Front. Energy 2012, 6(4): 311–340
DOI 10.1007/s11708-012-0214-x

FEATURE ARTICLE

Qin ZHANG, Yi ZHENG, Jing LIU

Direct writing of electronics based on alloy and metal (DREAM) ink: A newly emerging area and its impact on energy, environment and health sciences

Abstract Electronics, such as printed circuit board (PCB), transistor, radio frequency identification (RFID), organic light emitting diode (OLED), solar cells, electronic display, lab on a chip (LOC), sensor, actuator, and transducer etc. are playing increasingly important roles in people's daily life. Conventional fabrication strategy towards integrated circuit (IC), requesting at least six working steps, generally consumes too much energy, material and water, and is not environmentally friendly. During the etching process, a large amount of raw materials have to be abandoned. Besides, lithography and microfabrication are typically carried out in "Clean-room" which restricts the location of IC fabrication and leads to high production costs. As an alternative, the newly emerging ink-jet printing electronics are gradually shaping modern electronic industry and its related areas, owing to the invention of a series of conductive inks composed of polymer matrix, conductive fillers, solvents and additives. Nevertheless, the currently available methods also encounter some technical troubles due to the low electroconductivity, complex sythesis and sintering process of the inks. As an alternative, a fundamentally different strategy was recently proposed by the authors' lab towards truly direct writing of electronics through introduction of a new class of conductive inks made of low melting point liquid metal or its alloy. The method has been named as direct writing of electronics based on alloy and metal (DREAM) ink. A series of functional circuits, sensors, electronic elements and devices can thus be easily written on various either soft or rigid substrates in a moment. With more and more technical progresses and fundamental discoveries being kept made along this category, it was found that a new area enabled by the DREAM ink electronics is emerging, which would have tremendous impacts on future energy and environmental sciences. In order to promote the research and development along this direction, the present paper is dedicated to draft a comprehensive picture on the DREAM ink technology by summarizing its most basic features and principles. Some important low melting point metal ink candidates, especially the room temperature liquid metals such as gallium and its alloy, were collected, listed and analyzed. The merits and demerits between conventional printed electronics and the new direct writing methods were comparatively evaluated. Important scientific issues and technical strategies to modify the DREAM ink were suggested and potential application areas were proposed. Further, digestions on the impacts of the new technology among energy, health, and environmental sciences were presented. Meanwhile, some practical challenges, such as security, environment-friendly feature, steady usability, package, etc. were summarized. It is expected that the DREAM ink technology will initiate a series of unconventional applications in modern society, and even enter into peoples' daily life in the near future.

Keywords direct writing of electronics based on alloy and metal (DREAM) ink, direct writing of electronics, printed electronics, liquid metal ink, integrated circuit, consumer electronics, nano liquid metal

Received August 25, 2012; accepted October 12, 2012

Qin ZHANG, Yi ZHENG
Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Jing LIU (✉)
Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China; Department of Biomedical Engineering, School of Medicine, Tsinghua University, Beijing 100084, China
E-mail: jliubme@tsinghua.edu.cn

1 Introduction

The electronics industry which emerged in the early twentieth century has now become a global industry worth of billions of US dollars. Market studies from IDTechex clearly draft a promising near-future for printed electronics. It is disclosed that the market for printed and thin film electronics will be $9.46 billion in 2012, of which, 42.5% will be predominately organic electronics, such as organic light emitting diode (OLED) display modules [1]. Of the total market in 2012, 30% will be printed. Initially photovoltaics, OLED and E-paper displays grow rapidly, followed by thin film transistor circuits, sensors and batteries. By 2022 the market will reach $63.28 billion, with 45% printed and 33% on flexible substrates [1]. Portable mobile electronic devices such as cellphone, e-book readers and tablet PCs etc. are currently developing via a rather high speed along the direction of lighter quality, smaller volume, stronger function, steadier usability, lower price and higher frequency in replacement. So far, one of the most significant technologies to innovate electronic devices has focused on the fabrication of integrated circuit. Poly-crystalline silicon is a conventional IC material whose crystal grain size impacts the electronic properties of a silicon film. Processes to increase grain size require high temperatures which, however, are incompatible with flexible substrates [2]. The high processing temperatures of amorphous silicon make it hard to adapt to flexible substrates although thin flexible silicon film does can be fabricated [3]. Besides the high production costs of silicon electronics, the pollution it caused to the environment also makes it necessary to find more alternative ways. To this date, a kind of new technology named as printed electronics by which electronics was mass-printed on flexible surfaces has being increasingly explored [4]. A variety of electronic inks rooted in nano conductive particles have been tried, some of which even come into use. From these conductive inks, the fabrication process of electronics is simplified to two major steps: printing and solidification. Unfortunately, troublesome bottlenecks still exist which would impede rapid progress in the area. As is recognized by the society, preparation of such conductive inks is still somewhat complicated and their properties, correlating well with the dimension and dispersion of the conductive particles, are generally not stable as the ink is composed of several substances and it is often hard to guarantee the uniformity of the solution. Except for these issues, the currently available properties such as electric conductivity are heavily limited due to the bonding mechanism of the particles after solidification. Most important of all, nearly all these methods are still a little far away from truly direct writing of electronics. For example, although the nano silver conductive ink has been applied in flexible electronics, its conductive characteristics mainly come from silver particles whose loading ratio is however rather limited, while the solutions mainly served as carrier to quickly mold conductive materials as specific circuits or patterns. Furthermore, preparation and finalizing of nano silver particles emulsions suitable for printed electronics which must be accomplished in advance is crucial and relatively not easy, making this kind of conductive inks somewhat complex.

In order to realize a reliable and truly direct fabrication of electronics, a fundamentally different strategy was recently proposed for direct electronics writing through introduction of the room temperature liquid metals or alloys [5–13]. The method was later named as direct writing of electronics based on alloy and metal (DREAM) ink. A series of functional circuits, sensors and electronic devices can thus be easily written on a group of either soft or rigid substrates in a moment. Gao et al. demonstrated the capability of writing various electric circuits with liquid metal as conductive wires [5]. The process is so simple that it looks just like signing a name or drawing a picture on a paper. Further, Li et al. extend the method to direct printing of sensors such as thermocouples by liquid metal [6]. In fact, the basic idea of the DREAM ink technology is rather generalized in principle and has been extended to a series of inexpensive ways for printing functional electronics such as flexible printed circuit board (PCB) [7] electrical elements such as resistor, inductor, capacitor and their combination [8], semi-conductive devices such as diode, triode or transistor [9], waste heat harvesting device [10], kinetic energy harvesting device [11], paper microfluidics device [12], and printable solar battery [13] etc. Considering the increasing significance of the DREAM ink for electronics fabrication, this paper is dedicated to present a systematic summary of the DREAM ink method, aiming to disclose its basic features and illustrate further research and development opportunities.

2 State-of-the-art printed electronics

2.1 Existing technologies

Different from conventional methods of making integrated circuit such as physical vapor deposition (PVD) including RF-sputtering [14], pulse laser deposition [15] as well as magnetron sputtering [16] and wet deposition etc, the recently appeared printed electronics technology has made a great stride towards highly efficient and simplified electronics fabrications. Such method is generally composed of two working procedures: printing and solidification. This is a great benefit over former practices. For example, the high production cost of PVD due to inevitable vacuum process and requirement of substractively wet chemical patterning restrict its application in large scale [17] while acid and alkali waste are discharged during wet deposition consequently polluting the environment.

The printability of electronics provides a valuable opportunity for low-cost fabrication, which makes a number of new consuming electronic products possible, including printed electronic labels, printed integrated circuits, printed organic light-emitting diodes, and printed solar cells etc. Figure 1 illustrates several typical applications of such printed electronics. In this regard, graphics printing is quite economical owing to its high throughput and the fact that the whole production process can be completed in an indoor environment. As is known to all, the printed electronics is a printing method for fabricating electronics on various substrates usually using common printing equipment or other low-cost devices, consequently obtaining a determined pattern on the substrates, such as screen printing, gravure printing, lithography and inkjet printing etc. But to realize high quality printing, the viscosity, surface tension and solids content must be strictly controlled. In addition, the wettability, adhesion, solubility and solidification process also significantly affect the final results. The additives often used in the conventional printing inks are unavailable because they often affect the function of electronic inks. Figure 2 outlines some major differences between printed electronics and conventional electronics. Clearly, the merits of the printed electronics are rather evident.

2.2 Conventional conductive inks

Since plastic substrates, such as polyethylene terephthalate (e.g., Mylar®), typically limit device processing temperature to less than 150°C [16], organic semiconductors have been explored extensively. However, the electronic properties of organic semiconductors are unfortunately interior to those of a-Si. Cho et al. demonstrated that an emerging class of polymer electrolytes known as ion gel could serve as printable, high-capacitance gate insulator in organic thin-film transistors [19]. To improve the electronic properties of organic semiconductor, some metals such as gold, silver etc. are added into organic compounds. Aernouts et al. examined a newly developed PEDOT/PSS-based transparent electrode for organic solar cells subsequently improved by the application of a metallic ag-grid deposited in between the substrate and the transparent electrode [20]. Arias et al. deposited semiconductor using a regioregular polythiophene, poly [5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] by inkjet printing [21]. Li et al. used multiple regioregular polythiophene polymers with a variety of side chains, end groups and secondary polymer chains as active sensing layers in a single chip chemresistor sensor array device [22].

Conductive inks composed of a polymer matrix, conductive fillers, solvents and additives can generally be divided into two categories: inorganic and organic conductive inks based on its conductive fillers that are mainly conductive metal nanoparticles (such as gold [23], silver [24–28], copper [29–32] etc.), conductive metal

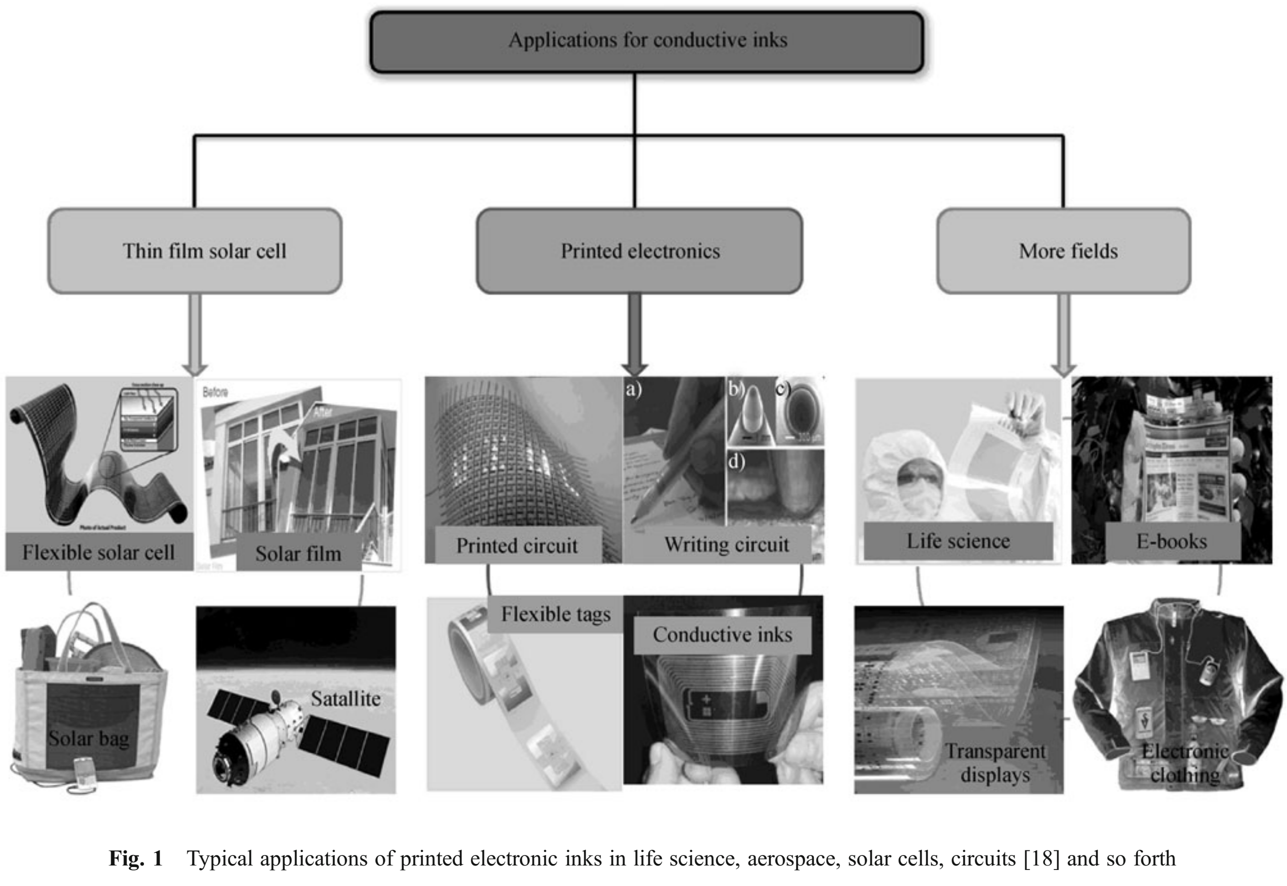


Fig. 1 Typical applications of printed electronic inks in life science, aerospace, solar cells, circuits [18] and so forth

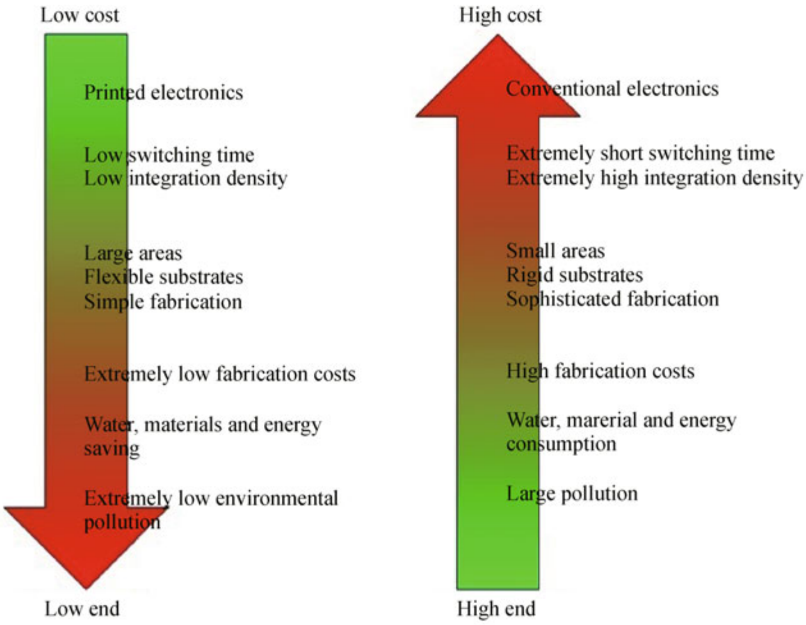


Fig. 2 Differences between printed electronics and conventional IC electronics

precursors (organometallic compound), carbon nanotubes [33–38], conductive polymer PEDOT/PSS [20], graphene, transparent oxides [39], metal nitrides, GaAs [40], chalcogenides [41,42], and so on. The electric conductibility of the ink is determined by the type of conductive material, the size and the shape of the particles, the time of solidification, the type of adhesive and the dispersing state etc. At present, inorganic conductive ink is more widely used in conductive ink printing than organic conductive ink. Figure 3 depicts the output of several printing cases using different conductive inks.

Among the many typical metal particle candidates, nanogold shows a series of distinctive capabilities such as stable chemical properties, high electric conductivity, good

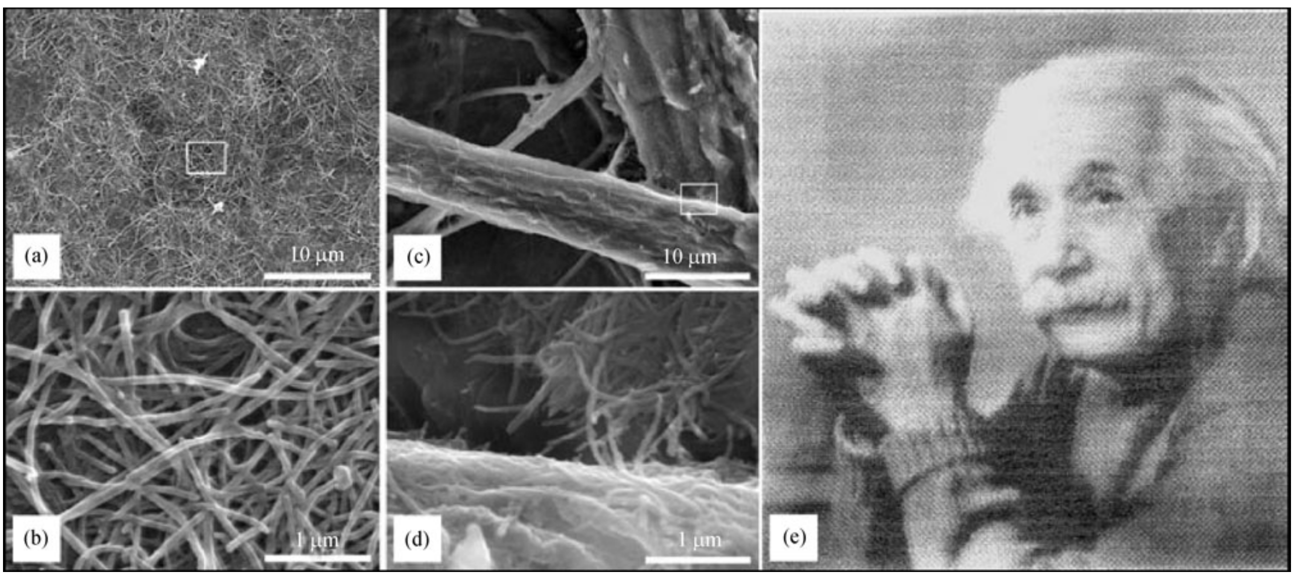


Fig. 3 Output of several printing cases using different conductive inks

(a) Multiple prints of carboxylated multi-walled carbon nanotube; (b) Canon bt-400 plastic; (c),(d) 80 g/m^2 paper surfaces; (e) scanned image of a photograph (105 mm × 110 mm) printed (×5) on Xerox color copier paper (100 g/m^2) using the water-based CNT ink [33] oxidation resistance and corrosion resistance, etc. But its high price makes the application range rather narrow. Nanosilver is superior to other metal since silver oxide has good electric conductivity and there is no need to cautiously avoid the surface oxidation of the particles. Copper conductive ink is one of the most widely adopted conductive inks at present. Nanocopper has good electric conductivity with its price lower than that of gold and silver. Organic phosphorus compounds and mixture of copper powder and antioxidants are widely used in practical application to improve stability and reliability as a result of the poor electrical properties of the copper oxide. Carbon nanotubes (CNTs) have good physical properties such as excellent mechanical strength, high thermal conductivity, optional semiconducting/metallic nature and advanced field-emission behavior which guarantee its application in a number of different devices. Recent advances in nanotube chemistry enable both the dissolution and dispersion of CNTs in various solvents [33]. Metal oxides such as zinc oxide [43] and indium tin oxide (ITO) [44–46] have been explored.

