in different dimensions, using the interaction of laser and carbon micro-nano materials to control the local instantaneous properties of the material, and achieve high- precision and high-efficiency manufacturing of multi-dimensional micro-nano functional structures [27–29]: laser direct writing quickly prepares good monodisperse zero-dimensional graphene quantum dots [Fig. 6.10 (a)]; laser micro-nano processing one-dimensional graphene microfibers to obtain walking robots [Fig. 6.10 (b)]; laser rapid radiation direct writing of two-dimensional graphene films to obtain graphene memory diodes [Fig. 6.10 (c)]; laser-assisted deposition to prepare functional three-dimensional graphene foams and other micro-nano functional structures [Fig. 6.10 (d)]. Using the above-mentioned new laser processing methods, a series of functional graphene-based devices have been constructed, which greatly expand the application of new materials such as graphene in the fields of capacitors, infrared sensors, fuel cells, and lithium-ion batteries.

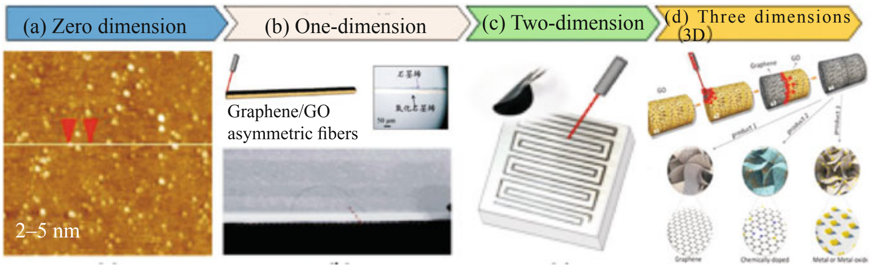

Fig. 6.10 Laser-assisted preparation method of graphene with different dimensions (**a** Zero-dimensional quantum dots; **b** One-dimensional graphene fiber; **c** Two-dimensional graphene film; **d** Three-dimensional graphene foam)

6.3.5 Manufacturing of Nanocrystalline Large-Area Assembly Structure

The nanocrystalline assembly structure provides greater flexibility and possibility for optimizing and regulating the properties of materials, and is of great significance to the development of chemical catalysis, solar energy conversion, and biomedicine. Utilizing the advantages of laser manufacturing, the research team of the Beijing Institute of Technology has established a method of laser-irradiated colloidal nanocrystals to assemble a large area to obtain a micron-scale nano-superstructure. The interaction between the resonant continuous laser and the Plasmon assembly nanostructure is manipulated to control the microstructure of materials the local photothermal activity of the structure, and realizes the *in-situ* welding of the precisely synthesized Plasmonic zero-dimensional nanocrystalline particles to obtain the superstructure. In order to realize the micro-nanomanufacturing and processing of the assembled structure of the zero-dimensional nanocrystalline, the inter-particle Efficient electron transmission and device applications have laid a solid material foundation [30–32]: the precise synthesis of Au@CdS, Au and other Plasmonic zero-dimensional particle assembly films using resonantly coupled continuous laser irradiation can realize the inter-nanoparticle interaction. Nano- welding to form a superstructure, and realize its application in light absorption and flexible devices (Fig. 6.11A); use precise synthesis of doped quantum dot (CdSe: Ag) film, continuous laser-assisted micro cd at 3.1 eV. The test and the transient spectrum test of the femtosecond (95 fs pulse, ~800 nm) laser realized the photo- induced magnetism in the non-magnetic Ag-doped CdSe quantum dots (Fig. 6.11B). Using the above-mentioned new laser irradiation processing method, the nano-particles are processed for micro-nano processing, which greatly expands the bottom-up assembly methodology of zero-dimensional plasmonic nanocrystals and doped quantum dots, and realizes its use in photoelectric detection, photomagnetic New applications in the fields of coupling and spintronics.

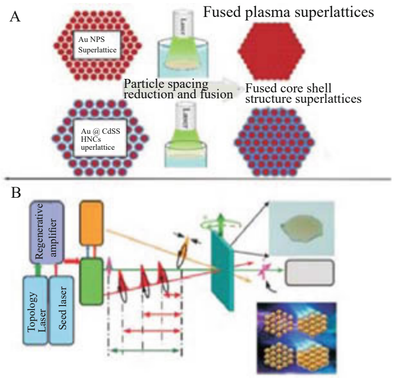

Fig. 6.11 **A** Use 532 nm (6.68–13.37 W·cm^{-2}) continuous laser irradiation to accurately synthesize plasmonic zero-dimensional particle assembly films such as Au @ CdS, Au, etc., to realize nano-welding between nanoparticles into a superstructure, and realize its application in light absorption (a) and flexible devices (b); **B** Use the precise synthesis of doped quantum dots (CdSe: Ag) film, continuous laser-assisted MCD test at 3.1 eV and femtosecond (95 fs pulse, ~800 nm) laser transient spectroscopy test, realized the light in non-magnetic Ag- doped CdSe quantum dots induced magnetism (a–e)

6.4 Laser Micro-Nanomanufacturing Equipment

The high-efficiency processing of large-area micro-nano 3D topography is a major international problem. The core technical problem is how to efficiently transform the massive design data into 3D micro-nano topography. Based on a new method of laser spatial shaping, the research team of Soochow University has proposed a lithography technology based on phase-space light hybrid modulation and digital light field, using "micro-nano structure light field" frame-by-frame digital rolling stack (integration) technology (12,000 frames)/sec, 1920 × 1080 data/frame, 3D navigation flight exposure mode, has overcome the major problems of efficient processing of complex micro-nano 3D topography on warped surfaces, and has successfully developed the "Large-area micro-nano 3D direct writing equipment MiScanV" (Fig. 6.12), filling the industry gap, and has successfully applied to large-area flexible functional materials, large-size capacitive sensors, new display devices, MEMS devices and other high-tech research fields for national defense and civil use. In the National "Twelfth Five-Year" Science and Technology Innovation Achievement Exhibition, large-area micro-nano 3D direct writing equipment has been exhibited as a landmark achievement in the advanced manufacturing field of the national "863 Program". At present, the equipment has been used in the development and manufacturing of micro-nano materials and devices in dozens of units such as China Electronics Technology Group Co., Ltd., Tsinghua University, Hong Kong Polytechnic University, and has been exported to Russia, Israel and other countries.

In response to the lack of technical means of "sub-nanometer precision control" in the development of photonic chips, 3D displays, and optical waveguide devices,

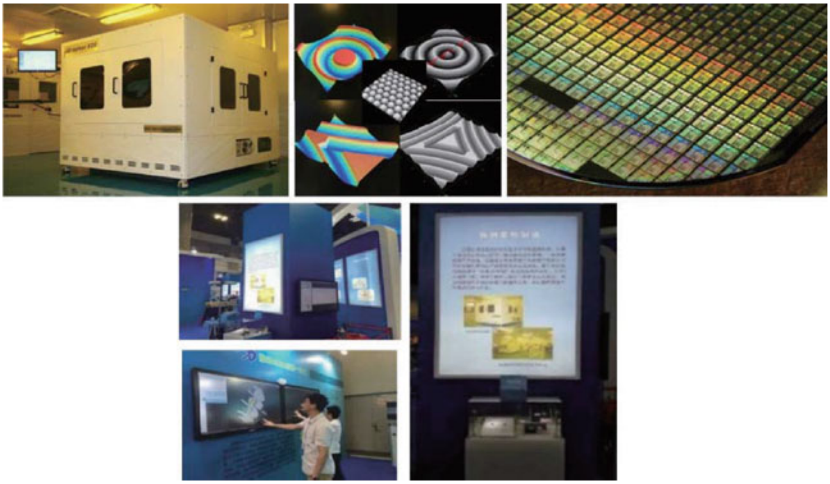

Fig. 6.12 Large-area micro-nano 3D direct writing device MiScanV and its iconic results

the research team of Soochow University has invented a new method of nanolithography with "five-dimensional micro-nano optical field control" (structural unit). The structure resolution is close to λ/4, which is 2 times higher than that of the projection lithography system; and has successfully developed a nanolithography equipment "NanoCryatal" with a structure modulation accuracy of <1 nm. The field size is 100–250 μm, the structure size in the light field is >90 nm, the format is 6–32 inches, the structured light field lithography mode, the rate is 100–500 mm^2/min, which fills the gap in the industry and realizes the industrial application (Shanghai Jiaotong University, The Hong Kong Polytechnic University and many companies).