According to the properties of the solvent, conductive ink can be divided into water-based ink, solvent ink and ultraviolet rays (UV) ink whose drying methods are very different. The drying method of solvent ink is volatilization drying. UV ink is dried by UV devices. The water-based ink usually uses infiltration drying. The latter two inks can meet the current requirements of environmental protection.

Without losing generality, the criteria to choose an appropriate ink can be summarized as follows:

1) Chemical compatibility of the solvent with print-head;

2) Matching substrates well: interface compatibility and adhesion between the ink and substrate, so as not to fall off;

3) Dimension of conductive particles and their time stability in ink suspension;

4) Low sintering temperature: typically at 100°C to 300°C, so that it can be printed on flexible organic board; and

5) Good and stable electrical resistance of films obtained by inkjet.

2.3 Printing methods

Conductive ink can be printed using either contact-mode template or noncontact direct writing methods onto a web-fed or sheet-fed substrate [47]. Contact printing technologies generally comprise flexography [48,49], gravure [50] and screen printing [51–53] and the ink is transferred onto substrate via an image-carrying master template. Inkjet printing is the most widely used direct writing in the process of which printing liquid is ejected from a nozzle onto substrates (Fig. 4). Inkjet printing method can be divided into impulse and continuous printing. Impulse printing is more commonly used and exists in two forms: piezoelectric systems that use nozzles controlled by electrical signals to eject tiny droplets of an ink onto a substrate, and thermal-bubble systems that launch inks onto substrates by rapid heating [54]. Both inkjet printers are remarkably accurate.

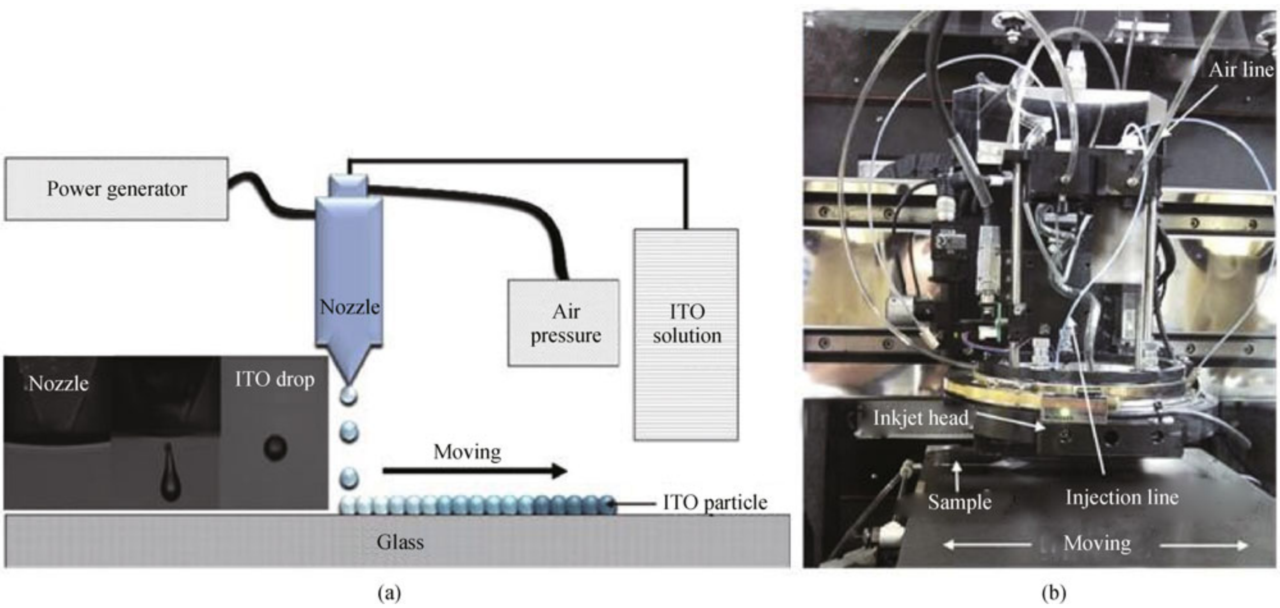


Fig. 4 Inkjet printing
(a) Schematic inkjet-printing process of the ITO nano particle with inset of the picture showing ITO solution jetting; (b) inkjet-printing system for coating of ITO electrode at atmospheric pressure [45]

A typical ink jet print head has 300 to 600 nozzles, and can form dots of many different colors of ink that are as small as 50 microns in diameter [55]. The proper understanding and control of jet formation and subsequent motion of the jetted materials requires physical studies into acoustic modes in print heads, material properties at very high shear rates, instabilities of jets, drop motion, drop formation, stretching of fluid ligaments, the role of polymers in jet break up, electrical charging of drops and the aerodynamic and electrostatic interaction of jets and drops in flight [56]. Inkjet printing method has been used for making transistors, photovoltaics, antennas, sensors, OLEDs, PCBs and many other components and electronics. Additional noncontact direct-writing or printing methods such as aerosol jet printing have already been used in organic thin-film transistors (OTFTs) [19], solar cells [57] and more electronics [58,59]. The liquid material is placed into an atomizer, creating a dense aerosol of micro-droplets from 1 to 5 μm in diameter. The aerosol is then carried by a carrier gas such as N_2 flow to the printing head. An annular flow of sheath gas is then generated to collimate the aerosol [60].

Micropen belongs to flow-based direct writing. In the operation, a flowable material that can be liquid or particulate slurry is loaded into a syringe that is then connected to the writing head of the micropen. The plunger of the syringe is compressed by a pneumatic ram and the material is forced into the writing head called the ‘block’. The writing head comprises an A-frame fluidic pathway, a metal double piston cylinder and a micro-capillary writing tip. The flowable material fed into the ‘block’ is pressurized up to 13.8 mPa and dispensed through the writing tip [60]. Through certain technical modifications, these well-established approaches can partially be extended into the new areas of liquid metal printing enabled by DREAM ink method. Figure 5 presents the schematic diagrams of an aerosol jet direct writing system and micropen.

2.4 Sintering methods

For the existing printed electronics methods, sintering on the printed inks is a necessary step for making the final device. Nanoparticle ink sintering is usually done in an oven/furnace or on a hotplate. The sintering temperatures are typically around 100°C–400°C depending on the particle size and the binding strength of the ligand shell [28,31,61]. However, oven sintering possesses numerous shortcomings. For example, it is a time and energy consuming process; many low-cost substrate will suffer from deformation when exposed in high temperature; undesired gas emission from the heated substrate occurs, and the entire structure has to be sintered (the process is not area-specific) [62]. New alternative sintering methods including laser sintering [63], microwave sintering [64,65], chemical sintering [66–68], plasma sintering [69] electrical sintering (PES) [62] and substrate-fabricated sintering (SUFS) [47] were thus proposed. Laser sintering is somewhat similar to stereolithography in its basic architecture. The heat affected zone is reduced by using laser sintering. Without affecting the surrounding substrate, energy deposition becomes more efficient as the laser follows the conductive tracks and sinters them selectively. The sintered feature size and quality can be controlled by varying the beam size, applied laser power, and scanning speed [70]. Microwave sintering costs less than laser sintering and can provide rapid, uniform and volumetric heating. Microwave radiation can be absorbed effectively when coupling with charge carriers or rotating dipoles. Highly conductive materials generally have a very small penetration depth such as from 1.3 to 1.6 μm: for microwave at 2.54 GHz on silver, gold, and copper [71]. The SUFS method is based on the chemical removal of the nanoparticle stabilizing ligand through interaction with the coating layer of the printing substrate [47]. All these sintering methods can be possibly adopted when using the DREAM ink to fabricate complex electronics.

3 Liquid-metal-ink-enabled direct writing of electronics: Emerging direction

3.1 Proposition of DREAM ink technology

Printing electronics is a comprehensive field that requires high standards in material quality, ink, printer, and device

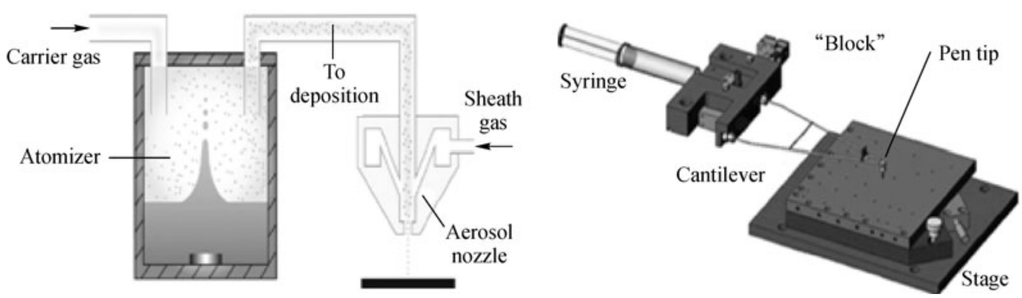


Fig. 5 Schematic diagrams of an aerosol jet direct writing system and micropen [60]

engineering. Nowadays, new types of conductive inks containing organic and inorganic conductive inks are being kept investigated such as conductive inks made of nano-silver, nano-copper, carbon nanotubes and so forth. Many fundamental problems have been solved, but many still remain. For instance, the electronic performance of existing conductive inks is not as good as the performance of (poly) crystalline silicon. In fact, the key to the success of printed electronics lies in high performance inks, which should be printable materials with excellent conductivity, environmental stability, and further unfolding to increase the potential of printed electronics [3]. Based on these considerations, the attention was turned to a new printed electronics strategy which is conceptually different from the conventional approaches [5–13]. The work initiated a generalized way to DREAM ink. So far, mechanisms for justifying the magnitudes of the electrical elements so as to compose various complex circuits through regulating their geometric sizes as well as components have been disclosed. According to this technology, what is seen is just what one wishes to print. The success of the method is attributed to the proposition of a new class of conductive inks made of low melting point metal or its alloy, which is flowable under normal temperature and directly printable (Fig. 6). It opens the possibility for directly writing various functional circuits via an extremely easy going and cost effective way, which can be as simple as signing a name or drawing a picture on the paper. If the user is not a good writer or drawer, he/she can just let the computer accomplish the task. That means, a pre-coded computer program will drive the printer, pre-filled with different liquid metal inks, to directly print the various electronic elements and the circuits. If under assistance of software such as Protel, even an inexperienced person can quickly print the electronic prototype from the original conception. This will significantly shorten the electronics design period which is rather helpful for the practices of modern electrical engineering. In that case, anyone can be a circuit maker. This may incubate the “Do it yourself” consumer electronics in the future. The considerable impacts of the DREAM ink can not only be felt in industries, but also in educational areas, such as universities, middle or even elementary schools where teachers can teach students the first-hand knowledge of circuits using the present metal ink. It is expected that this new frontier would produce a huge impact on a wide range of areas, especially in the field of energy, environment and health technology.

3.2 Basic features of DREAM ink

In the category of the DREAM ink, low melting point metal is an interesting material which appears as liquid in the temperature range spanning room temperature until 200°C. However, direct use of such fluid-like material, especially room temperature liquid metal, was significantly neglected in modern consumer electronics. After ten years’ continuous efforts, the many important features of room-temperature-liquid-metals were gradually disclosed. One of its significant applications is in the areas of chip cooling and energy [73–79]. Liu et al. proposed the concept of the DREAM ink which may lead to alternative electronics in different areas [5–13]. From this method, the liquid metals or its alloys serving as inks can be directly printed or written on the surfaces of different substrates with either

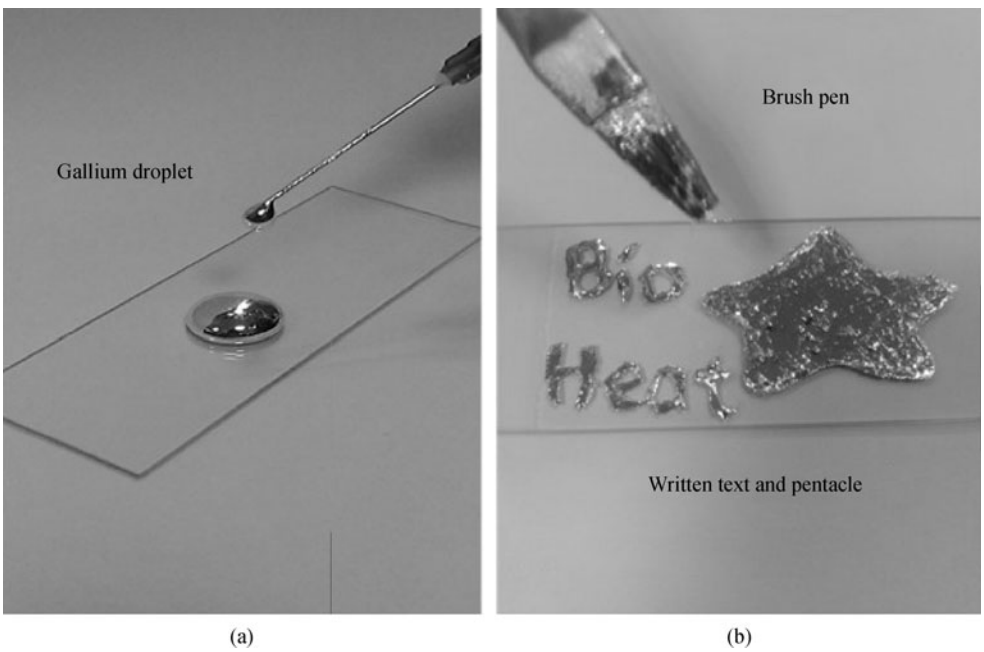


Fig. 6 Low melting point metals [72]

soft or rigid properties under normal temperature range, owing to the compatibility of such metal inks with particular metallic or non-metallic substrate materials (Fig. 7), in accordance with specific functional requirements, especially for flexible substrates. The applicability of the DREAM ink is rather generalized. For applications of a wide temperature range, desired metal inks with specific melting point can be made through altering the types of the alloy and adjusting the components of the matching metal. Some of such ink candidates for further application references are presented in the Appendix.

Generally speaking, liquid metals and alloys possess better thermal and electrical conductivity than other substances under low temperature or normal circumstances [80]. At the same time, liquid metals possess good flexibility that is particularly suitable for applying on flexible substrates. In the past few years, attention in the category of liquid metal was mainly paid to its thermal performance. Typical progresses having been made are liquid metals chip-cooling technology [81,82], kinetic energy harvesting [83], waste heat harvesting [84,85], phase change material to absorb heat from electronics devices [86] and so forth. Those studies concerned too much on the thermal aspects of metal flow while the electrical applications were neglected. As is well known, the main components of conventional wires in circuits are metal. As a result, liquid metals should also possess prominent performance if used in electronics. It is such dual capability that makes it an excellent conductive ink to directly write various electronics. So far, the experiments made in the authors' lab have demonstrated the capability of directly writing of various text, pattern (Fig. 8), and electrical circuits (Fig. 9) in a moment using the liquid metal ink. The electrical components such as capacitor and inductor directly written on paper show a good stability and widespread adaptability, especially in applications of some high frequency circuits [8] (Fig. 10). Besides, an oscillating circuit directly written on paper through combining the liquid metal ink and existing non-metal ink was found to work stably which implies that nearly each kind of functional circuit can possibly be written. Further, some metals or alloys in liquid state have been disclosed to have excellent wettability and viscosity properties through varied processing [87–91]. In addition, metals or their oxide may contain unique magnetic or optical properties. Therefore, it can be anticipated that great potentials of metal inks in printed electronics are in incubation.

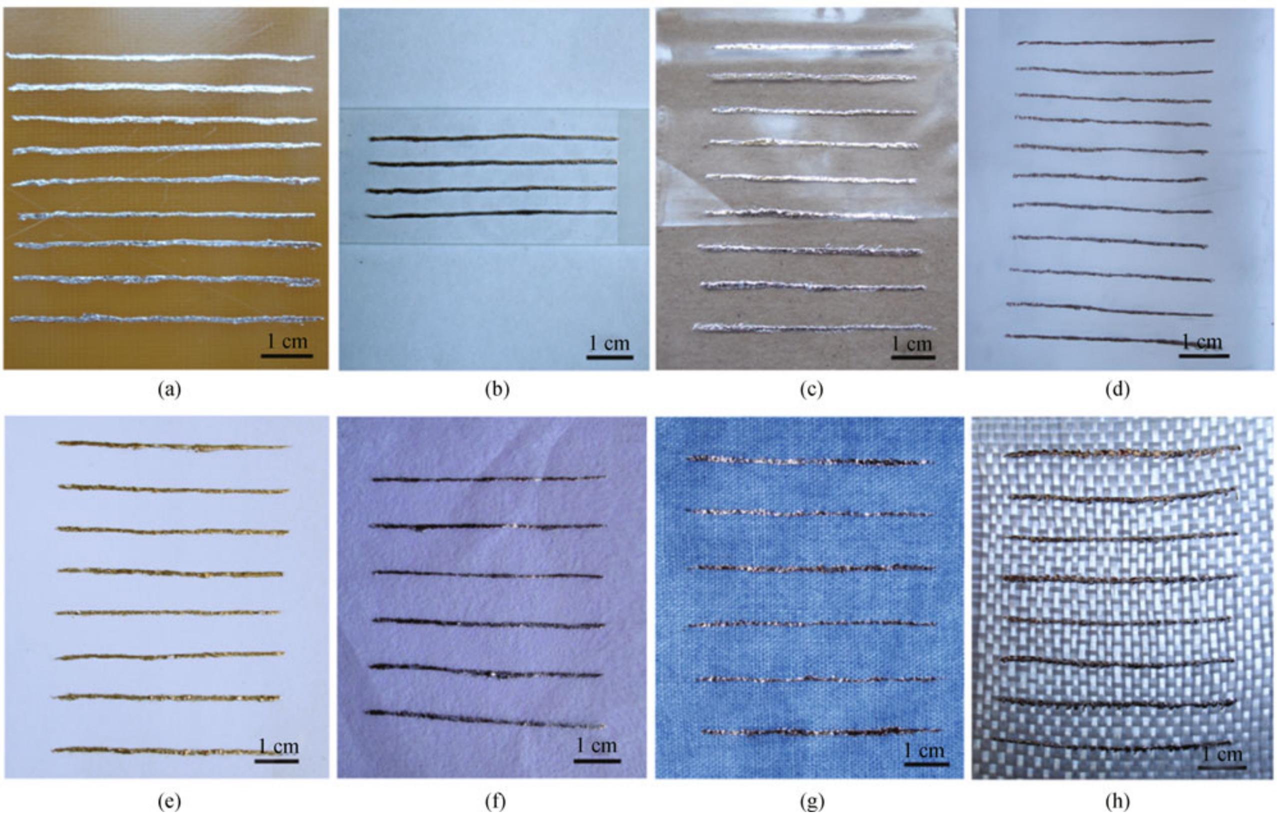
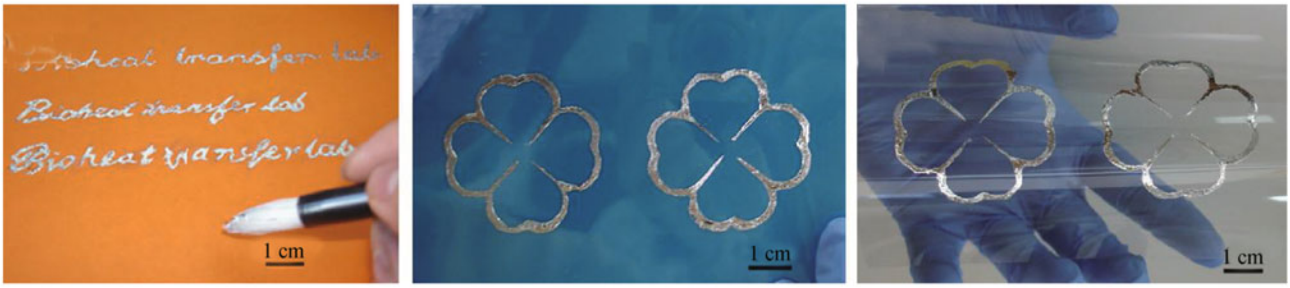
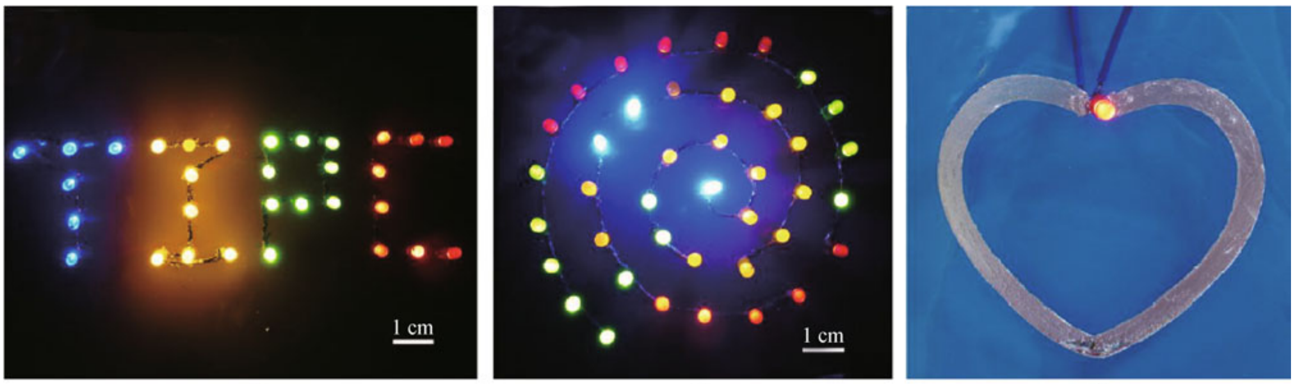


Fig. 7 Demonstrated wettability of $GaIn_{10}$-based liquid metal inks written on different substrate materials [5]
(a) Epoxy resin board; (b) glass; (c) plastic; (d) silica gel plate; (e) typing paper; (f) cotton paper; (g) cotton cloth; (h) glass fiber cloth



(a) (b) (c)

Fig. 8 Optical images of conductive text or patterns written on different substrates by using $GaIn_{10}$-based liquid metal ink



(a) (b) (c)

Fig. 9 Optical images of LEDs with $GaIn_{10}$-based liquid metal ink as electrical interconnects written on different substrates

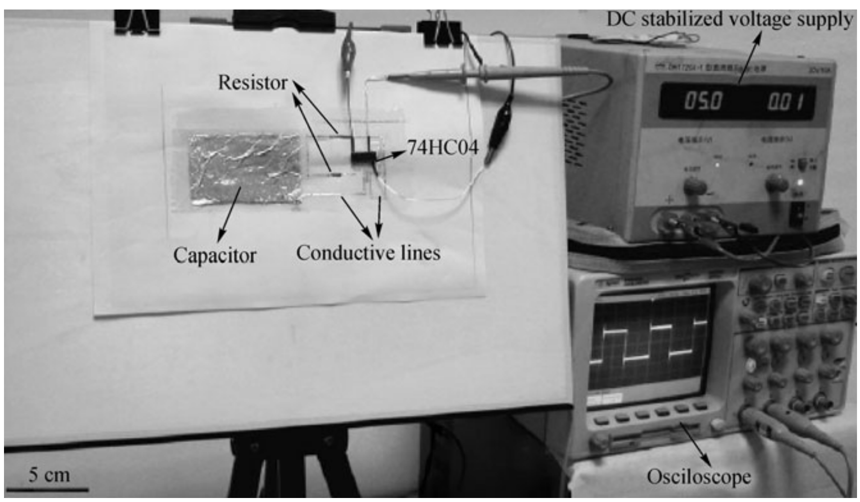


Fig. 10 Directly writing electrical elements such as resistor, inductor and capacitor on paper to form a functional circuit [8]

3.3 Merits of DREAM ink technology

Conventional conductive materials, such as tin, zinc, silver, indium and so on, are metals that are ductile and easily bent when deposited as thin films which are used for fabricating the flexible circuits. However, they must be evaporated at an extremely high temperature due to their higher melting point, and therefore have a requirement for strong energy. While for the room temperature-liquid-metal-ink, whose direct applications have been significantly neglected until now, mainly comes from the gallium and its alloys and is first proposed in our lab to fabricate conductive lines for flexible circuits by directly writing. What is more important is that the liquid metal ink has a better flexibility than the conventional materials because of its semi-liquid state at room temperature.

One of the biggest innovations of the DREAM ink technology is "direct writing". The conventional circuit boards are deposited on the substrate by evaporation, sputtering, airbrushing, and so on. For example, a few works used evaporation and sputter deposition to pattern metals on the surfaces of paper. As is well known, evaporation and sputter deposition are applicable to a variety of metals, but requires expensive equipment, a high vacuum, and lower rates and higher energy requirements. In contrast, direct writing is made possible by using high-performance metal ink especially $GaIn_{10}$-based conducting material. Compared with conventional technologies, the DREAM ink is more effective and economical for fabrication of flexible circuits. In addition, a conventional typical one-sided flexible PCB prepared by evaporation and sputter deposition method mainly comprises five layers: a base layer of polyimide; a layer of adhesive; a layer of copper; a second layer of adhesive; and a cover layer of polyimide. The preparing processes are complicated and wasteful for time and money. While for direct writing in the DREAM ink, a flexible circuit board is only 4 layers, at the very most. Most importantly, direct writing is inexpensive and can be applied at room temperature without specialized equipment. Therefore, it has overwhelming advantages especially for small-quantity production and prototyping. Its adoption in electronics industry opens a brand new area of direct and quick writing of flexible electronics which can be as simple as signing a name or drawing a picture on the paper.

In fact, currently, a lot of research has been conducted on conductive ink. For example, some works prepared highly concentrated silver nanoparticle ink using an aqueous system that contains silver nitrate as the silver precursor, poly (acrylic acid) (PAA) as the capping agent, and diethanolamine as the reducing agent. The silver ink was used to directly write electrodes on substrates. However, compared with silver ink, the liquid metal exhibits more values. The first, and perhaps the most important, merit of liquid metal lies in the extremely simple process of preparation. In additional, such materials own many unique favorable virtues such as low melting point, being directly printable, conductive, biocompatible, low cost, and so on. More importantly, various functional electrical devices can be directly written on paper by using liquid metal ink combined with various inks possessing different functions in the future and these kinds of circuits may form the first step in the integration of electronics in materials which are present in all areas of modern society.

The new technology is of particular importance for world energy saving. This is because traditional integrated circuits making industry generally consumes too much water, energy and gas. Meanwhile, it also produces too much pollutant which seriously affects the environment. Writing or printing liquid metal directly on the paper will change this game. Without complex preparation, craftwork, high energy requirement, the new method consumes much less energy. Considering that electronics industry is among the largest industry over the world, it is expected the DREAM ink technology will help reshape many related areas to a large extent.

3.4 Thermophysical properties

3.4.1 Low melting point

As conductive inks with prominent performance, the melting temperature of metal inks plays a significant role in stringent requirements of printed electronics. This is because high printing temperature poses challenges to substrates and equipments, which would lead to high heat resistance of surfaces and more energy consumption. In this regard, room-temperature-liquid- metals possess huge superiority for such requirements. Except for these interesting inks, the other low melting point metals and alloys (says, less than 200°C) which are susceptible to be easily liquefied on normal conditions could also serve as excellent candidate inks for effective solution of the crucial issues other than the room temperature case. And there are many options for such metals or alloys.

It is worth mentioning that, the melting points of the DREAM ink can be modified by changing the chemical compounds ratios of alloys or adding some elements into metals or alloys according to specific needs. As an example, Fig. 11 presents the low melting point values

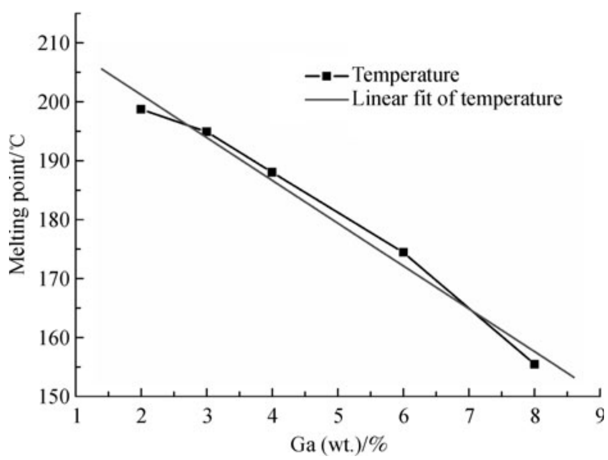


Fig. 11 Melting point of Sn-Zn-Ga alloy as a function of the addition of Ga [92]

for Sn-Zn-Ga alloy, which indicates the relationship between the melting point and the addition of Ga. From Fig. 11, it can be seen that the melting point decreases with the increase in gallium and the temperature of the liquid appears approximately as a linear function of the dosage of Ga.

3.4.2 High thermal conductivity

Liquid metals and their alloys have a very wide range of applications in industries, often in the fields of metallurgy, chemical industry and nuclear industry. In recent years, with the development of the atomic energy industry, plasma technology, rocket technology and aerospace technology, many of the low melting point metals are found to be excellent heat carrier medium of liquid, vapor or ionized state. To date, liquid metal, which owns far more higher thermal conductivity than that of water, can be used as coolant in many areas of high heat flux especially highly integrated computer chip [93,94] and optoelectronic devices. As an idealistic coolant, it has a rather wide working temperature range and can remain at liquid state from room temperature to above 2000°C, which can enable the DREAM ink to have a pretty wide printing temperature range. For instance, gallium has a melting temperature of 29.8°C and a thermal conductivity of 29.4 W/m^2 in atmospheric environment, with a specific heat capacity of 409.9 J/(kg·°C). Ma and Liu studied the liquid metal cooling device for the self thermal management of computer chip [73]. The liquid metal can be used as either coolant or thermal interface material. Figure 12 shows such a schematic diagram.

3.5 Flow properties

The viscosity of the inkjet ink is generally 0.00l–0.01 Pa·s, preferably 0.001–0.005 Pa·s. Inks with relatively low viscosity can form approximate Newtonian liquid without producing false viscous phenomena which will benefit the transport of ink droplets from the nozzle, as well as the formation of ink droplets and the integrity of the ink droplets. Former research proved that the viscosity of liquid gallium was up to 1100°C [96]. According to the measurement, gallium has a viscosity of 0.002037 Pa·s at the temperature of 30°C and decreases with the temperature rising. Clearly, this makes gallium one of the best candidates for the DREAM ink. Figure 13 presents the relationship between the viscosity of gallium and temperature.

3.6 Electrical or semiconductive properties

Generally speaking, metals have superior electrical performance than most non-metallic substances. The electric conductivity is generally reduced as temperature increases. Simultaneously, different composition ratios of alloys and different additive content would lead to different electrical resistivity. Therefore, electrical conductivity can be modified through such designs to fit for various application requirements. Table 1 lists the electrical resistivity of SnSb alloys around room temperature with different indium content [97].

Furthermore, some compounds from the low melting point metals such as Ga_2O_3, GaAs, GaN and so forth have special semiconducting properties. For example, Ga_2O_3 is

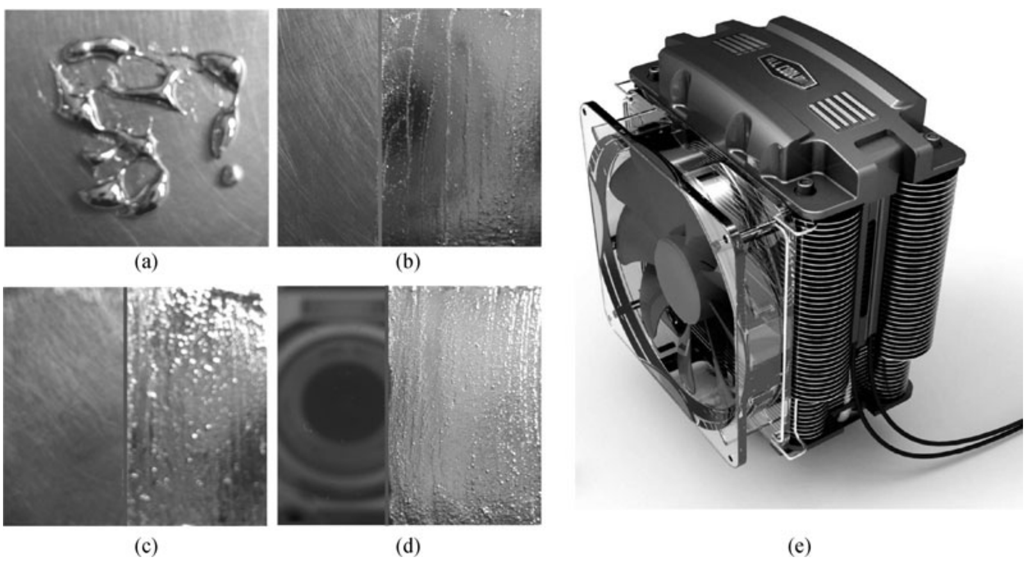


Fig. 12 Schematic diagram of liquid metal and cooling device
(a)–(d) Liquid metal as thermal interface materials [95]; (e) enhanced coolant in cooling device [79]

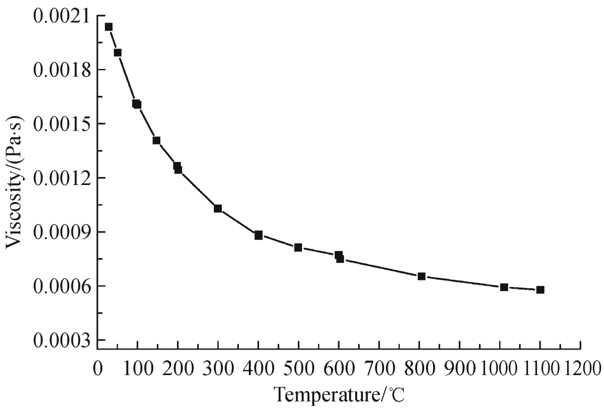


Fig. 13 Viscosity of gallium changes with temperature [96]

Table 1 Electrical resistivity of SnSb alloys with different indium content

Alloys	$\rho/(\mu\Omega\cdot cm)$
Sn-10Sb	26.25 ± 2.1
Sn-10SB-0.5In	27.55 ± 1.7
Sn-10SB-1.0In	29.33 ± 1.5
Sn-10SB-1.5In	30.25 ± 1.6
Sn-10SB-2In	32.37 ± 1.8

a transparent oxide semiconductor material that has capacious potential applications in optoelectronic device. It can be used as insulating layers for gallium-based semiconductor materials. Although as a metal with toxicity, GaAs has some better electronic properties than Si, such as high saturation electronic rate and high electron mobility. It is a significant semiconductor material which can be manufactured as microwave integrated circuit (MMIC), infrared light emitting diode, semiconductor laser unit and solar cell (photovoltaic characteristic). GaN is also a semiconductor that can be used in high power and high speed photoelectric devices. It has, in fact, been largely applied in LED as N/P semiconductors. Figure 14 demonstrates the atomic structure of GaAs and GaN while Fig, 15 illustrates the applications of those compounds based on Ga.