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Chapter 7
Other Nanomanufacturing Principles and Technological Breakthroughs

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Focusing on the core research goals of nanoprecision manufacturing, nanoscale manufacturing, and cross-scale manufacturing in nanomanufacturing, this Major Research Plan is aimed at subdivided areas such as nanomaterial manufacturing, special nanoprocessing methods, nanodevice integrated manufacturing, and nanometering and measurement. The corresponding layout and project support have been achieved, and breakthroughs in principles and methods have been achieved, providing support for the overall development of China's nanomanufacturing field.

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7.1 Preparation and Application of Functional Nano-Materials/Structures

In response to the major needs of nanomaterials manufacturing, this Major Research Plan has carried out project deployment in the "functional nanomaterials to construct nanostructures", and has developed preparation technologies surrounding precious metal nanomaterials, carbon materials, semiconductor nanomaterials, polymer materials, etc., and has formed serving such as high-sensitivity biosensing, high-precision bioimaging, high-efficiency energy conversion and collection, has established a typical manufacturing method based on nano-printing functional materials, and has realized the complete process chain of the mass production from material preparation to prototype devices.

7.1.1 Preparation of Functional Nanomaterials/Structures

The research team of Jilin University [1–3] has taken advantage of the complementarity of polymer materials and metal and inorganic non-metallic materials to propose a technical scheme for constructing two-dimensional ordered micro-nano structures. The hydrothermal synthesis method is used to prepare low-toxic, high-efficiency fluorescent polymer carbon dots, and polymer molecules that are responsive to solvents, ions, pH and cross-linking are introduced into the alternating layers to obtain one-dimensional photonic crystals with different response characteristics. Based on one-dimensional photonic crystals, silver ions are reduced *in situ* by ultraviolet light to generate a three-dimensional micro-nano structure in a one-dimensional multilayer film structure; a two-dimensional ordered micro-nano structure with non-spherical symmetry and unidirectional infiltration is constructed, forming a one-way valve device of a microfluidic system; using colloid etching technology combined with SI-ATRP *in-situ* polymerization to prepare a two-dimensional multi-level micro-nano ordered structure to construct a multiscale, gradient feature protein pattern and to prepare single-stranded DNA nanocone arrays and two-dimensional multi-level DNA patterned micro-nano structures that can be used for target DNA sensing.

The research team of the Chinese Academy of Medical Sciences [4–6] has fabricated high-precision, cross-scale planar gold nanoarrays based on DNA templates, enriching the theoretical foundation of nanomanufacturing and the manufacturing methods of technology and equipment. Through different modes of action such as electrostatic force, chemical bonding and biological recognition, the controllable self-assembly of gold nanorods has been realized, and the electromagnetic field distribution and Raman enhancement effect of gold nanorods have been studied. The research work has received the continuation of this Major Research Plan, has developed a new design method for universal nano-assembly, and has constructed a drug-loaded chitosan-gold nanorod assembly. The evaluation results of in vitro cell experiments show that the side-by-side nanorods have a good effect in tumor treatment, opening up a new treatment approach for tumor treatment research—chemotherapy-photothermal therapy integration, and it is effective for large molecular weight molecules (such as polyethylene glycol with molecular weight 1000–12,000), metal ions (such as mercury ion, the detection limit of 0.1 nm), small molecules (such as theophylline, the detection limit of 0.05 μm) have been tested with high specificity and sensitivity.

The research team of Sun Yat-sen University [7–10] has that established an electrochemical preparation method for large-area orderly growth of nanosemiconductor materials, and has realized the preparation of nanosemiconductor materials such as/CdTe, PbS/PbTe ZnO/ZnS, ZnTe/CdO, CdS on macro-scale substrates such as Cu, Ni, Ti, and ITO, playing an important role in promoting the development and application of nanosemiconductor materials science. The research team has Synthesized $MnO_2/Mn/MnO_2$ sandwich structure of nanotube arrays, and has discussed its application in the field of energy storage; has proposed the preparation method of TiN nanowire array electrode material, and has used solid polymer electrolyte to take the place of liquid electrolyte to improve cycle stability. After 15,000 cycles, its stability remains above 83%. This research work has been supported by the continuation of this Major Research Plan, and has carried out the nanoscale manufacturing of large-area ordered transition metal-based energy storage materials based on electrochemical methods and the research of flexible energy storage devices. In the research of hybrid supercapacitor anode materials, new vanadium oxide anode energy storage materials and hybrid supercapacitors, manganese-based flexible wearable asymmetric energy storage devices, stretchable flexible supercapacitors, etc. have made progress. Some representative results are shown in Fig. 7.1.

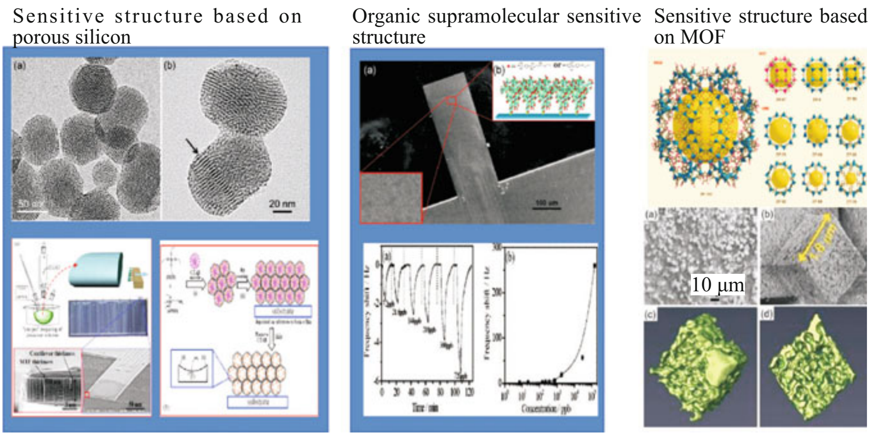

Fig. 7.1 Some representative results of nanomaterial manufacturing

7.1.2 Nano-Material Hybrid Printing Technology and Application

Based on the manufacturing of functional nanomaterials, the research team of the Suzhou Institute of Nanotechnology and NanoBionics, Chinese Academy of Sciences [11–14] has developed a flexible transparent conductive film nanomaterial hybrid printing manufacturing technology, which has broken through the traditional technology of conductivity and penetration. The problem of mutual restriction of rates has broad application prospects in the fields of large-area and low-cost manufacturing of flexible displays, light-emitting, thin-film solar cells, low-cost radio frequency identification, sensors and other fields. The team has studied the uniformity and consistency of the manufacturing technology of large-area printed nanosensor arrays, laying the foundation for the further realization of large-scale mass production of electronic devices. A new hybrid printing technology combining nanoimprint and nanoink filling, the material was invented and a variety of printing processes from inkjet printing to screen printing and gravure printing were established. This invention won the 2014 China Patent Gold Award; in terms of industrial promotion, developed a printed nanosilver metal grid flexible transparent conductive film touch sensor which was applied to touch screens of mobile phones and tablet computers; printed nanosilver flexible transparent conductive film has achieved mass production, electronic skin sensors and formaldehyde sensors have reached the level of practicality, and product development has been carried out in related companies. Part of the result is shown in Fig. 7.2.

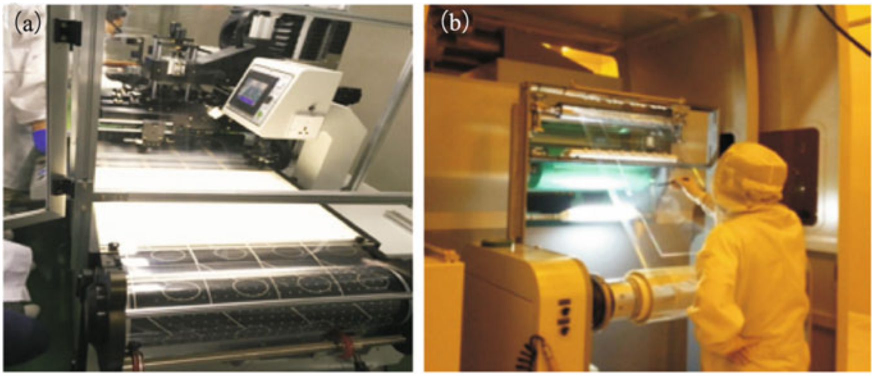

Fig. 7.2 Nano-printing manufacturing technology of mass-production electronic devices (**a** Printed field-effect transistor functional circuit; **b** Printed transparent conductive film touch sensor)

7.2 Maskless Manufacturing of Nanostructures

With the funding and support of this Major Research Plan, and focusing on the needs of nanomanufacturing, Chinese researchers have conducted fruitful explorations in nanomachining, near-field lithography, maskless lithography, nano-milling, and multi-photon processing, understanding the processing principle of maskless manufacturing technology, and forming unique nanostructure manufacturing methods and technical routes, which enrich the technical connotation of my country's nanomanufacturing.