3.7 Magnetic properties

Liquid metals can be adopted to write electromagnetic sensors for monitoring working fluid by way of their electromagnetic characteristic. The electromagnetic sensors can be used in electromagnetic pumps such as gallium pump and electromagnetic launder. Figure 16 displays the structure of an electromagnetic pump and its working mechanism. Actually, cooling systems based on liquid metal with high requirements on small mechanical vibration and low noise are equipped with electromagnetic pump. Further, gallium has been proven to be a good magnetic nanoparticles carrier fluid. Park et al. prepared silica-coated ferromagnetic nano particles dispersed in a gallium fluid with good magneto-rheological (MR) characteristics [98]. Such MR fluids have a low viscosity like Newtonian fluid in zero magnetic field while a high viscosity and a low liquidity in strong magnetic field. Ito et al. successfully dispersed micron-sized iron or nicked metal powders in liquid gallium and measured the viscosity and elasticity of the prepared liquid as a function of magnetic flux density which demonstrated that liquid Ga is a useful base for preparing a new type MR fluid [99]. The properties of the DREAM ink that can be conveniently driven and controlled by electromagnetic pump promise the convenient ways to print.

3.8 Mechanical properties

In electronic industry, available materials should satisfy required mechanical characters for maintaining running

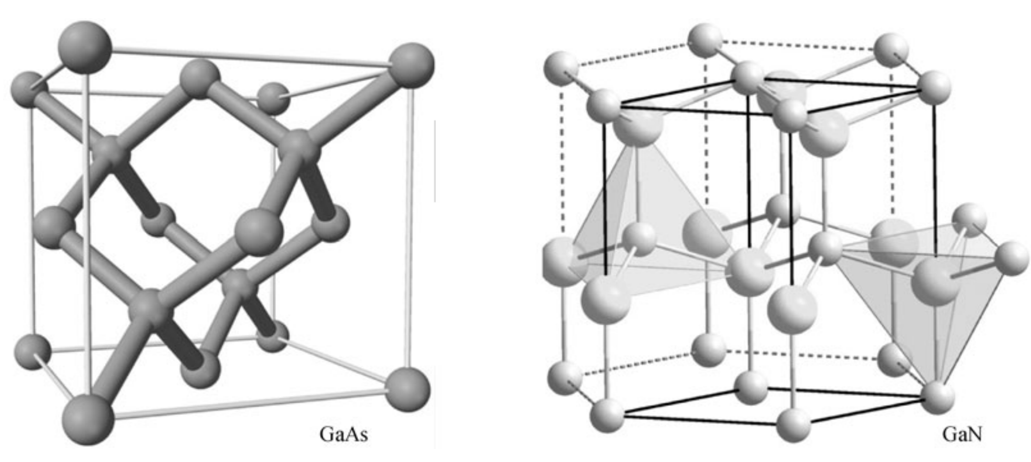


Fig. 14 Atomic structures of GaAs and GaN

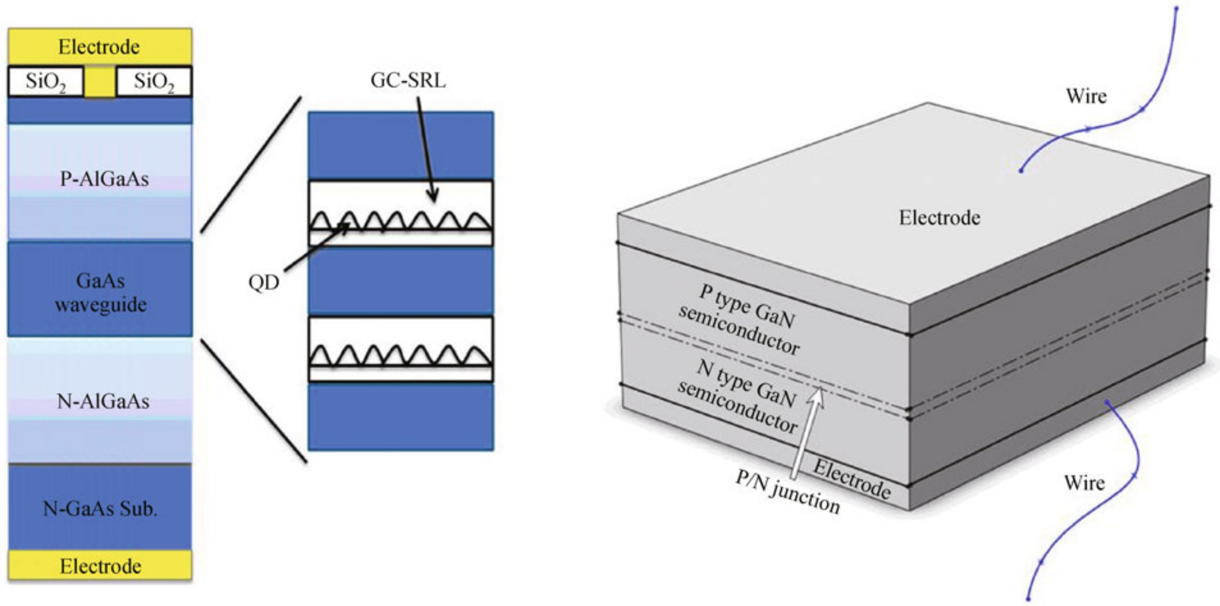


Fig. 15 Applications of GaAs, GaN as semiconductor

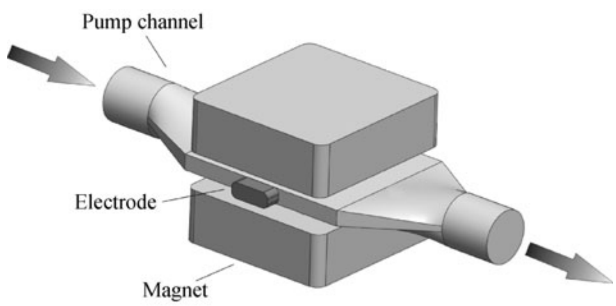


Fig. 16 Electromagnetic pump and its working mechanism

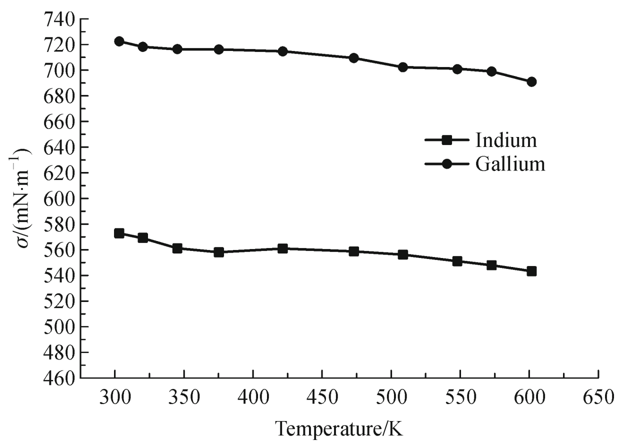


Fig. 17 Surface tensions (σ) of gallium and indium as functions of temperature by the sessile drop method [94]

efficiency. The room temperature metals or related alloys have a few flaws in those aspects, which should be overcome in real applications. The properties mainly include surface tension, mechanical strength, viscosity, wetting characteristics and so forth.

3.8.1 Surface tension

Surface tension has an important impact on the formation of liquid drops during inkjet process and printing quality. If surface tension is too high, it is difficult for inks to form droplets and some long breaks may occur, which can directly influence the output of printing. However, if surface tension is too low, it will lead to instability of droplets and make it easier to form stellate sputtering points. The magnitude of the surface tension of the materials should be controlled for the inks to meet the requirements of both spreading smoothly on substrates and forming enough small droplets during the ink-jet process. Figure 17 shows the discipline between surface tension and temperature. It can be observed that with the increase of temperature, the surface tension of gallium decreases gradually in company with indium [94].

3.8.2 Mechanical strength

The mechanical properties of the DREAM ink determine its application scope and service life. Mechanical strength of alloys mainly includes tensile strength, yield strength, young's modulus and shear strength etc. Different applied loads (such as tension, compression, torsion, impact,

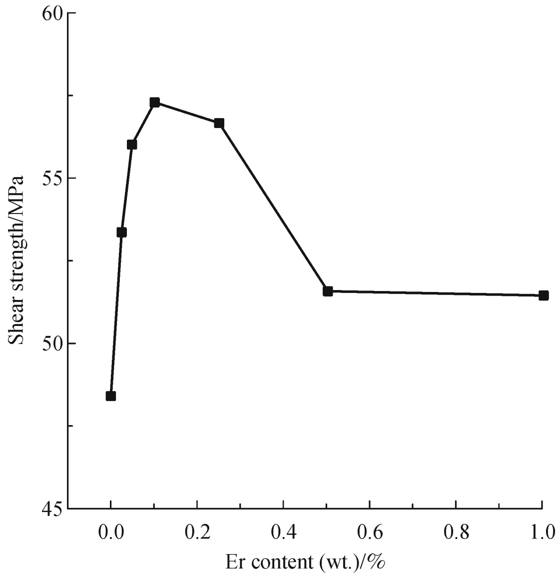


Fig. 18 Shear strength of $Sn_{3.8}Ag_{0.7}CuEr$ alloy as a function of Er content [100]

circulating load, etc.) usually have different requirements on performance of materials. Figure 18 indicates that the shear strength of alloys is closely related to the content of additives. According to the measurements, Er additive improves the shear strength of Sn3.8Ag0.7CuEr to some extent [100]. The tensile fracture strength (*f*), tensile fracture strain ($\varepsilon_{t,f}$), and compressive yield strength ($\sigma_{c,y}$) of $Sn_{90-x}Sb_{10}In_x$ melt-spun alloys are listed in Table 2 [97].

3.9 Chemical properties

Liquid metals hold high chemical stability and does not burn when meeting with the air. Their low saturated vapor pressure renders applications in environment with high vacuum. However, it also indicates difficulties on solidification of the DREAM ink and all solidification methods at low temperature should be investigated. Some liquid metals such as gallium are amphoteric metals that can be dissolved in both acid and alkali. At room temperature, it usually emerges as dense oxide film on the surface of gallium to prevent further oxidation. Gallium or its oxide can react with sodium hydroxide under normal condition with reaction equations as follows:

1) When heated, Ga can react with NaOH solution, producing hydrogen and $NaGaO_2$:

$$2Ga + 2NaOH + 2H_2O = 2NaGaO_2 + 3H_2 \qquad (1)$$

2) Ga_2O_3 may also react with NaOH, producing water and $NaGaO_2$:

$$Ga_2O_3 + 2NaOH = 2NaGaO_2 + H_2O \qquad (2)$$

Therefore, when storing gallium-based inks or writing on substrates, great attentions should be paid to putting it away from acid and alkali. Meanwhile, similar follow-up measures utilizing those properties may also be taken to produce required substances after writing inks on substrates. Also, gallium can react with other nonmetallic such as ammonia, hydrogen sulfide, arsenic, halogen, phosphorus and so on, to form compounds under special conditions.

Simultaneously, gallium possesses strong corrosivity to a few metals such as aluminum. Figure 19 shows the corrosion phenomenon of gallium to aluminum. Therefore, gallium is suitable to be placed in containers made of quartz, graphite or polyethylene material. Evidently, such property should be considered in advance as far as the printing surface is concerned.

3.10 Additional significant properties

Other significant properties such as electromagnetic, optical and acoustic properties cannot be ignored either. Ga_2O_3 is a transparent oxide semiconductor material which has a wide range of potential applications in optoelectronics devices. Copper indium gallium selenide (CIGS) thin-film solar cells' share in the thin-film photovoltaics (TFPV) market is on the growth. CIGS is a direct band gap material whose magnitude of visible light absorption coefficient is up to 105 cm^{-1}, suitable for thin film solar cells. Other liquid metal compounds such as indium phosphide, gallium arsenide are also TFPV materials. GaN material series are an ideal short-wavelength light emitting device material, covering the spectral range from red to the UV band gap. Few research has been conducted on the acoustic properties of liquid metals so far. Therefore, the acoustic properties of liquid metals will not be discussed here for brevity.

Table 2 Mechanical properties of $Sn_{90-x}Sb_{10}In_x$ melt-spun alloys [97]

Alloys	Young's modulus *E*/GPa	Shear modulus/GPa	Bulk modulus/GPa	Lame's constant/GPa	$\varepsilon_{t,f}$
Sn-10Sb	52.25	19.49	54.42	41.42	0.195
Sn-10Sb-0.5In	58.78	21.73	61.22	46.60	0.184
Sn-10Sb-1.0In	59.89	22.34	62.38	47.78	0.182
Sn-10Sb-1.5In	62.64	23.37	65.25	49.66	0.178
Sn-10Sb-2In	65.22	24.33	67.93	51.71	0.175

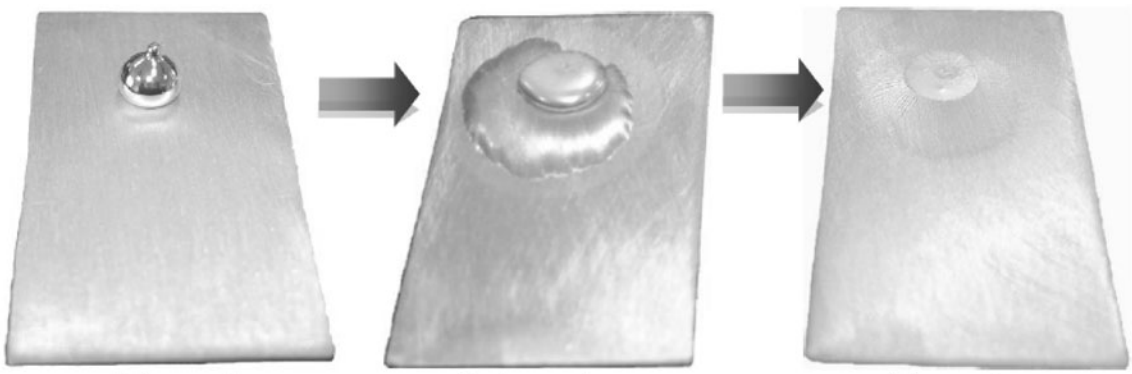


Fig. 19 Corrosion behavior between 6063 aluminum-alloy and liquid gallium [101]

3.11 Metal candidates for DREAM inks

Finding applicable room-temperature-liquid-metal for the DREAM ink is rather crucial for this newly emerging printed electronics area. The above-described room-temperature-liquid-metals or low melting point alloys mainly contain gallium, sodium, potassium, mercury (toxic), gallium indium alloys, gallium tin alloys, indium tin alloys, gallium indium tin alloys, gallium indium tin zinc alloys, gallium indium tin zinc bismuth alloys, sodium-potassium alloys and so forth. For a better reference in future practices, Appendix lists some basic physical properties of varied low melting point metal and alloys (less than 200°C) [102,103]. Of course, some parameters still need further researches to clarify and demonstrate their availability.

From Appendix, it can be easily found that for the alloys with same components, different mass ratios may have varied properties, even though only a slight change can be obtained; when adding trace elements to some alloys, the properties can be improved as desired; and Ga, In and Ga-based, In-based alloys have relatively low melting point. Therefore, particular attention should be paid to the research and applications of such printed electronics in the years to come. According to discoverable laws, one may even prepare more applicable and versatile liquid alloy inks in the near future.

4 Basic strategies to modify DREAM ink

So far, the DREAM ink has been demonstrated to work well to make a group of different electronic devices. However, the directly printable metal inks still lack many important physical or chemical properties. As a result, some special functions such as semiconductivity, magnetic or optical properties etc. cannot be directly available. For the purpose of acquiring ink materials with various performances, a series of feasible approaches as follows were proposed for modifying the printed metal inks so as to realize the expected functions as desired. It is believed that investigations along these directions are expected to lead to new fundamental discoveries and technical progresses.

4.1 Alloying

Alloying indicates to make compounds inks with metallic character by means of mixing those metals with some chemical substances, heating to a homogenous liquid and then solidified, which results in the atomic level arrangements changes of metal elemental substance. Hence, the features of metals can be improved for meeting specific performance requirements. Metal alloying, changing the alloy compositions or adding some elements into alloys may make excellent physical properties such as reduced melting point, changed electrical conductivity, thermal conductivity, viscosity and the like. Research has been conducted to find some alloys [100–106] for substituting lead-containing solders. In this regard, the DREAM inks have homologous functions with the previously developed alloy solders via utilizing the characteristics of alloys. This is an effective way to engineering a group of candidate materials as suitable inks for printed electronics. Figure 20 presents the appearance and melting point of Ga and eutectic GaIn alloy, respectively.

4.2 Combination

It is a reasonable approach to make new conductive inks by adding some organic solutions or metal particles into inks in order to obtain specific composites. The additives usually contain nonmetallic elements, carbon black powder [107], organometallic compounds [108] and other solutions. Those methods may be taken into consideration to fabricate more liquid metal based inks which are potentially feasible to many electronic elements.