7.2.1 Nano Cutting Mechanism and Ion Implantation Auxiliary Processing

According to the basic theory and control problems of high efficiency and low damage in nano cutting manufacturing, the research team of Tianjin University has carried out theoretical research on nano cutting and has developed a nano cutting with independent intellectual property rights. New cutting technology and new methods provide an important reference method for nanoprecision complex surface machining and play an important supporting role in the development of my country's advanced manufacturing industry [15–18].

The mechanism of material removal is studied from the perspective of micromechanics, the nanocutting process is modelled and mesoscopically simulated using the micro-macro mosaic theory, and the three-dimensional molecular dynamics and multiscale analysis method and simulation platform of nanocutting are established, and model differences and size effects in the cutting process and the nanocutting is systematically analyzed. It has proposed the nano-pushing mechanism of material removal in the nanocutting process, and has explained the reason for the formation of nanolevel precision surfaces; has proposed a new method of ion-implantation-assisted nanomachining; has developed the theory and technology of surface nitriding-assisted machining methods and ultrasonic-assisted cutting methods. The research effectively reduces the wear of diamond tools and realizes ultra-precision cutting of carbon steel materials; researches the preparation method of nanoedge cutting tools based on focused ion beams, and realizes the high-efficiency and high-precision preparation of nanoedge micro-tools; proposes nano the minimum cutting edge radius of the tool that generates chips during cutting is 10 nm, which provides a basis for the accuracy of tool preparation; a new method for ion implantation to change the surface properties of the processed material and achieve high-efficiency nanocutting has been developed, and the stable cutting of the thinnest chip is 6 nm. Part of the result is shown in Fig. 7.3.

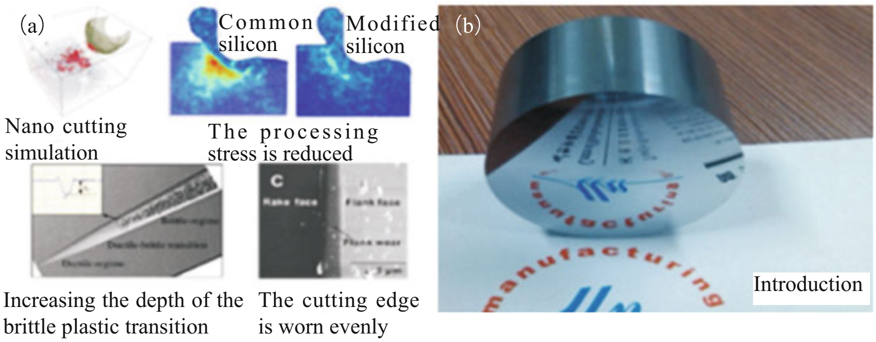

Fig. 7.3 Nano-cutting method of nanostructure (**a** Cutting performance changes after ion implantation; **b** Machining results of typical nanocutting devices)

7.2.2 Rotary Near-Field Lithography of Nanostructures

The research team of Tsinghua University has developed a new type of rotary near-field lithography method, which uses the excellent focusing characteristics of the surface plasmon lens in the near-field range, combined with the air flotation produced for the lithography head forms of high-speed rotation of the workpiece, so as to form a stable near-field condition to realize high-resolution, high-efficiency, large-area nanostructure processing [19–21].

The team thoroughly has studied the propagation characteristics of surface plasmons in the near-field range of 30 nm, the theory of rarefied gas lubrication under nanogap, the law of surface force action, and the rapid reaction mechanism of photoresist in nanosecond intervals, and studied head dynamics design theory, has broken through the core technology of rotary near-field lithography manufacturing, established a nanopattern rotary near-field lithography prototype manufacturing system, and has achieved low-cost manufacturing and high efficiency for patterns with a certain degree of complexity and a characteristic line width of 50 nm. With the speed of 11.3 m/s, line pattern processing at 16.85 nm and half-pitch processing at 50.71 nm and 75 nm have been achieved. Part of the result is shown in Fig. 7.4.

7.2.3 Maskless Etching Fabrication of Nanocones

The research team of the Institute of Physics, Chinese Academy of Sciences, aiming at the low-cost consistency of nanocones and the bottleneck of mass manufacturing, has realized the surface nanocone's unmasked plasma etching manufacturing technology, by controlling the temperature field, ion energy and surface ion sputtering process to optimize the key manufacturing process and to realize the large-area, uniform, universal and controllable manufacturing of surface nanocones [22–24].

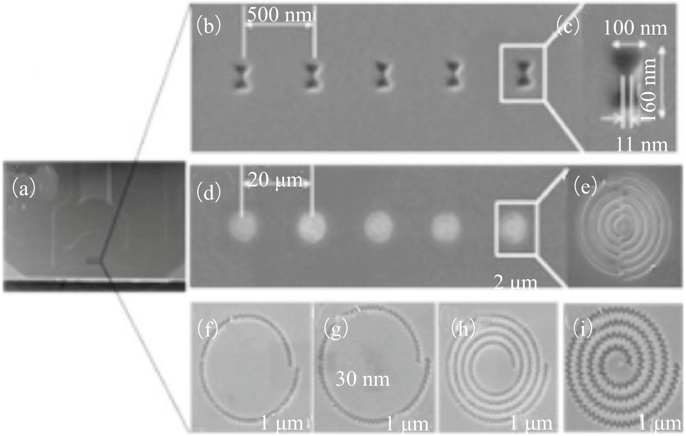

Fig. 7.4 Processing result of surface plasmon lens

The team has developed a maskless plasma etching device, proposed an optimized design method for key components such as dual plasma regions, filament arrangement shape, and bias control power supply, and has developed an independent technology for maskless etching of surface nanocones, obtaining the key process of surface nanocone without the mask and controllable fabrication, and realizing the large area (4 inches), density uniformity (5%), controllability (cone height 0.2–3 μm, cone angle 15°–45°, nanocone cone density above 10^6), universality (suitable for a variety of materials), patterning and batch manufacturing. The surface nanocone photoelectric properties and applications are studied, and wide-band super anti-reflection properties (reflection rate less than 1%), excellent and stable electronic field emission properties (current density exceeding 10 mA/cm^2), wide-band optical detection and highly sensitive sensing (sensitivity increased by 5 times) are achieved, having enhanced surface-enhanced Raman scattering effect (field enhancement factor $>10^8$ and detection capability >5 nm) and controllable super-wetting characteristics (from super-hydrophilic to super-hydrophobic and super-adhesive characteristics), and can be used as a three-dimensional electrode structure application in supercapacitors and lithium batteries, thus the overall performance of energy devices is greatly improved (can be recycled 10,000 times). Some results are shown in Fig. 7.5.

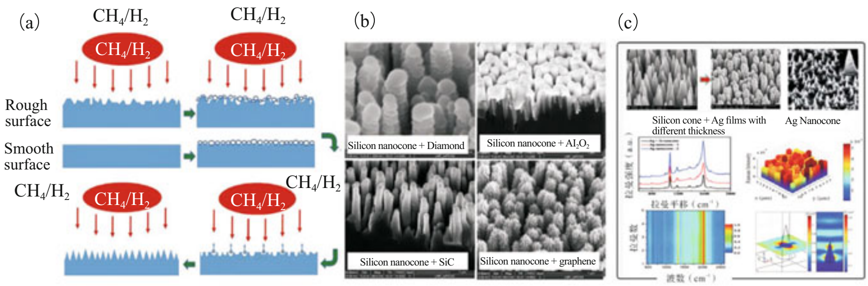

Fig. 7.5 The surface nanocone structure can be controlled without a mask (**a** The principle of formation of nanocone by unmasked plasma etching; **b** The structure of silicon nanocone is used as a functional template; **c** Surface enhanced Raman scattering characteristics of metal nanocone array structure)

7.2.4 Principles and Methods of Constrained Etching for Nano-Features

In response to major requirements such as large-scale integrated circuits and modern optical precision systems, researchers have proposed original constrained etching principles and methods, which are applied to the fields of nanoprocessing of high-quality optical materials and the flattening and hardening of the copper interconnection surface of large-size silicon wafers, and the basic theories and methods for restricting etching nanoprocessing equipment have been established.

The precision manufacturing team of Dalian University of Technology [25–29] aiming at the problem of flattening the surface of large-size silicon wafer copper interconnections with low-strength Cu/Low-k structures in the manufacturing of very large-scale integrated circuits, proposed a new stress flattening method based on the principle of constrained etching processing and developed three original flattening methods: an electrochemical polishing method based on diffusion control reaction, film constrained etching polishing method based on polymer, and chemical polishing method based on light-induced constrained etching, achieving large area (mm/cm level) flattening processing.

Aiming at the large-area uniform processing problem caused by the micro-nano gap formed by the electrode and the surface of the workpiece, an etching processing method sensitive to the gap has been innovatively developed. By designing and regulating the reaction process in the large-area micro-nano gap, the diffusion process in chemical confinement etching has been accurately controlled, and a gap-sensitive etching processing method that does not rely on constraining agents has been developed to achieve large-area constrained etching planarization; an electrochemical polishing method based on diffusion control reaction is proposed to reduce the roughness *Ra* from 100.5 nm to 3.6 nm taking the rough copper surface polishing as the research object and under the condition of 0.2–1.1 V triangular wave voltage, 0.5 μm processing gap and 24 min processing conditions. It has developed a large-area smooth electrode preparation and nanoprecision chemical etching platform, has realized the flattening of the copper surface in the 50 mm area, the PV value dropped from 260 nm to 120 nm, and the roughness *Ra* value dropped from 82 nm to 4 nm; innovatively has proposed an electrochemical etching planarization method based on redox polymer nanofilm, using redox hydrogel polymer to build a large-area tool electrode surface and a micro-nanolevel gap between the surface of the workpiece, and using the unique physical and chemical properties of redox water gel polymer to control the reaction process in this special space and realize nanometer-precision etching processing. The glassy carbon electrode with surface roughness *Ra* of 3.8 nm is used as the tool electrode to realize 50 mm for the flattening of the surface of the regional copper workpiece, with the PV value decreasing from 3.95 μm to 1.93 μm, and the roughness *Ra* value decreasing from 2.6 nm to 2.2 nm. Part of the result is shown in Fig. 7.6.

The research team of Shanghai Jiaotong University [30–32], aiming at the demand for nanomachining of hard optical materials in the process of 3D bas-relief patterning in the manufacturing of micro-nano optical components, focusing on the basic theories and keys of restricting etchant layer technology and electrochemical nanomachining technology, has carried out related research on nanomanufacturing, thus the processing resolution of GaAs, quartz and other optical materials reaches the nanoscale, forming a set of simple process, suitable for a variety of materials, nanoprecision copying and processing of bas-relief array patterns. The new equipment has promoted the progress of 3D micro-nanomanufacturing technology. Aiming at the Br_2/L-cystine constrained etching system of GaAs, using the feedback mode of the scanning electrochemical microscope and the collection mode experiment, combined

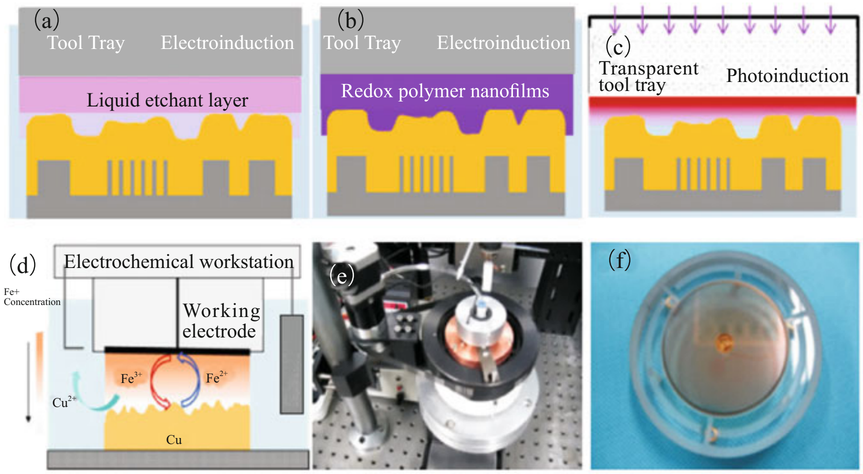

Fig. 7.6 Constrained etching chemical planarization on the surface of a large-area copper interconnect layer (**a** Electrochemical liquid layer system polishing; **b** Electrochemical film layer system polishing; **c** Photochemical liquid layer system polishing; **d** Schematic diagram of copper EGCP polishing; **e** EGCP prototype system development; **f** Physical photos of electrodes after polishing)

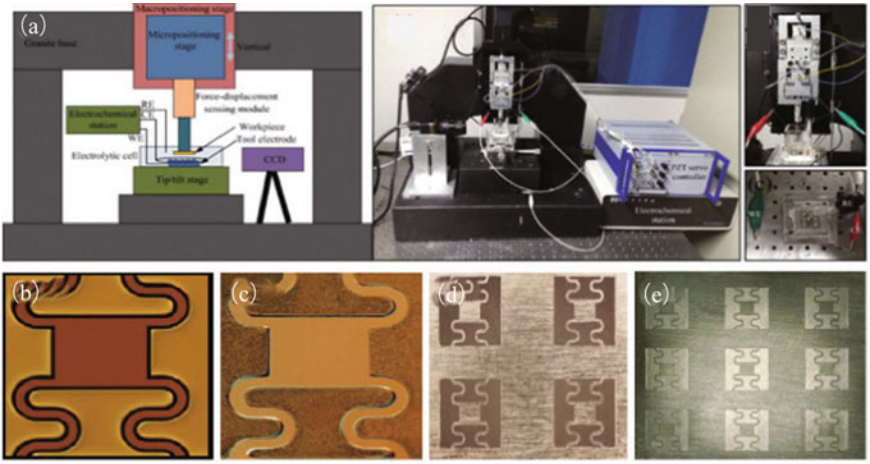

Fig. 7.7 The micro/nano structure replicated by CELT on GaAs, nickel, aluminum, and silicon substrates by electrolysis (**a** CELT micro-nano processing system; **b** Silicon template pattern; **c** GaAs pattern; **d** Pattern on aluminum; **e** Graphic on nickel)

with COMSOL multiphysics simulation, the etching reaction and the constrained reaction rate constant are determined. The main factors affecting the machining accuracy and the uniformity of large-area machining have been explored by simulation and experiment. By optimizing the component concentration of the etching system and the machining process parameters, the high production rate replication processing of nanometer precision of the microlens array on GaAs is realized on the developed machining device; in addition, electrochemical wet stamp constrained etchant layer technology and metal-assisted constrained etchant layer technology have been developed, three-dimensional micro-nano structures on semiconductors and metals have been processed, including refractive and diffractive micro lens arrays and surface-enhanced infrared components. Some results are shown in Fig. 7.7.

7.2.5 *Multi-Photon Fabrication of Metal Micro-Nano Structures*

The research team of the Institute of Technology of Physics and Chemistry of the Chinese Academy of Sciences has explored the control principle of nanoscale multi-photon photochemical reduction reaction based on the nonlinear optical effect-multi-photon effect for the processing and preparation of three-dimensional metal micro-nano structures, and has developed the new method, new technology and new equipment principle of an original and transcendent optical diffraction-limited three-dimensional metal micro-nano structure processing, providing important support

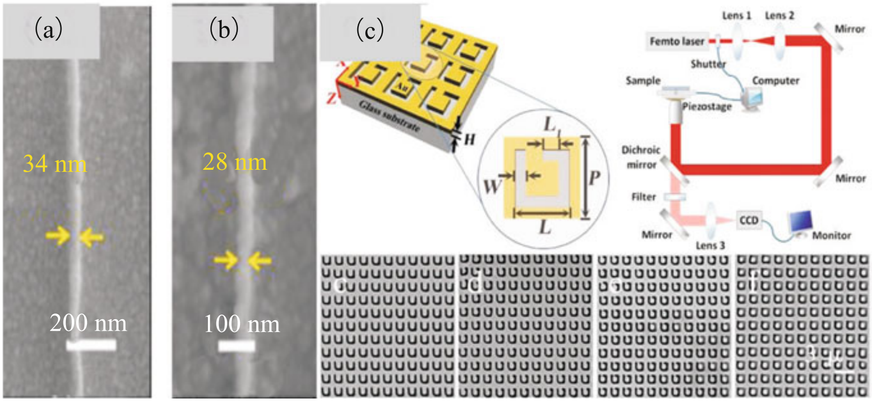

Fig. 7.8 Multiphoton processing of metal micro-nano structures (**a**–**b** Manufacturing of silver nanowires with line widths of 34 nm and 28 nm; **c** Manufacturing of two-dimensional chiral complementary metamaterials)

for the development of China's cutting-edge technology research and high-tech applications [33–35].