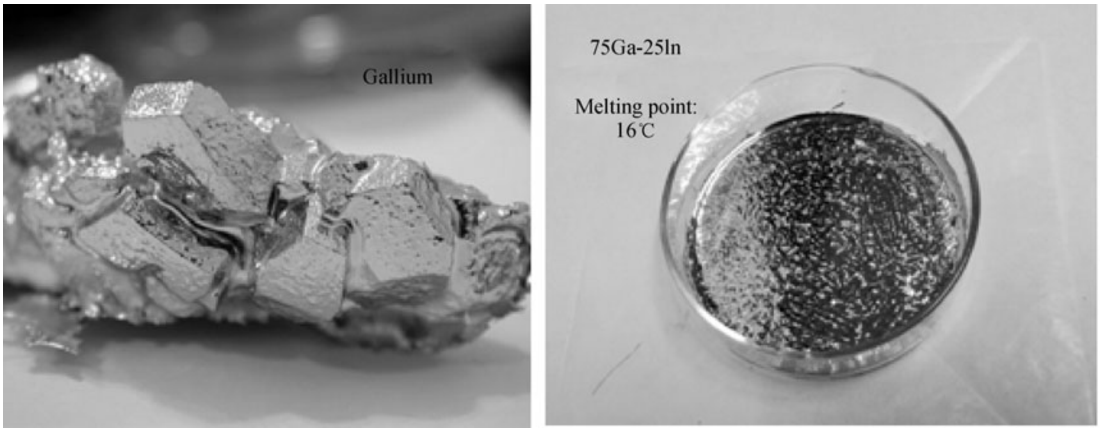


Fig. 20 Low melting point metals of Ga and eutectic GaIn alloy [103]

For example, a latest silver electronic ink successfully prepared by researchers from the University of Illinois in United States [18], is just such an easy-configuration ink composed of silver and ammonia. After printing, the liquid evaporates and the remaining trace serves as conductive material. The silver solution ink has some evident advantages over conventional conductive inks such as easier-printing, lower sintering temperature and so on. However, such method is still a little far away from the sense of direct writing. Overall, it is interesting to note that the developing trends of various conductive inks are running towards the final target: liquid metal. It is apparent that the combination between liquid metal and other matched solution or material would lead to more useful inks. This measure turns out to be a significant approach to modify the liquid metal inks for many desired physical/chemical properties and printing technologies.

4.3 Nano liquid metal

As has been proposed by Ma and Liu, adding nanoparticles into liquid metal can help make high performance metal fluid [109]. Clearly, the different physical and chemical properties of the liquid metal inks are also expected to be modified by loading with nanoparticles. Here, nanostructure method also means printing nanostructure by using metal inks. Nanoparticles can be some metallic particles such as copper, silver, nickel, etc. or some magnetic oxides such as Fe_3O_4. And some inorganic or semiconducting particles such as silicon, silicon oxide, silicon carbide, etc. are also very useful. Different particles can be added into the liquid metal inks in different amounts to fulfill various specific needs and functions. However, homogeneity and stability of particles' dispersion, which will directly affect the quality of the inks, should be carefully investigated. Some dispersants can be taken into account to enhance the uniform and stable dispersion of particles. Dispersants adsorb at the solid-liquid interface, significantly reducing the interfacial free energy, so that the solid powder can disperse uniformly in liquid instead of gathering into clusters. Currently, the commonly-used dispersants can be divided into two categories: inorganic dispersants including silicates (e.g., water glass) and alkali metal phosphates (e.g., sodium tripolyphosphate, sodium hexametaphosphate and sodium pyrophosphate, etc.); organic dispersants including three ethyl hexyl phosphoric acid, sodium lauryl sulfate, methyl amyl alcohol, cellulose derivatives, polyacrylamide, guar gum, fatty acid polyethylene glycol esters and so forth. To find suitable dispersants compatible with the DREAM ink will be another important problem which is worth of tremendous efforts. Overall, liquid metal is expected to serve as a super solution to make various electronic inks.

4.4 Oxidation

Liquid metal oxides such as gallium oxide and indium oxide are important transparent semiconductor materials already widely used in LCDs, solar cells, etc. So far, the adhesion of pure liquid metal is not sufficient enough to satisfy the different needs of substrates. As a result, the

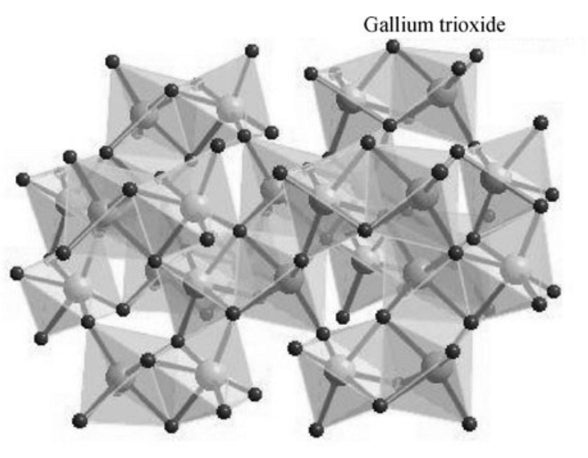


Fig. 21 Prototypical structure of gallium trioxide

liquid metal should be doped with nanooxides or partly oxidized to increase the adhesion. Figure 21 presents the prototypical structure of gallium trioxide. Researches on oxidation of printed metal ink homogeneously at low temperature after being printed are very significant. Selective oxidation by the methods of laser, microwave, and electricity should be taken into account in the near future.

4.5 Nitridation

As is known to all, GaN is an ideal candidate for high power and high temperature field-effect transistors (FETs), lasers and LEDs etc., because of its wide band gap and thermal stability. Figure 22 presents the diagrams of gallium dust and transparent hexagonal crystals of GaN. Conventionally, making a GaN film is always a high energy consuming process. As an alternative, it is suggested in this paper to print the Ga film first and then nitrify it. After printing liquid metal ink on substrates, nitridation can be followed up according to specific designs. This should be an important way to gain printable semiconductors. One conventional fabrication approach of polycrystalline GaN utilizing gallium is to place gallium in the atmosphere of ammonia in a heater. However, the heating temperature is too high and cannot be applied on ordinary flexible substrates. The liquid metal inks based on gallium can be printed on substrate and solidified later by similar method as shown by the following chemical equation:

$$Ga + NH_3 = GaN + 3/2H_2 \quad (3)$$

The localized reaction temperature between gallium and nitrogen is high, however, well controllable. For example, Argoitia [110] obtained polycrystalline GaN films utilizing liquid gallium and nitrogen by electron cyclotron resonance plasma at a low pressure. Some other methods such as nitridation by laser, microwave, plasma sintering, etc. need further investigation.

4.6 More chemical modification approaches

In addition to the chemical methods as described above, metals or alloys can also possibly react with carbon, arsenic or other chemical elements. When heated, gallium will react with halogen, sulfur and selenium rapidly. Some of such basic approaches for modifying the pre-printed metal film are suggested as follows.

4.6.1 Preparation of Ga_2S_3, Ag_2S, $AgGaS_2$ film

At present, $AgGaS_2$ thin films have already been prepared by complex procedures. Zhang and Huang [112] prepared $AgGaS_2$ thin films by the “ionic layer absorption and reaction” (SILAR) method. CH_3CN and $Na_2S_2O_3$ are used as solvent and sulfuration source respectively, $AgNO_3$ and $GaCl_3$ as cationic reagents. The Ga^{3+} ions absorbed on the

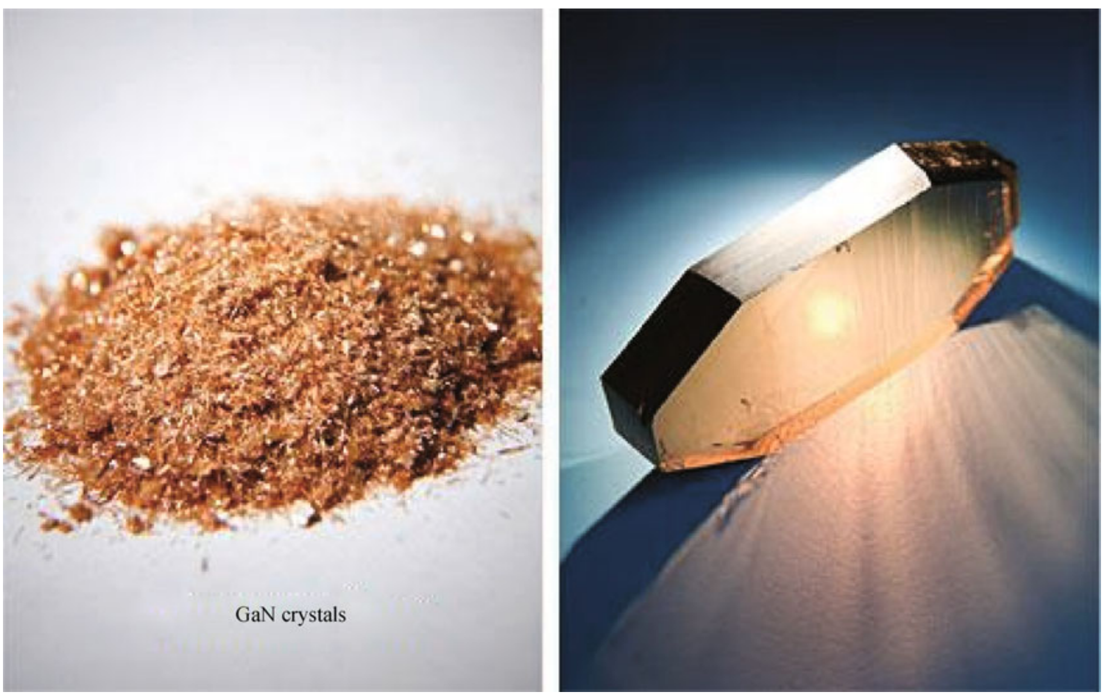


Fig. 22 Gallium dust and transparent hexagonal crystals of GaN
(a) Ammono’s first GaN crystals were tiny, and metallic impurities gave them a brownish tint; (b) after nearly two decades of refinement, Ammono’s growth technique now yields wondrously fine hexagonal crystals up to 2 inches across [111]

substrate can react with the H_2S formed from $Na_2S_2O_3$ solution according to the reactions below:

$$2H^+ + S_2O_3^{2-} \rightarrow H_2S_2O_3 \quad (4)$$

$$H_2S_2O_3 + H_2O \rightarrow H_2S + 2H^+ + SO_4^{2-} \quad (5)$$

$$2Ag^+ + H_2S \rightarrow Ag_2S + 2H^+ \quad (6)$$

$$2Ga^{3+} + 3H_2S \rightarrow Ga_2S_3 + 6H^+ \quad (7)$$

After repeating such SILAR deposition cycles 200 times, all the obtained samples were annealed in Ar atmosphere at different temperatures for 4 h. Finally, $AgGaS_2$ films with about 1μm thickness are obtained according to

$$Ag_2S + Ga_2S_3 \rightarrow 2AgGaS_2 \quad (8)$$

At room temperature, $AgGaS_2$ with yellow color is a kind of ternary semiconducting compounds. Therefore, after directly writing gallium aluminum-based liquid alloys on substrates, measures such as reacting with concentrated nitric acid solution may be taken to produce Ga^{3+} and Ag^+ ions, then hydrogen sulfide gas may get in contact with those ions to generate $AgGaS_2$. However, plentiful further studies must be carried on to assess the feasibility of this method.

4.6.2 Preparation of GaAs

Even though GaAs is toxic to some extent, it has excellent electrical characteristics and is now widely used in solar cells. GaAs can be prepared by direct reaction from the elements, as used in a number of industrial processes [113]:

Crystal growth uses a horizontal zone furnace in the Bridgman-Stockbarger technique, in which gallium and arsenic vapors react and free molecules deposit on a seed crystal at the cooler end of the furnace.

Liquid encapsulated Czochralski (LEC) growth is used for producing high purity single crystals that exhibit semi-insulating characteristics.

Alternative methods for producing films of GaAs include [113,114]:

Vapor phase epitaxy (VPE) reaction of gaseous gallium metal and arsenic trichloride:

$$2Ga + 2AsCl_3 \rightarrow 2GaAs + 3Cl_2 \quad (9)$$

Metal-organic chemical vapor deposition (MOCVD) reaction of trimethylgallium and arsine:

$$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4 \quad (10)$$

Molecular beam epitaxy (MBE) of gallium and arsenic:

$$4Ga + As_4 \rightarrow 4GaAs \quad (11)$$

or

$$2Ga + As_2 \rightarrow 2GaAs \quad (12)$$

Naturally, the pre-printed gallium thin film allows the above series of chemical reactions until finally makes the desired GaAs film.

4.6.3 Preparation of GaSe

When heated, Ga can react with Se. Previously, an open framework gallium selenide, $Ga_4Se_7(en)_2\cdot(enH)_2$, has been prepared by the direct reaction of gallium and selenium in ethylenediamine (en) [115].

Apart from the above discussed gallium material, other low melting point metals such as indium can also react with As, N and so on. In short, those compounds are important semiconductor materials in electronic industry. If they can be printed directly, the DREAM ink based on liquid metals will bring about tremendous impacts on modern electronics and energies. Even though, those compounds cannot be directly printed out yet, the innovative solution may be feasible. Gallium or a few related alloys can be written on suitable substrates firstly, then subsequent processing may be carried on to get the required capability with specific functions by the above-described methods, but manufacturing process should be further simplified as much as possible for printing succinctly. This warrants future investigations along this direction.

4.6.4 Ion implantation

Ion implantation is thought to be a feasible way for material modification. Ion implantation is a new generation technology for the surface treatment of materials in which a high-energy ion beam enters into solid material, causing a series of physical and chemical changes, to improve surface properties of the solid materials. For GaAs, p-type doped ions including Zn^+, Cd^+, Mg^+ and Be^+, while n-type doped ions including S^+, Se^+ and Si^+ can be implanted to make idealistic devices. But annealing in the implantation will increase the ceiling temperature of the whole process, consequently narrowing the range of substrate materials, and complicate the solidification process.

5 Impacts of DREAM ink and emerging applications

The metal inks can be applied in many electronic products such as PCB, radio frequency identification (RFID), OLEDs, solar cells, electronic displays, transducer and electronic packaging etc. Of course there are still many other potential applications. For instance, a conception about a mash up of electronics, print and indie music has been discussed [116]. Collapsible thin-film solar cell is a kind of thin-film solar cell which is made using noncrystalline silicon combined with a pin photodiode technology. These series of products are soft, portable, durable and also have high photoelectric conversion efficiency. They can be widely used in power supply of electronic consumer goods, remote monitoring/communication, military affairs and spaceflight. Ink-jet printing can be applied for different materials deposition on the same substrate with no interference among each deposition step. This could be relevant for the fabrication of sensor arrays on a chip. The DREAM ink, as an emerging method, will trigger a brand new round of electronic industrial revolution, engendering tremendously positive impacts on energy, environment, material, manufacturing and other industries [117].

5.1 Significance in energy saving

The new technology is expected to significantly reduce the cost of printed electronics and improve productive efficiency. The manufacturing process of traditional integrated circuits is cumbersome and complex. The high-cost processing of conventional integrated circuit containing oxidation, photolithography, diffusion, epitaxial, sputtering, vacuum deposition requires a large number of material, water, gas and energy consumptions. Figure 23 presents the schematic diagram of consumption containing energy and materials in conventional electronics. One of the most significant differences between the conventional electronics industry and printed electronics lies in processing technologies which are subtractive and addictive strategies, respectively. The revolution of the DREAM ink technology is addictive crafts that print liquid metal inks directly on varied surfaces. Figure 24 compares the conspicuous differentiation between the two above-mentioned technologies [117].

Though the existing conductive inks for printed electronics will greatly simplify the process, many issues still remain unsolved, such as worse performance than conventional electronics, complex configuring of the conductive nano-solutions, higher printing temperature and perhaps bigger nozzles. Therefore, the DREAM ink provides a game changing method to further advance the development of printed electronics with their direct

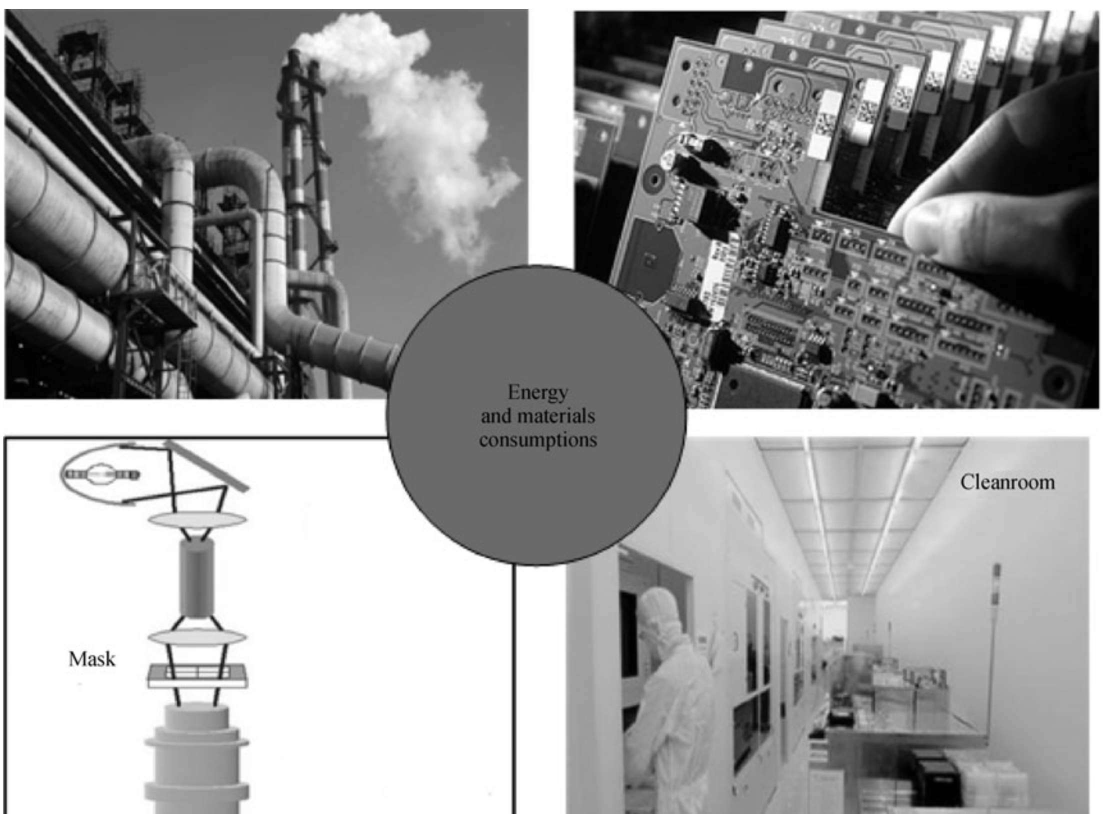


Fig. 23 Schematic diagram of consumption in conventional electronics

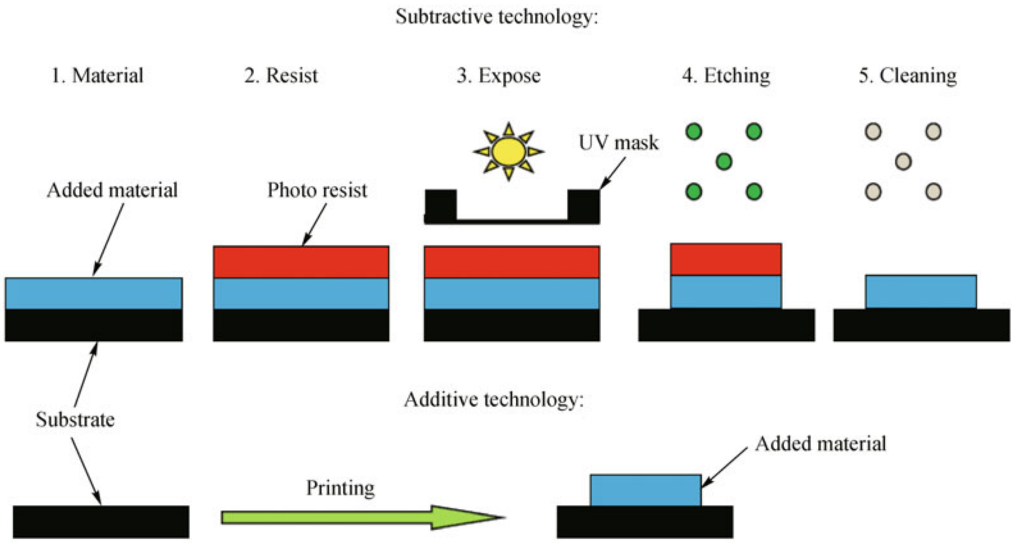


Fig. 24 Differences between subtractive and additive technologies [117]

addition feature, higher conductivity, lower-cost, materials savings, easier preparation, lower-energy consumption, easier preparation and higher efficiency.

5.2 Impact to environment

The typical fabrication methods for traditional integrated circuits have high environmental requirements during manufacture and a few process technologies can produce environmentally harmful gases and particles. Hence, the IC is usually manufactured in cleanroom that discharges hazardous substances to the outside environment. Meanwhile, lead-containing solders used in package process have been prohibited to apply by related regulations due to its potential toxicity to humans and environments. Furthermore, the recycling use of IC wastes which can directly pollute the environment is also a huge problem to be solved. Figure 25 illustrates some of such potential harms to the environment.

The newly appeared liquid metals as enabled by the DREAM inks, whose preparation progress can be completed at room temperature or normal conditions, have no particular requirements on circumstances. Liquid alloys themselves have the function of solders or printed electronics. Therefore, using the DREAM ink does not even need solders. In conclusion, as long as vital issues in science and technologies can be broken through, the DREAM ink will bring about unpredictable beneficial influences on the environment.

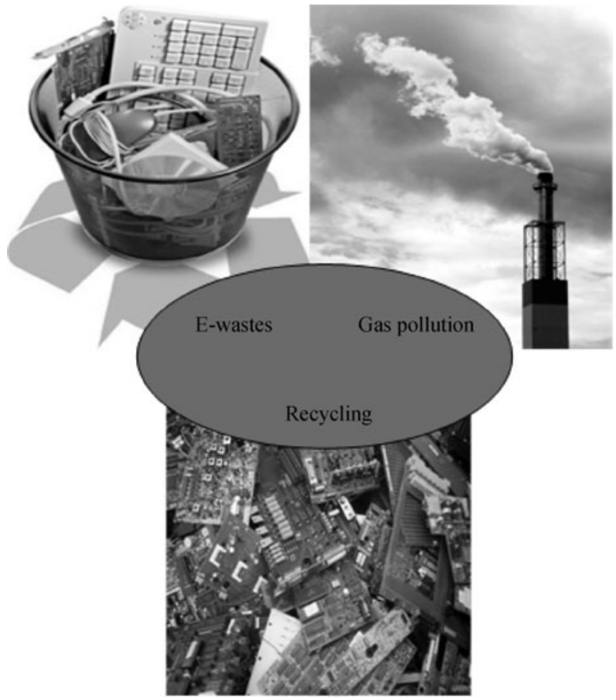


Fig. 25 Environmental pollutions of traditional integrated circuits

5.3 Impact to health technology

As liquid metal inks can be printed on flexible substrates, portable devices to monitor a person's health status that could one day be incorporated into intelligent "hospital-on-a-chip" systems can be more easily fabricated. Electric circuits and solar cells can be printed that can compose a complete system to exam physiological conditions at anytime and anywhere on bags or on clothes. Other human comfort systems like small portable fans on clothes can be connected with metal ink as electric wires. Electronic tags thus printed can serve as identifications of people. In the authors' lab, it has been demonstrated that some non-toxic metal inks can be written on skin as electrode to monitor a person's heartbeat or thermal couples to monitor body temperatures.

To date, chemical sensors printed on elastic waistbands [118] and printable sensors [119] detecting underwater hazards have already been fabricated. Tiny sensors based on the DREAM ink are no more an imagination but a feasible and significant application in the near future.

5.4 Emerging applications

The DREAM ink method opens up many potential applications, although a large part can still not be clearly outlined at this time. Most importantly, the lower printing temperature endows it with more direct writing choices. It is even possible to immediately build up circuits on paper or other flexible surfaces. The conductivity of the ink will stay excellent whether subject to folding or bending. In short, liquid metal ink brings new impetus and opportunities for further development of printed electronics. Owing to the simple structure, easy manufacturing, stable performance, low-cost and high efficiency, low curing temperature for the ink, the potential application areas contain printed electronics especially flexible printed electronics, sensor field, measurement industry, displays, micro-chips, electronic clothing, aerospace field, even the life science fields. Figure 26 presents some emerging applications along this direction.

Particularly, in view of the excellent semiconducting properties and photovoltaic characteristics of some metal oxides, new printable P or N type inorganic semiconductors may even be developed to take the place of Si [9]. Thus it is possible to produce new-style thin film solar cells conveniently and efficiently by printing on varied substrates such as papers, clothes, briefcase, cars, and even the palisade structure of the buildings [13]. Some metal oxides such as Ga_2O_3 may act as the P/N type semiconductor, further researches are being implemented.

6 Challenging scientific and technological issues

The high performance of the DREAM ink warrants its

Fig. 26 Some emerging applications [120]

future applications in printed electronics. However, printed electronics is a comprehensive area that many disciplines meet. Before applications are completely approved in electronic industry, lots of scientific issues and technological challenges must be overcome in advance.

The followings are a few of the scientific issues that must be addressed:

1) The key issues lie in materials. Although previously listed potential candidates for the DREAM ink contain a number of alloys, a large portion of alloys' physical properties remain to be investigated to make more appropriate inks in wider temperature ranges. Even though by changing the component ratio of alloys or adding a few varied elements into the alloys, the performance may be improved as desired [121–123], further studies must be carried out to verify whether the liquid metals or alloys can meet the application requirements. Figure 27 presents the schematic diagram from original liquid to final product.

In the first place, although the conventional IC has a number of disadvantages, its manufacturing technology is relatively mature. Simultaneously, enough research has been conducted on the physical properties of alloy solders, such as mechanical, tensile properties and so forth [124–128]. But lots of issues still remain to be solved. Furthermore, solders are mainly used at welding spots at local areas to connect circuits, yet the DREAM inks are generally printed on different surfaces in large scale, especially on flexible substrate which relates to three-dimensional printings as is shown in Fig. 28. More in-depth studies are yet to clarify the performance of those alloy solders on varied surfaces, including the insurance of the continuity and uniformity of liquid metals materials. When printing metal inks on substrates, some important

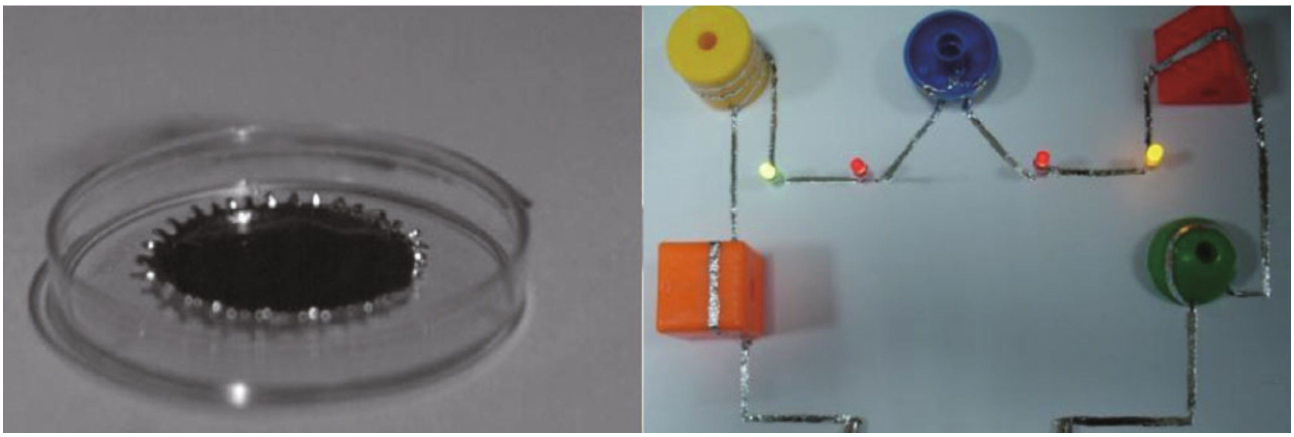


Fig. 27 Schematic diagrams of application issues

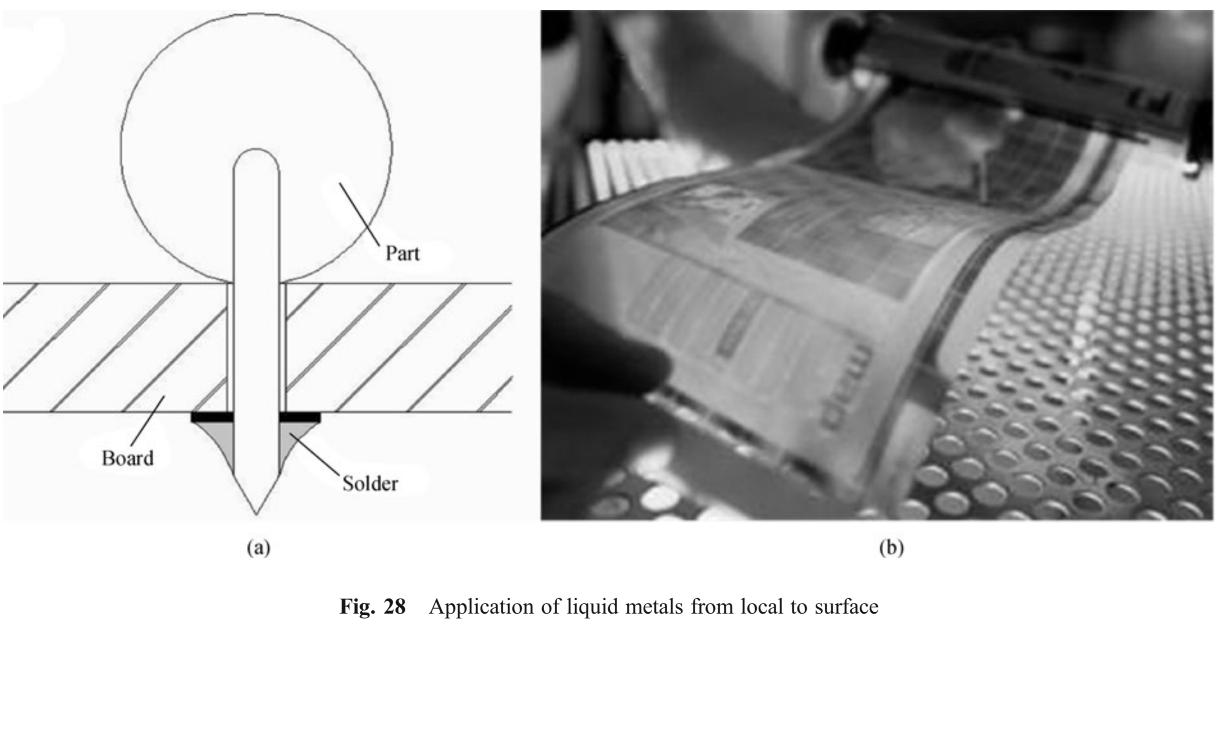


Fig. 28 Application of liquid metals from local to surface

mechanisms exist such as the prevention of the liquid metal from flowing and deforming owing to liquidus characteristics which may deteriorate the electrical performance of products, and the insurance of the long-term use etc. Besides, the migration of liquid metal droplets must be forecasted and reduced before meeting substrates. Furthermore, the distorted images need to be modified.

Secondly, just like conventional conductive inks, liquid metals are solidified from liquidus on substrates, during which some metals are likely to be oxidized. Thus the electrical conductivity of metals may be deteriorated due to oxidations that have poor electrical properties. There are little concerned investigations to protect it in the air conveniently. As liquid metal follows the principles of solidification before writing on the substrates, the substrates and other materials on substrates as functional components will be impacted in the process of solidification. Suitable solidification methods are in need of development. Without such endeavors, the material of substrates will just be limited in a narrow range.

Last but not the least, the properties of metals such as electrical conductivity, viscosity are closely related to the temperature [129–131]. Therefore, research should be conducted to clarify whether the products are able to meet the application requirements in a certain temperature and humidity ranges of environment, including magnetic field and optics as well.

2) The interconnection and compatibility between varied liquid metals and substrates are other crucial aspects that may hinder the application of these new inks. In addition, when printed on flexible surfaces, valuable information must be obtained to know about whether materials can maintain high performance after bending or reversing the flexible substrates. For example, pure gallium adhesion with some substrates such as paper is not very satisfactory and partially oxidized gallium can be tried instead, however, sacrificing electrical properties. There will be an optimal solution between adhesion improvement and suitable electrical characteristics maintenance. Clearly, finding the optimal solution is very critical. Contact resistance between liquid metal inks and substrates may change with temperature and humidity of environment. Guaranteeing the adhesion and contact resistance stable in certain range for a time long enough in different environments will be a great challenge before being put into practical use.

Simultaneously, a few technical challenges remain to be overcome. First of all, most low melting metals and alloys are very expensive. Though sodium-potassium alloy is relatively cheap, they can only be used in specific conditions since they are chemically very active and can be dangerous if leaking. Therefore, the recycling must be taken into account for the noble metal inks such as gallium. Second, there should be simple and corresponding equipment to expose the advantages of the DREAM inks for printed electronics and the device related issues, such as proper sizes, backflow and corrosion of nozzle must be taken seriously. Next, of course not all the conventional printing methods can be applied for DREAM ink. Those probably suitable approaches should be attempted and then modified to meet various writing requirements. Finally, the toxicity of products by the DREAM inks and intermediates of the fabrication process must also be paid enough attention to.

7 Future prospects

Printed electronics is an emerging technology with huge potential to change the way people interact with each other and the everyday stuff they use [116]. The simple and convenient usage of the DREAM ink is promising. People would change their idea about paper which will integrate with many functions besides the traditional writing. Besides, people can even print all these functional paper with their desktop inkjet printers as they desire. A form of washable fabrics that could sense and emit light and sounds will no longer be surprising. Electronic clothing coated with liquid metal thin films may appear to generate power at random in the sun. The wall of buildings can be painted directly as LEDs or even solar cells which will harvest solar energy and generate huge electricity for people's daily life. Meanwhile, a tremendous revolution will also come into being in education areas where both teachers and students will benefit a lot. With liquid metal inks, the teachers can make their class more interesting and vivid while the students can paint as they image. But different from the traditional practices, what they paint will be so lively that it can really give off sound, light and even smell. Many electronics will enter into an era of rapid prototyping. Combined with pre-loaded computer software with designed programs and automatic control printer, required components may even able to be rapidly manufactured at the lowest cost by only selecting codes corresponding to specific patterns. All these will bring about a fantastic new electronics world.

Acknowledgements The authors wish to appreciate the valuable help from Dr. Yunxia Gao at the Technical Institute of Physics and Chemistry, Chinese Academy of Sciences for the preparation of Figs. 8–10.

Appendix

Further researches are needed to confirm the metal inks' feasibility in direct writing of electronics. Required by the environmental regulations, the lead-containing alloys are limited or even forbidden to apply in electronics industry. The following two tables (Tables 3 and 4) selectively list a series of potential candidates for DREAM ink.