The team has proposed a new method of dual-wavelength, dual-beam, multi-photon metal nanostructure processing, which has solved the problem of the diffusion of metal nanoparticles generated by multi-photon photochemical reduction during processing, and has realized metal structure processing with a feature size of 28 nm. It provides an effective way for the low-cost, large-area, and rapid manufacturing of metal nanostructures and devices; in addition, it reveals a new micro-nano processing mechanism that regulates the nonlinear interaction between light and matter, and proposes equal arc scanning methods and shell scanning technology, the processing accuracy having been increased from 100 nm to 20 nm, and the surface roughness of the plane and curved surface modeling being less than 5 nm. Some results are shown in Fig. 7.8.

7.3 New Nano Device Manufacturing

During the implementation of this Major Research Plan, focusing on the design and manufacturing of new nanodevices, Chinese researchers have conducted in-depth research in the fields of two-dimensional material (such as graphene, molybdenum disulfide) nanodevice manufacturing and three-dimensional nanodevice manufacturing, forming several original manufacturing principles and manufacturing methods.

7.3.1 Principle and Manufacturing of Two-Dimensional Material Devices

In response to the challenge of processing functional devices below 10 nm, the research team of Nanjing University of Aeronautics and Astronautics has combined theoretical calculations and high-resolution electron microscopy *in-situ* observations and has found that the electron beam caused the adjacent pores of the molybdenum disulfide monolayer to undergo spontaneous phase change before polymerization, resulting in size generation homogeneous molybdenum sulfide nanobelt with a width of only 0.35 nm. The nanobelt is more stable than the complete molybdenum disulfide base material under electron beam irradiation, so it can be generated neatly and in a large range within the electron beam irradiation range. Hopefully, it can be used as a template to change the "top-down" nanomanufacturing technology from 10 nm node breaking through to the sub-nanometer level [36], as shown in Fig. 7.9 (a). This method also predicts the sub-nanometer template processing capabilities of a variety of low-dimensional materials with similar capabilities. After the publication of the paper, it has attracted rapid international attention. Researchers at the Oak Ridge National Laboratory in the United States has called it "Pioneer Results", and on this basis, sub-nanometer manufacturing has been controlled in a controlled manner. This technical method provides a new way for "top-down" to control sub-nanostructures, and has been invited by Nat Nanotechnol to write News and View [37].

The team has discovered for the first time the possibility of the construction of new graphene devices and the possibility of water-voltage effects such as wave potential and drag potential [38, 39]. By improving the deposition preparation process of large-area high-quality graphene and the design of energy conversion devices, systematic experiments and theories have clarified the huge experimental results differences and mechanism contradictions in the research of carbon nanomaterials capturing fluid energy since 2001. It is found that when graphene is inserted into the ion-containing solution, a voltage will be generated across the graphene. This phenomenon is named "wave potential", as shown in Fig. 7.9 (b).

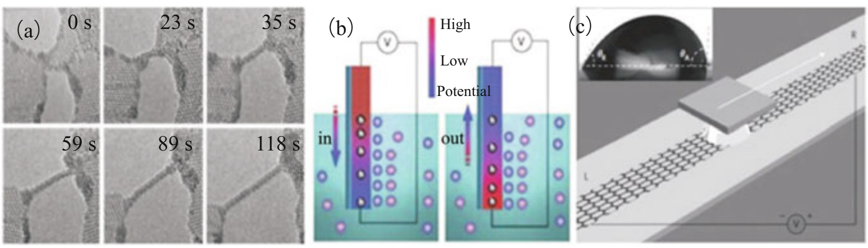

Fig. 7.9 Sub-nano-templating processing capabilities of low-dimensional materials and the construction of new graphene devices, as well as wave potential and drag potential (**a** Molybdenum sulfide sub-nano structure; **b** Wave potential in graphene; **c** Drag potential in grapheme)

When the graphene is inserted into the solution at a uniform speed, the fluctuation potential is proportional to the length of the graphene in the inserted solution. Combining first-principles calculations have revealed the mechanism of this phenomenon: the response speed of the anions near the liquid surface to the cation adsorption/desorption on the graphene surface lags behind the movement speed of the electrons in the graphene, resulting in a potential difference in the graphene. This potential difference is proportional to the speed of movement and is related to the species of ions. Based on the graphene wave potential work, it has been found that when the ion-containing droplet is dragged on the surface of the graphene, there will be two changes in the graphene along the direction of the droplet. This phenomenon is named "drag potential", as shown in Fig. 7.9 (c), and this drag potential is proportional to the movement speed and number of droplets, which can be used to detect the movement speed of droplets on the graphene surface [40, 41]. The wave potential and the drag potential reveal the principle of electricity generation by the movement of the electric double layer boundary. They have been commented by the British Institute of Physics Nanotechnology Network as "expanding the 200-year-old electrokinetic theory established since 1807", laying the foundation for photovoltaic energy capture and the design of the sensor.

7.3.2 Cross-Scale 3D Interconnection and Integrated Manu-Facturing of Nanostructures and Devices

In response to the needs of cross-scale structures and devices for three-dimensional nanooperation and interconnection technology, the nanomanufacturing team of Harbin Institute of Technology has proposed an innovative method for measuring and three-dimensional operations of cross-scale structures and devices based on dual AFM probes, has constructed a prototype of the device and has realized the three-dimensional arrangement, operation and interconnection of nanostructures and devices, and has provided technical support for nanoelectronics manufacturing and NEMS manufacturing [42–45]. For the three-dimensional operation and assembly of nanowires/tubes, we have designed and established a dual-probe AFM-based nanorobot system and control system with independent intellectual property rights, which have realized the three-dimensional nanowire/nanotube operation, assembly and interconnection. As shown in Fig. 7.10, on the developed nanorobot system, simulation calculation and measurement including precise calibration of the system, adhesion force and friction force have been carried out, and the three-dimensional operation and assembly experiment of nanowires of 50–200 nm have been successfully realized; in addition, for three-dimensional nanomanipulation and assembly, the force modulation mode dip pen nanoetching technology (FM-DPN) has been carried out, and the quantitative relationship between the diameter of the DPN node and the force between the tip and the substrate has been obtained, and the interconnection methods between different dimensional nanostructures have been explored.

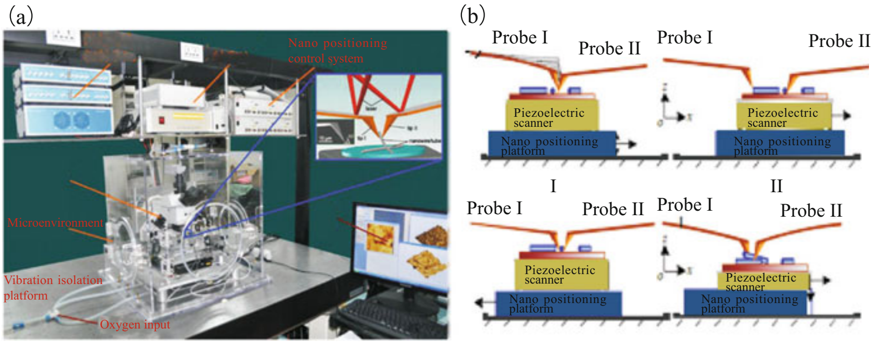

Fig. 7.10 Three-dimensional manipulation and assembly of nanomaterials based on AFM probes (**a** The physical object of the nanorobot system; **b** The process of three-dimensional nanomanipulation and assembly)

The research team of Huazhong University of Science and Technology has conducted in-depth research on the design, manufacturing methods and principles of carbon-based and silicon-based bionic micro-nano integrated structures. For the three-dimensional multi-level multi-layer micro-nano structure of the biological surface, the design optimization of the cross-scale bionic micro-nano structure has been carried out, and the cross-scale micro-nanomanufacturing technology of the bionic three-dimensional multi-level multi-layer micro-nano structure has been developed [46–49]. As shown in Fig. 7.11, the research is carried out for the large-scale manufacturing of high-performance composite micro-nano electrode arrays, and large-area C-MEMS/CNT/MnO_2 composite three-dimensional micro-nanoporous electrode array structure has been prepared, realizing high-performance new micro-supercapacitors, and providing new micro-nano integrated manufacturing principles and methods for the application of nanotechnology in the field of micro-energy.

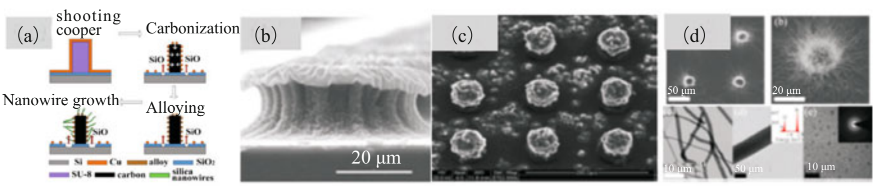

Fig. 7.11 Micro-nano integrated structure design and large-area manufacturing (**a** Micro-nano structure generation mechanism; **b** Al wrinkles; **c** Nanowire and PPY integrated structure; **d** Carbon electrode and nanowire integrated structure)

7.4 Precision Measurement and Traceability in Nano-Manufacturing

The nanometering and measurement is important links in the precision guarantee of manufacturing methods, manufacturing processes, and manufacturing equipment in nanomanufacturing, and is one of the key elements of nanomanufacturing. This Major Research Plan has carried out project deployment for metrology and measurement in nanomanufacturing, ensuring the overall development of China's nanomanufacturing system.

7.4.1 Nano/Sub-Nano Error Transmission and Traceability

The research team of Xi'an Jiaotong University has researched metrological traceability and testing theory in nanomanufacturing, aiming at standard evaluation systems for the preparation and measurement comparison of nanosamples, the analysis and characterization of nanoroughness, the relationship between nanoroughness and nanodevice/system performance, and the measurement of geometric characteristic parameters of the sidewalls of nanostructures [50–52]. Nano step height samples of 8 nm, 18 nm and 44 nm have been prepared. The prepared series of step height samples have been used as standard samples of this scale and became the benchmark for nanometer measurement/traceability; a mathematical model for evaluating nanoroughness has been established, the nanometer roughness evaluation model has been established, the structural features and functional features have been extracted and analyzed, and the measurement method of nano/sub-nanometer roughness of nanostructures has been established; the preparation method of AFM probe-based on carbon nanotube has been proposed, and the large aspect ratio nanostructure measurement method based on carbon nanotube the probe has been developed, realizing the measurement of large aspect ratio nanostructures. Some results are shown in Fig. 7.12.

The research team of the University of Science and Technology of China has conducted a systematic analysis of the influencing factors of SPM nanometer

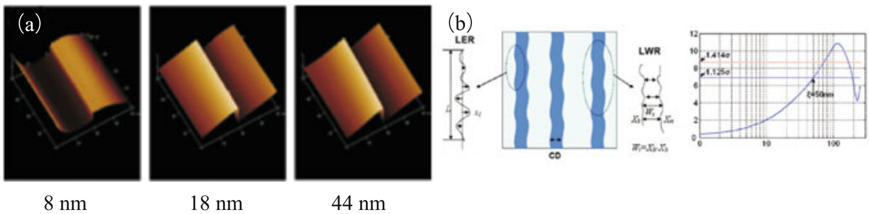

Fig. 7.12 Metrological traceability and testing based on nanosamples (**a** Step height model calibrated by German PTB; **b** Preparation and characterization of LER/LWR model)

measurement and has explored researches on measurement and compensation, principle and application of atomic grating. The SPM drift to restrict the scanning probe microscope (SPM) nanometer measurement and nanofabrication scanning rate and drift. On this basis, the above research results are upgraded to national and international standard documents. For the first time in the world, a quantitative measurement method based on the *X*, *Y*, and *Z*-direction drift of the SPM measurement image is proposed, which can achieve high-resolution measurement with a drift of less than 0.01 nm. The formulation of the international standard "Scanning Probe Microscope Drift Measurement Method", is not only applicable to the drift rate evaluation method based on SPM measurement images, but also has important reference value for the stability evaluation of nanometer measuring instruments.

With the development of giant component processing, large-scale industrial testing, large-scale scientific instruments, etc., the development of large-scale, nano-precision positioning drive control technology and instrument equipment with excellent performance has become an urgent need to solve in the development of nanomanufacturing equipment and nanomeasurement instruments. Based on the research foundation of nanoimprint, the research team of Xi'an Jiaotong University has researched the manufacturing process of high-precision ultra-long metal gratings, and has realized the development of ultra-long gratings with a measuring range greater than 3 m and the development of a reading system with an accuracy better than 0.2 μm/m.

7.4.2 Nanomaterials and Nanostructure Detection and Characterization

The research team of Huazhong University of Science and Technology has put forward the basic idea of computational metrology. Measuring the nanostructure topography parameters of the generalized ellipsometer as an example, it has systematically studied and solved the measurability, error analysis, and measurement uncertainty evaluation in computational measurement and other basic scientific problems and key technical problems [53–55]. The research team independently has developed a broad spectrum generalized ellipsometer principle prototype covering the wavelength range of deep ultraviolet to infrared. Its performance and technical indicators have reached the international advanced level, and it is suitable for online and accurate measurement of large-area nanostructure manufacturing processes. At the same time, it has independently developed China's first high-precision wide-spectrum muller matrix ellipsometer, and has invented core components and key technologies such as wide-spectrum achromatic compensator and instrument precision calibration algorithm. The self-developed high-precision wide-spectrum muller matrix ellipsometer has been successfully applied in more than 10 units at home and abroad, such as the Belgian Microelectronics Research Center, breaking the long-standing situation that China's high-end ellipsometer market has been completely

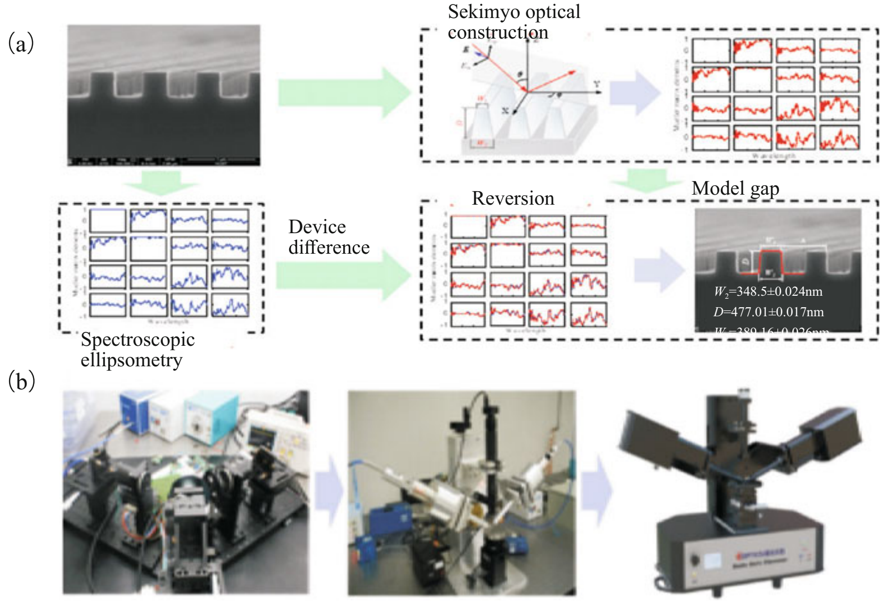

Fig. 7.13 The principle prototype of a broad-spectrum generalized ellipsometer independently developed (**a** Nanostructure ellipsometric scattering calculation and measurement theory and method; **b** Self-developed high-precision wide-spectrum muller matrix ellipsometer)

monopolized by foreign companies. Foreign ellipsometer manufacturers have cut prices by more than 30% within two years, which has produced significant social and economic benefits. Some of the results are shown in Fig. 7.13.

With the further development of physics, chemistry, materials, and other disciplines, new principles and new methods of nanomanufacturing continue to emerge. In addition to mainstream nanomanufacturing methods, encouraging interdisciplinary and continuous funding of innovative principles and manufacturing methods are the driving force for the continuous extension of nanomanufacturing and to provide method reserves and technical support for occupying the commanding heights of nanomanufacturing in the future.

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Chapter 8
Outlook

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Through continuing efforts committed in principle innovation and cutting-edge technology tackling, this Major Research Plan has promoted China's manufacturing technology from the fields micro-manufacturing to nanomanufacturing, laid the foundation for China's nanomanufacturing, and has played an important role in achieving the strategic mission in China's manufacturing and exerting international influence in the field of nanomanufacturing. However, how nanomanufacturing can further serve China's major strategies, solve the "stuck neck" problem, lead to the forefront of international research, and improve the originality and visibility of results is still a hot potato we are facing. How to continuously improve and upgrade the proposed nanomanufacturing theoretical model is still a technical difficulty that needs to be faced for a long time. Therefore, China should encourage specific

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research and explore new nanomanufacturing methods and new processes to adapt to the rapidly expanding nanomanufacturing research; based on the formed interdisciplinary research group, we should fully collaborate and focus on the "stuck neck" technology to serve China's major strategic needs; moreover, we should stabilize and develop the nanomanufacturing research team, and establish an integrated innovation platform for sustainable development. In the future layout of nanomanufacturing, Chinese researchers should not forget their original aspirations and move forward. Based on the research results of the major nanomanufacturing research plan, they should extend the manufacturing scale to the atomic scale and explore the theories and key technologies that support atomic-level manufacturing, clarify the mechanism of atomic-level manufacturing of a wide range of materials, and establish processes and equipment based on the above-mentioned new principles that is how we realize several internationally leading nanomanufacturing theories and technologies.