Table 3 Main physical properties of low melting point lead-free metal and alloy [72,102,103]

Alloys categories	Combination	Melting point (Solidus/liquidus)/°C	Density /($g \cdot cm^{-3}$)	Electrical conductivity /(10^6 $S \cdot m^{-1}$)	Thermal conductivit /($W \cdot cm^{-1} \cdot °C^{-1}$)	CTE/($10^{-6} \cdot °C^{-1}$)
Bi-Cd(Toxic)	60Bi-40Cd	144	9.31			
Bi-In	67Bi-33In	109	8.81			
Bi-In-Sn	57Bi-26In-17Sn	79	8.54			
	54Bi-29.7In-16.3Sn	81	8.47			
Bi-In-Cd	48.5Bi-41.5In-10Cd	78	8.49			
Bi-Sn	50Bi-50Sn	138/152				
	52Bi-48Sn	138/151				
	57Bi-43Sn			2.61	0.19	15
	58Bi-42Sn	138	8.56			
	95Bi-5Sn	134/251	9.64			
Bi-Sn-Ag	56Bi-43.5Sn-0.5Ag	Ternary eutectic				
	57Bi-42.9Sn-0.1Ag	138/140	8.57			
	57Bi-42Sn-1Ag	139/140				
	57Bi-41Sn-2Ag	140/147				
Bi-Sn-Ag-Sb	56Bi-40.5Sn-2Ag-1.5Sb	137/145				
	55.5Bi-40Sn-3Ag-1.5Sb	137/147				
	55Bi-40Sn-3Ag-2Sb	138/150				
	54Bi-39Sn-3Ag-4Sb	138/154				
Bi-Sn-Ag-Sb-In	54Bi-39Sn-3Ag-2Sb-2In	99/138				
Bi-Sn-Ag-Sb-Cu	54Bi-39Sn-3Ag-2Sb-2Cu					
Bi-Sn-Cu	55Bi-43Sn-2Cu	138/140				
Bi-Sn-Fe	54.5Bi-43Sn-2.5Fe	137				
Bi-Sn-Cd	54Bi-26Sn-20Cd	102/103	8.78			
Bi-Sn-In	56Bi-42Sn-2In	126/140				
	57Bi-42Sn-1In	132/138				
	57Bi-41Sn-2In	127/140				
Bi-Sn-In-Cu	56.7Bi-42Sn-1In-0.3Cu	132/138				
Bi-Sn-Sb	57Bi-41Sn-2Sb	141/150				
	57Bi-42Sn-1Sb	138/149				
Bi-Sn-Zn	55Bi-43Sn-2Zn	Ternary eutectic				
Bi-Sb	95Bi-5Sb	About 275/308				
Ga	100 Ga	30	5.90	1.792	0.29	
Ga-In	75.5Ga-24.5In	16	6.35			
	95Ga-5In	16/25	6.15			
Ga-In-Sn	62.5Ga-21.5In-16Sn	11	6.50			
Ga-In-Sn-Zn	61Ga-25In-13Sn-1Zn	7/8	6.50			
In	100 In	157	7.31	13.9	0.86	29
In-Ag	97In-3Ag	143	7.38	13.34	0.73	22
	90In-10Ag	141/237	7.54	12.818	0.67	15
In-Bi	66.3In-33.7Bi	72	7.99			
	95In-5Bi	125/150	7.40			
In-Bi-Sn	48.8In-31.6Bi-19.6Sn	59				
	51.0In-32.5Bi-16.5Sn	60	7.88	1.914		22
In-Bi-Cd	61.7In-30.8Bi-7.5Cd	62	8.02			
In-Sn	90In-10Sn	143/151	7.31			
	60In-40Sn	118/127				
	52In-48Sn	118	7.30	6.786	0.34	20
	50In-50Sn	118/125	7.30	6.786	0.34	20

(*Continued*)

Alloys categories	Combination	Melting point (Solidus/liquidus)/°C	Density /($g \cdot cm^{-3}$)	Electrical conductivity /(10^6 $S \cdot m^{-1}$)	Thermal conductivit /($W \cdot cm^{-1} \cdot °C^{-1}$)	CTE/($10^{-6} \cdot °C^{-1}$)
In-Sn-Zn	52.2In-46Sn-1.8Zn	108	7.27			
In-Sn-Cd	44In-42Sn-14Cd	93	7.46		0.36	24
In-Cd	74In-26Cd	123	7.62			
In-Ga	99.3In-0.7Ga	150	7.31			
	99.4In-0.6Ga	152	7.31			
	99.5In-0.5Ga	154	7.31			
	99.6In-0.4Ga	153	7.31			
Sn-Bi	55Sn-45Bi	138/164				
	60Sn-40Bi	138/170	8.12	2.9	0.30	
Sn-Bi-Ag	90.5Sn-7.5Bi-2Ag	190/216				
	90.8Sn-6.1Bi-3.1Ag	137/215				
	86.5Sn-10Bi-3.5Ag	137/208				
	81.7Sn-15Bi-3.3Ag	137/200				
	78Sn-19.5Bi-2.5Ag	138/196				
	63.2Sn-30Bi-6.8Ag	137/282				
	56Sn-41Bi-3Ag	138/166				
Sn-Bi-Ag-Cu	90Sn-7.5Bi-2Ag-0.5Cu	193/213	7.56			
	90.8Sn-5Bi-3.5Ag-0.7Cu	198/213				
Sn-Bi-Cu	50Sn-48Bi-2Cu	138/153				
Sn-Bi-Cu-Ag	48Sn-46Bi-4Cu-2Ag	137/146				
Sn-Bi-In-Ag	80Sn-11.2Bi-5.5In-3.3Ag	170/221				
	80.8Sn-11.2Bi-5.5In-2.5Ag	169/200				
Sn-Bi-Zn	65.5Sn-31.5Bi-3Zn	133/171				
Sn-Cd(Toxic)	67.8Sn-32.2Cd	177	7.68			
Sn-In	52Sn-48In	118/131	7.30			
	58Sn-42In	118/145	7.30			
	70Sn-30In	120/about175				
Sn-In-Ag	77.2Sn-20.0In-2.8Ag	175/186	7.25	5.684	0.54	28
	73.2Sn-20In-6.8Ag	113/242				
	80Sn-14.4In-5.6Ag	189/199				
Sn-In-Ag-Cu	88.5Sn-8In-3Ag-0.5Cu	196/202				
Sn-In-Bi	82Sn-15In-3Bi	113				
	80Sn-10In-10Bi	153/199or170/200				
Sn-In-Bi-Ag	80Sn-10In-9.5Bi-0.5Ag	179/201				
	78.4Sn-9.8In-9.8Bi-2Ag	163/195				
Sn-In-Zn	77.2Sn-20In-2.8Zn	106/180				
	83.6Sn-8.8In-7.6Zn	181/187	7.27			
Sn-Zn	91Sn-9Zn	199	7.27	8.7	0.61	
Sn-Zn-Bi	89Sn-8Zn-3Bi	192/197				
	88Sn-7Zn-5Bi	185/194				
Sn-Zn-In	87Sn-8Zn-5In	175/188				
Sn-Zn-In-Bi	86.5Sn-5.5Zn-4.5In-3.5Bi	174/186	7.36			

Table 4 Pb-containing alloys (Containing a few Pb, selective use for environmentally friendly purpose) [103]

Alloys categories	Combination	Melting point (Solidus /liquidus)/°C	Density/($g\cdot cm^{-3}$)	Electrical conducztiv-ity/($10^6 S\cdot m^{-1}$)	Thermal conductivit /($W\cdot cm^{-1}\cdot °C^{-1}$)	CTE/($10^{-6}\cdot °C^{-1}$)
Bi-In-Sn-Pb	51.6Bi-37.4In-6.0Sn-5.0Pb	95/129	8.58			
Bi-Sn-Pb	56.8Bi-41.2Sn-2.0Pb	128/133	8.60			
	57.4Bi-41.6Sn-1.0Pb	135E	8.58			
	55.1Bi-39.9Sn-5.0Pb	121/136	8.67			
In-Pb-Ag	80.0In-15.0Pb-5.0Ag	149/154	7.85	7.54	0.43	28
Sn-Bi-Pb	60.0Sn-25.5Bi-14.5Pb	96/180	8.25			
Sn-Pb	85.0Sn-15.0Pb	183/205	7.70			
	90.0Sn-10.0Pb	183/213	7.55			
	95.0Sn-5.0Pb	183/222	7.42			

Dr. Jing Liu is a professor with the Department of Biomedical Engineering of Tsinghua University (THU) and the Technical Institute of Physics and Chemistry, Chinese Academy of Sciences (CAS). He received his B.E. degree in Power Engineering and Control and B.S. degree in Physics in 1992, and Ph.D. in Thermal Science in 1996 from THU. He then served as assistant professor at THU, a postdoctoral research associate at Purdue University, and a senior visiting scholar at Massachusetts Institute of Technology. He has been a professor with the CAS since July 1999 and a professor with THU since August 2008. Dr. Liu has authored nine popular books on cutting edge frontiers in energy and bioengineering areas (among which Micro/Nano Scale Heat Transfer has been reprinted five times), fourteen invited book chapters, over three hundred peer reviewed journal papers, and about seventy international conference presentations or invited lectures. He holds more than 100 patents.

Prof. Liu's research interests include microenergy, mobile health technology, thermal management, bioheat and mass transfer, and micro/nano fluidics. He contributed significantly to the bioheat transfer area through numerous conceptual innovation, methodology development and technical inventions and is a world-renowned expert in this area. His work is also fully reflected in energy and related areas, where he pioneered a series of non-conventional technologies especially the liquid metal based thermal management, waste heat recovery, electricity generation and direct writing electronics etc. Dr. Liu is a recipient of 2010–2011 Best Paper of the Year Award from ASME Journal of Electronic Packaging, the National Science Fund for Distinguished Young Scholars of China, National Science and Technology Award for Chinese Young Scientist, Mao Yi-Sheng Science and Technology Award for Beijing Youth, and five times highest teaching award from CAS etc.

References

1. Harrop P, Das R. Player and Opportunities 2012–2022. FRID Market Research Report. 2012
2. Sun Y G, Rogers J A. Inorganic semiconductors for flexible electronics. Advanced Materials, 2007, 19(15): 1897–1916
3. Leenen M A M, Arning V, Thiem H, Steiger J, Anselmann R. Printable electronics: Flexibility for the future. Physical Status Solidi A, 2009, 206(4): 588–597
4. Cui Z. Printed Electronics: Materials, Technologies and Applications. Beijing: Higher Education Press, 2012 (in Chinese)
5. Gao Y X, Li H Y, Liu J. Direct writing of flexible electronics through room temperature liquid metal ink. PLoS One, 2012, 7(9): e45485
6. Li H Y, Yang Y, Liu J. Printable tiny thermocouple by liquid metal gallium and its matching metal. Applied Physics Letters, 2012, 101 (7): 073511
7. Liu J, Li H Y. A liquid metal based printed circuit board and its fabrication method. China Patent 201110140156.6, 2011
8. Gao Y X, Li H Y, Liu J, Yan X M. Liquid metal ink enabled direct writing of functional circuits: A super-simple way for alternative electronics, 2012, in review
9. Liu J. Printable semiconductive device and its fabrication method. China Patent 2012103572802, 2012
10. Liu J, Li H Y. A thermal energy harvesting device and its fabrication method. China Patent 201210241718.0, 2012
11. Liu J. Piezoelectric thin film electricity generator and its fabrication method, China Patent 2012103225845, 2012
12. Liu J. Liquid metal ink printed microfluidic lab on paper and its fabrication method. China Patent 2012103625068, 2012
13. Liu J. Printable solar cell and its fabrication method. China Patent 2012103224715, 2012
14. Horikawa T, Mikami N, Makita T, Tanimura J, Kataoka M, Sato K, Nunoshita M. Dielectric properties of (Ba, Sr)TiO_3 thin films deposited by RF sputtering. Journal of Applied Physics, 1993, 32 (1): 4126–4130
15. Sun X W, Kwok H S. Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition. Journal of Applied Physics, 1999, 86(1): 408–411
16. Carcia P F, McLean R S, Reilly M H, Nunes G. Transparent ZnO thin-film transistor fabricated by RF magnetron sputtering. Applied Physics Letters, 2003, 82(7): 1117–1119
17. Gross M, Linse N, Maksimenko L, Wellmann P J. Conductance enhancement mechanisms of printable nanoparticulate indium tin oxide (ITO) Layers for Application in Organic Electronic Devices.

Advanced Engineering Materials, 2009, 11(4): 295–301
18. Russo A, Ahn B Y, Adams J J, Duoss E B, Bernhard J T, Lewis J A. Pen-on-paper flexible electronics. Advanced Marerials, 2011, 23(30): 3426–3430
19. Cho J H, Lee J, Xia Y, Kim B, He Y, Renn M J, Lodge T P, Frisbie C D. Printable ion-gel gate dielectrics for low-voltage polymer thin-film transistors on plastic. Nature Materials, 2008, 7(11): 900–906
20. Aernouts T, Vanlaeke P, Geens W, Poortmans J, Heremans P, Borghs S, Mertens R, Andriessen R, Leenders L. Printable anodes for flexible organic solar cell modules. Thin Solid Films, 2004, 451–452: 22–25
21. Arias A C, Ready S E, Lujan R, Wong W S, Paul K E, Salleo A, Chabinyc M L, Apte R, Street R A, Wu Y, Liu P, Ong B. All jet-printed polymer thin-film transistor active-matrix backplanes. Applied Physics Letters, 2004, 85(15): 3304–3306
22. Li B, Santhanam S, Schultz L, Jeffries-EL M, Iovu M C, Sauvé G, Cooper J, Zhang R, Revelli J C, Kusne A G, Snyder J L, Kowalewski T, Weiss L E, McCullough R D, Fedder G K, Lambeth D N. Inkjet printed chemical sensor array based on polythiophene conductive polymers. Sensors and Actuators B, Chemical, 2007, 123(2): 651–660
23. Nur H M, Song J H, Evans J R G, Edirisinghe M J. Ink-jet printing of gold conductive tracks. Materials in Electronics, 2002, 13(4): 213–219
24. Lee H H, Chou K S, Huang K C. Inkjet printing of nanosized silver colloids. Nanotechnology, 2005, 16(10): 2436–2441
25. Woo K, Kim D, Kim J S, Lim S, Moon J. Ink-jet printing of Cu-Ag-based highly conductive tracks on a transparent substrate. Langmuir, 2009, 25(1): 429–433
26. Smith P J, Shin D Y, Stringer J E, Derby B, Reis N. Direct ink-jet printing and low temperature conversion of conductive silver patterns. Journal of Materials Science, 2006, 41(13): 4153–4158
27. Kim D, Jeong S, Park B K, Moon J. Direct writing of silver conductive patterns: Improvement of film morphology and conductance by controlling solvent compositions. Applied Physics Letters, 2006, 89(26): 264101
28. Kim D, Moon J. Highly Conductive ink jet printed films of nanosilver particles for printable electronics. Electrochemical and Solid-State Letters, 2005, 8(11): 30–33
29. Kim Y, Lee B, Yang S, Byun I, Jeong I, Cho S M. Use of copper ink for fabricating conductive electrodes and RFID antenna tags by screen printing. Current Applied Physics, 2012, 12(2): 473–478
30. Tang X F, Yang Z G, Wang W J. A simple way of preparing high-concentration and high-purity nano copper colloid for conductive ink in inkjet printing technology. Colloid and Surfaces A. Physicochemical and Engineering Aspects, 2010, 360(1–3): 99–104
31. Park B K, Kim D, Jeong S, Moon J, Kim J S. Direct writing of copper conductive patterns by ink-jet printing. Thin Solid Films, 2007, 515(19): 7706–7711
32. Lee B, Kim Y, Yang S, Jeong I, Moon J. A low-cure-temperature copper nano ink for highly conductive printed electrodes. Current Applied Physics, 2009, 9(2): 157–160
33. Kordás K, Mustonen T, Tóth G, Jantunen H, Lajunen M, Soldano C, Talapatra S, Kar S, Vajtai R, Ajayan P M. Inkjet printing of electrically conductive patterns of carbon nanotubes. Small, 2006, 2(8–9): 1021–1025
34. Denneulin A, Bras J, Carcone F, Neuman C, Blayo A. Impact of ink formulation on carbon nanotube network organization within inkjet printed conductive films. Carbon, 2011, 49(8): 2603–2614
35. Huang D, Liao F, Molesa S, Redinger D, Subramanian V. Plastic-compatible low resistance printable gold nanoparticle conductors for flexible electronics. Journal of the Electrochemical Society, 2003, 150(7): 412–417
36. Kaempgen M, Chan C K, Ma J, Cui Y, Gruner G. Printable thin film supercapacitors using single-walled carbon nanotubes. Nano Letters, 2009, 9(5): 1872–1876
37. Maksimenko I, Kilian D, Mehringer C, Voigt M, Peukert W, Wellmann P J. Fabrication, charge carrier transport, and application of printable nanocomposites based on indium tin oxide nanoparticles and conducting polymer 3,4-ethylenedioxythiophene/polystyrene sulfonic acid. Journal of Applied Physics, 2011, 110(10): 104301–104308
38. Sekitani T, Nakajima H, Maeda H, Fukushima T, Aida T, Hata K, Someya T. Stretchable active-matrix organic light-emitting diode display using printable elastic conductors. Nature Materials, 2009, 8(6): 494–499
39. Lee D H, Chang Y J, Herman G S, Chang C H. A general route to printable high-mobility transparent amorphous oxide semiconductors. Advanced Materials, 2007, 19(6): 843–847
40. Fortuna S A, Wen J G, Chun I S, Li X. Planar GaAs nanowires on GaAs (100) substrates: Self-aligned, nearly twin-defect free, and transfer-printable. Nano Letters, 2008, 8(12): 4421–4427
41. Panthani M G, Akhavan V, Goodfellow B, Schmidtke J P, Dunn L, Dodabalapur A, Barbara P F, Korgel B A. Synthesis of $CulnS_2$, $CulnSe_2$, and $Cu(In_xGa_{(1-x)})Se_2$ (CIGS) nanocrystal “inks” for printable photovoltaics. Journal of the American Chemical Society, 2008, 130(49): 16770–16777
42. Guillemles J F, Kronik L, Cahen D, Rau U, Jasenek A, Schock H-W. Stability issues of $Cu(In,Ga)Se_2$-based solar cells. Journal of Chemical Physics B, 2000, 104(20): 4849–4862
43. Volkman S K, Mattis B A, Molesa S E, Lee J B, de la Fuente Vornbrock A, Bakhishev T, Subramanian V. A novel transparent air-stable printable n-type semiconductor technology using ZnO nanoparticles. In: IEEE International Electron Devices Meeting. Berkeley, USA, 2004, 769–772
44. Dasgupta S, Gottschalk S, Kruk R, Hahn H. A nanoparticulate indium tin oxide field-effect transistor with solid electrolyte gating. Nanotechnology, 20008, 19(43): 435203.1–435203.6
45. Jeong J A, Kim H K. Characteristics of inkjet-printed nano indium tin oxide particles for transparent conducting electrodes. Current Applied Physics, 2010, 10(4): 105–108
46. Gross M, Linse N, Maksimenko I, Wellmann P J. Conductance enhancement mechanisms of printable nanoparticulate indium tin oxide (ITO) layers for application in organic electronic devices. Advanced Engineering Materials, 2009, 11(4): 295–301
47. Allen M L. Nanoparticle sintering methods and applications for printed electronics. Dissertation for the Doctoral Degree. Espoo, Finland: Aalto University, 2011
48. Siden J, Fein M K, Koptyug A, Nilsson H E. Printed antennas with variable conductive ink layer thickness. IET Microwaves,

Antennas and Propagation, 2007, 1(2): 401–407
49. Yan H, Chen Z H, Zheng Y, Newman C, Quinn J R, Dötz F, Kastler M, Facchetti A. A high-mobility electron-transporting polymer for printed transistors. Nature, 2009, 457(7230): 679–686
50. Pudas M, Hagberg J, Leppävuori S. Gravure offset printing of polymer inks for conductors. Progress in Organic Coatings, 2004, 49(4): 324–335
51. Shaheen S E, Radspinner R, Peyghambarian N, Jabbour G E. Fabrication of bulk heterojunction plastic solar cells by screen printing. Applied Physics Letters, 2001, 79(18): 2996–2998
52. Pardo D A, Jabbour G E, Peyghambarian N. Application of screen printing in the fabrication of organic light-emitting devices. Advanced Materials, 2000, 12(17): 1249–1252
53. Ito S, Chen P, Comte P, Nazeeruddin M K, Liska P, Péchy P, Grätzel M. Fabrication of screen-printing pastes from TiO_2 powders for dye-sensitised solar cells. Progress in Photovoltaics: Research and Applications, 2007, 15(7): 603–612
54. Bao Z N, Rogers J A, Katz H E. Printable organic and polymeric semiconducting materials and devices. Journal of Materials Chemistry, 1999, 9(9): 1895–1904
55. Renn M J. Direct Write System. US7270844 B2. 2007
56. Martin G D, Hoath S D, Hutchings I M. Inkjet printing—The physics of manipulating liquid jets and drops. Journal of Physics: Conference Series, 2008, 105(1): 012001
57. Mette A, Richter P L, Hörteis M, Glunz S W. Metal aerosol jet printing for solar cell metallization. Progress in Photovoltaics: Research and Applications, 2007, 15(7): 621–627
58. Ahn B Y, Duoss E B, Motala M J, Guo X, Park S I, Xiong Y, Yoon J, Nuzzo R G, Rogers J A, Lewis J A. Omnidirectional printing of flexible, stretchable, and spanning silver microelectrodes. Science, 2009, 323(5921): 1590–1593
59. Kahn B E. The M3D aerosol jet system, an alternative to inkjet printing for printed electronics. Organic and Printed Electronics, 2007, 1: 14–17
60. Hon K K B, Li L, Hutchings I M. Direct writing technology—Advances and developments. Manufacturing Technology, 2008, 57 (2): 601–620
61. Perelaer J, De Laat A W M, Hendriks C E, Schubert U S. Inkjet-printed silver tracks: Low temperature curing and thermal stability investigation. Journal of Materials Chemistry, 2008, 18(27): 3209–3215
62. Allen M L, Aronniemi M, Mattila T, Alastalo A, Ojanperä K, Suhonen M, Seppä H. Electrical sintering of nanoparticle structures. Nanotechnology, 2008,19 (17): 175201.1–175201.4
63. Ko S H, Pan H, Grigoropoulos C P, Luscombe C K, Fréchet J M J, Poulikakos D. All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. Nanotechnology, 2007, 18 (34), 345202.1–345202.8
64. Perelaer J, de Gans B J, Schubert U S. Ink-jet printing and microwave sintering of conductive silver tracks. Advanced Materials, 2006, 18(16): 2101–2104
65. Perelaer J, Klokkenburg M, Hendriks C E, Schubert U S. Microwave flash sintering of inkjet-printed silver tracks on polymer substrates. Advanced Materials, 2009, 21(47): 4830–4834
66. Magdassi S, Grouchko M, Berezin O, Kamyshny A. Triggering the sintering of silver nanoparticles at room temperature. ACS Nano, 2010, 4(4): 1943–1948
67. Wakuda D, Kim C J, Kim K S, Suganuma K. Room temperature sintering mechanism of Ag nanoparticle paste. In: Proceedings of the 2nd Electronics System-Integration Technology Conference. Greenwich, 2008, 909–914
68. Zapka W, Voil W, Loderer C, Lang P. Low temperature chemical post-treatment of inkjet printed nano-particle silver inks. In: International Conference on Digital Printing Technologies and Digital Fabrication. Pittsburgh: NIP24, 2008, 9: 906–911
69. Munir Z A, Anselmi-Tamburini U, Ohyanagi M. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. Journal of Materials Science, 2006, 41(3): 763–777
70. Ko S H, Pan H, Grigoropoulos C P, Luscombe C K, Fréchet J M J, Poulikakos D. All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. Nanotechnology, 2007, 18 (34): 345202
71. Thostenson E T, Chou T W. Microwave processing: Fundamentals and applications. Composites. Part A, Applied Science and Manufacturing, 1999, 30(9): 1055–1071
72. Li H Y, Liu J. Revolutionizing heat transport enhancement with liquid metals: Proposal of a new industry of water-free heat exchangers. Frontiers in Energy, 2011, 5(1): 20–42
73. Ma K Q, Liu J. Heat-driven liquid metal cooling device for the thermal management of a computer chip. Journal of Physics. D, Applied Physics, 2007, 40(15): 4722–4729
74. Liu J, Zhou Y X, Lv Y G, Li T. Liquid metal based miniaturized chip-cooling device driven by electromagnetic pump. In: ASME 2005 International Mechanical Engineering Congress and Exposition. Orlando, USA, 2005: 501–510
75. Deng Y G, Liu J. Hybrid liquid metal-water cooling system for heat dissipation of high power density microdevices. Heat and Mass Transfer, 2010, 46(11–12): 1327–1334
76. Deng Y G, Liu J. A liquid metal cooling system for the thermal management of high power LEDs. International Communications in Heat and Mass Transfer, 2010, 37(7): 788–791
77. Liu J, Zhou Y X. A computer chip cooling method which uses low melting point metal and its alloys as the cooling fluid. China Patent 02131419.5, 2002
78. Deng Z S, Liu J. Capacity evaluation of a MEMS based micro cooling device using liquid metal as coolant. In: The 1st IEEE International Conference on Nano/Micro Engineered and Molecular Systems. Zhuhai, China. 2006, 1311–1315
79. Deng Y G, Liu J. Design of practical liquid metal cooling device for heat dissipation of high performance CPUs. ASME Journal of Electronic Packaging, 2010, 132(3): 031009
80. Plevachuk Y, Sklyarchuk V, Yakymovych A, Svec P, Janickovic D, Illekova E. Electrical conductivity and viscosity of liquid Sn-Sb-Cu alloys. Journal of Materials Science Materials in Electronics, 2011, 22(6): 631–638
81. Li P P, Liu J. Self-driven electronic cooling based on thermosyphon effect of room temperature liquid metal. ASME Journal of Electronic Packaging, 2011, 133(4): 041009
82. Deng Y G, Liu J, Zhou Y X. Liquid metal based mini/micro

channel cooling device. In: ASME 2009 7th International Conference on Nanochannels, Microchannels, and Minichannels June. Pohang, South Korea, 2009, 253–259
83. Jia D W, Liu J, Zhou Y. Harvesting human kinematical energy based on liquid metal magnetohydrodynamics. Physics Letters. [Part A], 2009, 373(15): 1305–1309
84. Dai D, Zhou Y X, Liu J. Liquid metal based thermoelectric generation system for waste heat recovery. Renewable Energy, 2011, 36(12): 3530–3536
85. Li P P, Liu J. Harvesting low grade heat to generate electricity with thermosyphon effect of room temperature liquid metal. Applied Physics Letters, 2011, 99(9): 094106-1–094106-3
86. Ge H S, Liu J. Phase change effect of low melting point metal for an automatic cooling of USB flash memory. Frontiers in Energy, 2012, 6(3): 207–209
87. Islam R A, Chan Y C, Jillek W, Islam S. Comparative study of wetting behavior and mechanical properties (microhardness) of Sn-Zn and Sn-Pb solders. Microelectronics Journal, 2006, 37(8): 705–713
88. Wang H, Xue S B, Chen W X, Zhao F. Effects of Ga-Ag, Ga-Al and Al-Ag additions on the wetting characteristics of Sn-9Zn-X-Y lead-free solders. Journal of Materials Science: Materials in Electronics, 2009, 20(12): 1239–1246
89. Fu C C, Chen C C. Investigations of wetting properties of Ni-V and Ni-Co alloys by Sn, Sn-Pb, Sn-Cu, and Sn-Ag-Cu solders. Journal of the Taiwan Institute of Chemical Engineers, 2011, 42(2): 350–355
90. Zhao N, Pan X M, Yu D Q, Ma H T, Wang L. Viscosity and surface tension of liquid Sn-Cu lead-free solders. Journal of Electronic Materials, 2009, 38(6): 828–833
91. Noor E E M, Sharif N M, Yewa C K, Ariga T, Ismail A B, Hussain Z. Wettability and strength of In-Bi-Sn lead-free solder alloy on copper substrate. Journal of Alloys and Compounds, 2010, 507(1): 290–296
92. Zhang Y, Liang T X, Jusheng M A. Phase diagram calculation on Sn-Zn-Ga solders. Journal of Non-Crystalline Solids, 2004, 336 (2): 153–156
93. Ma K Q, Liu J, Xiang S H, Xie K W, Zhou Y X. Study of thawing behavior of liquid metal used as computer chip coolant. International Journal of Thermal Sciences, 2008, 48(5): 964–974
94. Chentsov V P, Shevchenko V G, Mozgovoi A G, Pokrasin M A. Density and surface tension of heavy liquid metal coolants: Gallium and indium. Inorganic Materials: Applied Research, 2011, 2(5): 468–473
95. Gao Y X, Liu J. Gallium-based thermal interface material with high compliance and wettability. Applied Physics: A, Materials Science & Processing, 2012, 107(3): 701–708
96. Thostenson E T. The determination of the viscosity of liquid gallium over an extended range of temperature. Proceedings of the Physical Society, 1936, 48(2): 299–311
97. Shalaby R M. Influence of indium addition on structure, mechanical, thermal and electrical properties of tin-antimony based metallic alloys quenched from melt. Journal of Alloys and Compounds, 2009, 480(2): 334–339
98. Park H S, Cao L F, Dodbiba G, Fujita T. Preparation and properties of silica-coated ferromagnetic nano particles dispersed in a liquid gallium based magnetic fluid. In: The 11th International Conference on Electrorheological Fluids and Magnetorheological Suspensions. Dresden, Germany, 2008
99. Ito R, Dodbiba G, Fujita T. MR fluid of liquid gallium dispersing magnetic particles. International Journal of Modern Physics B, 2005, 19(7–9): 1430–1436
100. Shi Y, Tian J, Hao H, Xia Z, Lei Y, Guo F. Effects of small amount addition of rare earth Er on microstructure and property of Sn-Ag-Cu solder. Journal of Alloys and Compounds, 2008, 453(1,2): 180–184
101. Deng Y G, Liu J. Corrosion development between liquid gallium and four typical metal substrates used in chip cooling device. Applied Physics: A, Materials Science & Processing, 2009, 95(3): 907–915
102. Lau J H, Wong C P, Lee N C, Lee R. Electronics Manufacturing: with Lead-Free, Halogen-Free and Conductive-Adhesive Materials. New York: McGraw Hill, 2002
103. Indium Corporation of America, Europe and Asia. Solder alloy chart. http://www.indium.com/products/, accessed on July, 2012
104. Hamadaa N, Uesugib T, Takigawab Y, Higashi K. Effects of Zn addition and aging treatment on tensile properties of Sn-Ag-Cu alloys. Journal of Alloys and Compounds, 2010, 527(25): 226–232
105. Laurila T, Vuorinen V, Paulasto-Kröckel M. Impurity and alloying effects on interfacial reaction layers in Pb-free soldering. Materials Science and Engineering: Reports, 2010, 68(1,2): 1–38
106. Ahmed M, Fouzder T, Sharif A, Gain A K, Chan Y C. Influence of Ag micro-particle additions on the microstructure, hardness and tensile properties of Sn–9Zn binary eutectic solder alloy. Microelectronics and Reliability, 2010, 50(8): 1134–1141
107. Yusof M S, Gethin D T. Investigation of carbon black ink on fine solid line printing in flexography for electronic application. China Printing and Packing Study, 2011, 3(3): 74–76
108. Shin D Y, Jungb M, Chun S. Resistivity transition mechanism of silver salts in the next generation conductive ink for a roll-to-roll printed film with a silver network. Journal of Materials Chemistry, 2012, 22(23): 11755–11764
109. Ma K Q, Liu J. Nano liquid-metal fluid as ultimate coolant. Physics Letters [Part A], 2007, 361(3): 252–256
110. Argoitia A, Hayman C C, Angus J C, Wang L, Dyck J S, Kash K. Low pressure synthesis of bulk, polycrystalline gallium nitride. Applied Physics Letters, 1996, 70(2): 179–181
111. Stevenson R. The world's best gallium nitride. http://spectrum.ieee.org/semiconductors/materials/the-worlds-best-gallium-nitride, accessed on July, 2012
112. Zhang J J, Huang Y. Preparation and optical properties of $AgGaS_2$ nanofilms. Crystal Research and Technology, 2011, 46(5): 501–506
113. Moss S J, Ledwith A. The Chemistry of the Semiconductor Industry. New York: Chapman and Hall, 1987
114. Smart L, Moore E. Solid State Chemistry: An Introduction. 3rd ed. Boca Raton: Taylor and Francis CRC Press, 2005
115. Dong Y J, Peng Q, Wang R J, Li Y. Synthesis and characterization of an open framework ballium selenide: $Ga_4Se_7(en)_2\cdot(enH)_2$. Inorganic Chemistry, 2003, 42(6): 1794–1796
116. Creative Times. Can printed electronics save the music industry?

http://www.creativetimes.co.uk/articles/can-printed-electronics-save-the-music-industry, accessed on July, 2012
117. Kunnari E, Valkama J, Keskinen M, Mansikkamäki P. Environmental evaluation of new technology: Printed electronics case study. Journal of Cleaner Production, 2009, 17(9): 791–799
118. Yang Y L, Chuang M C, Lou S L, Wang J. Thick-film textile-based amperometric sensors and biosensors Affiliation Information. Analyst (London), 2010, 135(6): 1230–1234
119. Malzahn K, Windmiller J R, Valdés-Ramírez G, Schöning M J, Wang J. Wearable electrochemical sensors for in situ analysis in marine environments. Analyst (London), 2011, 136(14): 2912–2917
120. California Institute for Telecommunications and Information Technology. Flexible, printable sensors detect underwater hazards.http://www.calit2.net/newsroom/article.php?id = 1870, accessed on July, 2012
121. Wu C M L, Yu D Q, Law C M T, Wang L. Properties of lead-free solder alloys with rare earth element additions. Materials Science and Engineering: Reports, 2004, 44(1): 1–44
122. Chen K I, Cheng S C, Wu S, Lin K L. Effects of small additions of Ag, Al, and Ga on the structure and properties of the Sn–9Zn eutectic alloy. Journal of Alloys and Compounds, 2006, 416(1–2): 98–105
123. Hung F Y, Wang C J, Huang S M, Chen L H, Lui T S. Thermoelectric characteristics and tensile properties of Sn–9Zn–*x*Ag lead-free solders. Journal of Alloys and Compounds, 2006, 420(1,2): 193–198
124. El-Daly A A, Swilem Y, Hammad A E. Creep properties of Sn-Sb based lead-free solder alloys. Journal of Alloys and Compounds, 2009, 471(1–2): 98–104
125. Zhang J S, Chan Y C, Wu Y P, Xi H J, Wu F S. Electromigration of Pb-free solder under a low level of current density. Journal of Alloys and Compounds, 2008, 458(1–2): 492–499
126. Zhang Y, Liang T X, Jusheng M A. Phase diagram calculation on Sn-Zn-Ga solders. Journal of Non-Crystalline Solids, 2004, 336 (2): 153–156
127. Zhou J, Sun Y S, Xue F. Properties of low melting point Sn-Zn-Bi solders. Journal of Alloys and Compounds, 2005, 397(1–2): 260–264
128. Chriašteľová J, Ožvold M. Properties of solders with low melting point. Journal of Alloys and Compounds, 2008, 457(1–2): 323–328
129. Plevachuk Y, Sklyarchuk V, Yakymovych A, Svec P, Janickovic D, Illekova E. Electrical conductivity and viscosity of liquid Sn-Sb-Cu alloys. Journal of Materials Science Materials in Electronics, 2011, 22(6): 631–638
130. Plevachuk Y, Sklyarchuk V, Hoyer W, Kaban I. Electrical conductivity, thermoelectric power and viscosity of liquid Sn-based alloys. Journal of Materials Science, 2006, 41(14): 4632–4635
131. Plevachuk Y, Mudry S, Sklyarchuk V, Yakymovych A, Klotz U E, Roth M. Viscosity and electrical conductivity of liquid Sn-Ti and Sn-Zr alloys. Journal of Materials Science, 2007, 42(20): 8618–8621