8.1 The Shortcomings and Strategic Needs of China's Nano-Manufacturing

8.1.1 The Shortcomings of China's Nanomanufacturing

1. Insufficient application of the results and unsolved "stuck neck" problems

Most of the new principles, new methods, new processes, and other achievements formed in this Major Research Plan have not yet obtained industrial applications, and the contribution to the "stuck neck" technology needs to be further improved. Aiming at solving the current "stuck neck" technologies (such as chip manufacturing and high-end equipment manufacturing) and possible future "stuck neck" technologies (such as artificial intelligence and genetic engineering), the bottleneck problems are refined from the principles, methods, and technologies, and provide solutions to meet the new needs of major national science/engineering (deep space, deep blue, and deep ground) in the future.

For fields such as the processing and characterization technology and equipment of nano devices that are currently relatively backward but are vital to future industrial competition, we, oriented by China's current strategic needs, must strengthen deployment and strive to break through technologies that restrict the development of nanotechnology. We will strive to achieve key leapfrogging in these areas as soon as possible and to be among the international frontiers.

2. Original results need to be strengthened in nanomanufacturing

The modern advanced manufacturing science and technology, is different from traditional manufacturing theories and technical categories, and relies more on new scientific principles and theoretical foundations. At present, the new principles and new methods of nanomanufacturing are slightly weak in China. Relevant scientific researchers must vigorously improve the original innovation ability, give full play to scientific imagination, seize the commanding heights of the original innovation strategy, and develop our nation's nanomanufacturing theory from "tracking" level to "leading" level.

3. In-depth interdisciplinary multi-discipline needs further exploration

Nanomanufacturing is a frontier field where multiple disciplines intersect deeply. For a further development, it is necessary for us to vigorously strengthen the cross-cooperation and research in the fields of manufacturing and mechanics, chemistry, information, energy, electronics, biology, etc., carry out in-depth cross-over from the scientific theory level, and form the ability to tackle major scientific issues and common key technologies. That is how we will become a world-class innovation highland and promote the development of China's nanomanufacturing technology.

4. Supports for emerging fields urgently needs to be improved

Taking the research and development of new materials, new energy, equipment manufacturing, information technology, aerospace, environmental protection, medicine and health as the driving force, our nation is committed to developing nanomanufacturing and characterization technology, and realizing the high degree of intersection and integration of nanomanufacturing technology. Moreover, we will continue to make efforts to explore the establishment of standards for nanoprocessing and characterization technologies, serve the industry, and realize the leading and service functions of a large platform.

8.1.2 The Development Strategy of China's Nano-Manufacturing

1. Strengthening the interdisciplinarity of basic research and attaching importance to innovation at the source

Focusing on the frontier research fields in nanomanufacturing that may give rise to major innovations and profoundly affect future development, we are committed to proposing new major scientific issues, forming new interdisciplinary fields, carrying out original basic frontier research, and striving to produce major scientific and technological achievements that affect human civilization and social progress. We are dedicated to integrating the research strength and research foundation of the nanomanufacturing projects that have been established, and facing the frontiers of international disciplines, major national needs, and the main battlefield of the national economy, and focusing on tackling key problems, solving major challenging scientific problems or breaking major application technologies. We focus on encouraging the intersection and integration of multiple disciplines, strengthening the cross-cooperation of nanotechnology and information, biology, energy, environment, and other fields, and developing key technologies with independent intellectual property rights.

2. Deepen nanomanufacturing research and strengthen the supporting role of major national science/engineering

We should deeply analyze the strategic needs of China's economic, social, and technological development, strengthen national goal orientation, and establish a sound coordination mechanism. In the field of basic research, scientists need to publish papers in the world's top scientific journals to win glory for the motherland at the forefront of world science and technology; in the field of application and development, scientists need to solve key problems facing national economic and social development and write scientific papers on the land of the motherland and contribute to the modernization of China. Mechanism research is combined with application and is specifically implemented in major national research tasks, making contributions to the development of international manufacturing frontiers and addressing major national needs.

3. Strengthen support for emerging fields

Nanomanufacturing is the foundation of the next generation of high-performance computers and information technology. The development of integrated nanosensor systems, etc., provides strong technical support for the information field, and determines the future development direction of China's microelectronics industry and the evolution of China's manufacturing to China's creation; in the field of environmental protection and energy, nanomanufacturing technology will provide new solutions for environmental protection applications and the world's demand for new energy; in the field of aerospace, the development of nanomanufacturing technology can not only increase the payload but also make the energy consumption index exponential. It is also expected to develop lightweight, high-strength, and thermally stable materials for the design and manufacture of airplanes, rockets, space stations, and planetary/solar exploration platforms; in the field of defense, security, and military applications, nanomanufacturing technology is developing, especially the further development of the electromechanical system will provide technical support for the development of China's military and national defense, as well as the manufacturing and product upgrades of military-industrial enterprises, and will lay a technical foundation for military scientists and technicians to develop nanoweapons.

8.2 Ideas and Suggestions for Continuous Research on Nanomanufacturing

8.2.1 Ideas of Continuous Research on Nano-Manufacturing

With the explosive rise of technological level and the promotion of the inherent needs of social and economic development, nanomanufacturing is no longer only satisfied with the development direction of a single dimension such as the manufacturing scale, but gradually develops in the direction of cross-scale and multi-material.

In terms of manufacturing accuracy, it is further approaching the physical limits of current manufacturing methods; in terms of manufacturing scale, its pursuit meets the needs of macro-systems; in terms of material system, it has developed from silicon-based semiconductors to a variety of semiconductor materials (III–V, II–VI) groups, carbon-based, polymers, low-dimensional structural materials, etc. In recent years, nanomanufacturing technology combined with other manufacturing technologies is also trying to develop ceramic materials and bulk metal materials for the manufacture of nanofunctional structures. In addition, the high-precision manufacturing of semiconductor materials makes it possible for people to freely manipulate charge, laying a solid foundation for the rapid development of the information industry. Nanomanufacturing advances human manufacturing capabilities to the atomic level. It not only provides a new way for precision manufacturing, but also provides a technical guarantee for engineers to design new materials and structures with excellent performance at the atomic and molecular levels. If nanomanufacturing can effectively combine cross-scale manufacturing to achieve effective control of ions, photons, and phonons, then nanomanufacturing will create many new products with disruptive technologies.

According to the international nanomanufacturing development trend, combined with China's current nanomanufacturing level and foundation, in the next 10 to 30 years, China's research on possible breakthroughs in the field of nanomanufacturing includes the following aspects.

1. Atomic-level manufacturing approaching physical limits

In the future, the precision and scale of nanomanufacturing will be fully expanded to the atomic level. Atomic-level manufacturing is manufacturing at the atomic level of processing scale, including atomic-level subtractive manufacturing (atomic layer removal, physical/chemical bond regulation) and atomic-level additive manufacturing (controllable assembly and growth at the atomic scale), building new materials from the atomic scale , new structure and new performance, extending manufacturing precision and scale from "nano" to "atom". The National Science Foundation's "Nanotechnology Development Research", the US Defense Advanced Research Projects Agency's "Atom to Product" (A2P) project, and the EU's Nanomanufacturing 2020 plan, etc., all list "atomic manufacturing" as the next 10–20-year development strategy.

For example, atomic-scale manufacturing provides technical feasibility for manipulating ions. The selective transmembrane transport of ions is the most important transport process in life. After natural evolution, a basic feature of ion channels is to achieve selective transmembrane transport; for the past 20 years, people have simulated the transmembrane transport of ions. During the transportation process, the feasibility of seawater desalination, seawater power generation, and high-energy-density ion batteries have been researched. The problem that plagues ion-selective transport is high-precision nanomanufacturing technology. The difference of different ion radii is 0.1–0.3 nm. If the manufacturing precision can reach a sub-nanometer, this provides a way for the rapid development of new energy technology. Furthermore, if mass, high-precision manufacturing of ion channels with feature size below 2 nm can be achieved, it will not only provide the possibility for ion selection, but also provide disruptive technologies for gene sequencing and protein sequencing. Nanopore-based single-molecule reading technology can quickly read the sequence without amplification. By directly reading the electrical signal of the base sequence passing through the nanopore, the base sequence can be determined. This is considered the next generation lowest cost and most competitive technology among gene sequencing and protein sequencing technologies.

In addition, conventional nanomanufacturing methods and technologies are mainly characterized by planar nanomanufacturing, that is, to ensure nanoprecision in the manufacturing plane. “Carbon” manufacturing takes new 2D/quasi 2D materials as the starting point, and uses the sub-nanometer precision of 2D materials outside the manufacturing plane to develop a new large-scale 3D nanoscale controllable macro, micro, and nano cross-scale manufacturing method. Given the excellent performance of two-dimensional materials in terms of structural stability, electrical conductivity, thermal conductivity, biocompatibility, etc., as well as the specific response to electric, optical, magnetic, and other external fields, large-scale carbon manufacturing based on two-dimensional materials can be foreseen, will achieve disruptive applications in major fields such as energy, information, life, and new materials.

With the funding of this Major Research Plan, Chinese researchers have reached the atomic scale in electronic control manufacturing, chemical mechanical polishing, and other aspects of processing, and have made important breakthroughs. Atomic-level manufacturing for future applications, based on the previous results, focuses on the development: (i) the first one is the quantum manufacturing theory of electron/ion regulation. Be in-depth interaction with physics, develop quantum manufacturing theory, develop nonmetallic ultra-fast laser manufacturing to metal electronic control manufacturing, and meet the extreme manufacturing needs of future strategies. (ii) The second one is chemical bond deconstruction manufacturing theory. In-depth intersecting with chemical disciplines, chemical mechanical polishing has been developed into a broad-spectrum material manufacturing method with a more universal chemical bond structure and reconstruction.

2. Large-scale precision manufacturing for universal objects

The development of nanomanufacturing technology has gone through a long process, from naturally occurring nanomaterials to artificially manipulated atoms and molecules of nanomaterials and devices. This is a process from unconscious to conscious, from conception to theoretical breakthrough to manufacturing application. In this process, innovation in manufacturing methods is the prerequisite and basis for achieving high-level nanomanufacturing. With the funding of this Major Research Plan, researchers have made important breakthroughs in laser micro-nanomanufacturing and nanoimprinting. Facing the future needs of nanomanufacturing to further expand the application, development should be focused based on the previous results: (i) the first one is precision manufacturing. Taking high-energy beam manufacturing as an example, how to effectively and accurately realize the control of high-energy beam spot, firing angle, energy density, firing angle and other parameters should be the focus to meet future ultra-high-precision atomic-level manufacturing needs. (ii) The second one is universal manufacturing. At present, the effective application of nanomanufacturing methods is only for one or a limited number of specific material systems. Based on further enriching and perfecting nanomanufacturing theory, how to improve the universality and large-scale nanomanufacturing process and technology for a variety of materials is of decisive significance for the future development of nanomanufacturing to a wide range of applications, and it will also be important research in the future direction.

3. Nanomanufacturing to meet the new needs of social development

The basic scientific research of micro-nanomanufacturing is the foundation to support the application of nanotechnology, and rapid development has been achieved in the fields of sensing and testing, new energy development, energy conversion and storage, and biotechnology. With the funding of this Major Research Plan, researchers have developed a series of nanomanufacturing processes that serve for chip process polishing, lithography machine lens polishing, target ball micro-hole manufacturing, meter-level two-dimensional metrology gratings, and spacecraft surfaces. Major national scientific/engineering tasks such as multi-level micro-nano structure skins provide a theoretical and technical basis for improving the level of nanomanufacturing technology and equipment in China. The endless scientific development has laid the foundation for the continuous innovation of technological products, and at the same time, it has continuously put forward higher requirements for technological progress. For example, with the unremitting efforts of physicists, the level of human manipulation of macroscopic quantum states has continuously set new records, and quantum computers have gradually become possible from the concept proposed by Richard Feynman. It is foreseeable that the popularization and application of quantum computers in the future will be inseparable from the innovation of nanomanufacturing technology. The large-scale and low-cost manufacturing demand for nanofibers, related functional nanostructure units, and devices will be just like our demand for chips today. The new generation of nanomanufacturing technology that faces the new needs of the development of human society and the new generation of nanometers and nano-detection-related theories, technologies and equipment derived therefrom will undoubtedly be the future research trend.

4. Brain-like intelligent manufacturing imitating life sciences

The main difficulty of nanomanufacturing for life sciences lies in the materials with "life" functional characteristics. It is generally difficult to process with the existing nanomanufacturing methods, and new processing methods need to be explored; in addition, the "life" functional characteristic of the processing process retention is also a problem of nanomanufacturing in the current life science field. Biological bodies have strong self-repair capabilities, but nanodevices are affected by factors such as heat, machinery, and chemistry. During the application process, the structure and shape are broken, and the service life and mechanical properties are affected. By imitating the principle of biological self-repairing damage, intelligent self-repairing micro-nano device is an important development trend in the future. Smart micro-nano devices based on self-healing materials can be widely used in fields including military equipment, electronic products, automobiles, and airplanes. This technological breakthrough is of great significance to maintaining the sustainable development of society. The international nanomanufacturing power has made a strategic layout for brain-like biomanufacturing: in 2013, the European Union launched the "Human Brain Engineering", which brought together more than 120 universities to jointly research key problems and invested more than 1 billion euros; in 2014, the United States deployed the "Brain Project", which was funded by NIH, NSF, DARPA, FDA, IARPA, and other institutions, and it is estimated that the investment in the next 10 years will exceed 4.5 billion US dollars to carry out brain-like biological manufacturing research; the United States launched the "Precision Medicine Program" in 2015, which was one of the NIH's four priority investment projects; in 2016, an annual investment of 215 million US dollars, was focused on research on brain-like engineering and nanoprecision medicine.

The international nanomanufacturing power has made a strategic layout for brain-like biomanufacturing. At the beginning of the project, this Major Research Plan focused on and funded the deep intersection of nanomanufacturing and life, chemistry, information, and other fields. A series of breakthroughs have been made in brain-like smart devices and bionic manufacturing. The brain-like bio-manufacturing for future applications can deeply intersect with life sciences to develop human organ re-creation, 5D additive manufacturing and imitating "DNA" manufacturing theories; the brain-like device manufacturing method based on the random neural network will fix the brain-like device. The correlation model is developed to random network interconnection, which improves the intelligence of brain-like devices from the bottom; it combines the principles of biological growth using environmental matter and energy under genetic control with atomic-level manufacturing technology, develops the theory of bionic atomic manufacturing, and it explores new material and energy possibilities. Control utilization and conversion, as well as the bionic manufacturing of brain-like intelligent systems.

8.2.2 Suggestions for Continuous Research on Nano-Manufacturing

The further development of nanomanufacturing requires strengthening basic research, integration of deep chemistry disciplines, the realization of original innovations, and focusing on solving the "stuck neck" problem in response to the needs of the country 's development strategy, and predicting the new "stuck neck" problem, forming a future exchange core technology. The main recommendations are as follows.

We should strengthen basic research and realize original innovation. Engineering research first emphasizes creative engineering (new materials, new structures, new machinery, new drugs, etc.), and secondly emphasizes condensing and solving key scientific problems. Not only to contribute to the solution of the current "stuck neck" problem, but also to predict the possible "stuck neck" problem in the next 10 to 30 years, and carry out basic research to avoid being "stuck" again. In addition, speed up the formation of the country's self-developed core nanomanufacturing technology, strengthen research efforts on independent software, independent research and development of scientific research instruments, equipment technology, etc., and form core technologies that can be exchanged with other powerful countries in the world.

We should deepen interdisciplinary collaboration and strengthen collaboration with cutting-edge disciplines such as materials, life, and AI. Intersecting with material science, we can actively explore the fields of additive/subtraction-based atomic manufacturing, material genomics, self-healing materials, etc. In addition, we can introduce other dimensional parameters in the material manufacturing process, and develop 4D or even 5D functions. Intersecting with life science, manufacturing can be matched with biological system functions (brain nerves, cell division, and differentiation, etc.), which is conducive to promoting the development and improvement of precision medicine and brain-like programs, and also plays a positive role in promoting the development of neural network chips and quantum computing chips.

We should serve major national strategic needs, strengthen original research, and achieve international leadership. For mature scientific and technological achievements, we should accelerate the development of technological breakthroughs, such as including the national key research and development plan or the layout of major special medium and large scientific projects. In addition, it is hoped that the country will encourage more industrialization policies for the implementation of new technologies, give full play to the combined advantages of emerging industries, industries, and local governments, and gather the country's multi-sectoral forces to achieve a mature technology industrialization process, and effectively solve major national scientific/engineering issues as well as the bottleneck problem.

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