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Laser nano-fabrication of large-area plasmonic structures and surface plasmon resonance tuning by thermal effect

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Abstract A simple and flexible technique aimed to generate large-area periodic nano-dot array features on metal thin films by laser interference lithography (LIL) has been demonstrated. In this paper, gold nano-dot arrays with a period of ~450 nm and a dot diameter of ~100 nm on quartz substrates coated with a gold film of 50 nm thick were fabricated. Multiple enhanced transmission peaks were observed in this patterned film. In addition to the characteristic peak of the gold surface plasmon resonance around 500 nm, multiple shoulder peaks that range from 550 to 700 nm were also observed in the nano-chain array structures. These shoulder peaks disappeared after thermal annealing. It was found that the nano-dots became smaller and well-separated nano-balls under the high temperature annealing process. These nano-structures have potential applications in solar cell, nano-lithography and biosensing.

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1 Introduction

Recently there has been great interest in enhanced optical transmission through large-area periodic metallic nano-structures due to its promising applications in photonics and optoelectronics. Since the first experimental observation, the role of the surface plasmon resonance (SPR) has been assumed but the detailed picture of the transmission enhancement is still being debated. Up to now, much effort has been made to understand and control the SPR of metallic nano-structures. Among them, the observation of multiple SPR peaks is highly desirable because of their potentials in tailoring SPR to various desired positions. Since the wavelength and intensity of SPR are highly sensitive to the nano-structure's material, size, size distribution, shape, period and surrounding environment, the tunable SPR wavelength in the visible and near infra-red regions has been achieved by changing these parameters of the metallic nano-structures [1–3]. The investigation has demonstrated both theoretically and experimentally that the SPR of metallic nano-particles depends much more on their geometry than on the size [4]. Therefore, most of the studies carried out so far have been focused on transforming the shapes of nano-structures to obtain tunable optical properties. A number of research groups have studied the core/shell nano-particles and came to conclusions that the SPR is sensitive to the shell thickness, which can shift forward and reverse from the visible to the infra-red spectral region [5]. More recently, much effort has been devoted to novel nano-structures and their unique tunability in SPR peak positions. For example, metal/dielectric spherical composites and non-spherical structures, such as nano-rods, nano-spins, the nano-star, and the split ring or crescent have been developed and exhibited interesting optical properties [6–9]. However, the fabrication of such complicated nano-structures brings about undesirable requirements for the process and equipment. We report here a simple and effective method to tune the SPR wavelength of large-area periodic Au nano-structures, which employs laser interference lithography (LIL), followed by thermal annealing treatment.

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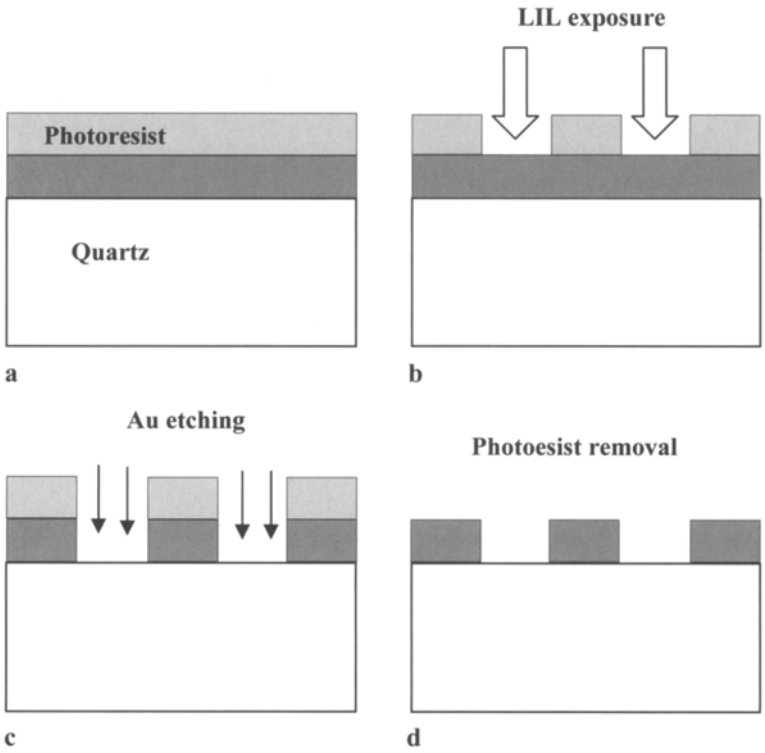

Fig. 1 Schematic illustration of the process steps to fabricate a large-area metallic periodic nano-structure. We show (**a**) the 1 mm quartz substrate coated with a gold thin film and photoresist; (**b**) the photoresist periodic patterns formed after LIL exposure and development; (**c**) patterns transferred to gold film by etching, and (**d**) photoresist removed by acetone

2 Sample preparation

Quartz substrates with 1 mm thickness were first ultrasonically cleaned in acetone for 5 minutes, followed by another 5 minutes of de-ionized water rinse. After being dried by nitrogen, the substrates were deposited with a 50 nm gold thin film, which was done in a high vacuum chamber of an e-beam thermal evaporator. Subsequently, the samples were spin coated with S1805 positive photoresist from Shipley at a spin speed of 6000 rpm to obtain a resist thickness of 500 nm. Immediate pre-bake of photoresist was then carried out on a hotplate at a temperature of 115°C for 1 minute to improve the adhesion of photoresist and at the same time to remove the solvent. The periodic patterns on the resist were then obtained by laser interference lithography as reported previously [10]. The sample was exposed by two coherent laser beams at an incident angle of 17° to achieve an array pattern with the period of 560 nm. This was carried out using Llyod's mirror setup with a 325 nm helium–cadmium (He–Cd) continuous laser as the light source with an output power of 4 mW. To obtain a nano-dot array, double exposure was done by rotating the sample at 90° after the first exposure. To avoid external vibrations, the whole experimental setup was placed on an optical table and enclosed during the exposure. The exposure time was controlled by a mechanical shutter. By adjusting the incident angle, the period of the photoresist pattern can be tuned to the desired value. After the periodic patterns were formed on the photoresist, Au etchant was used to etch the gold

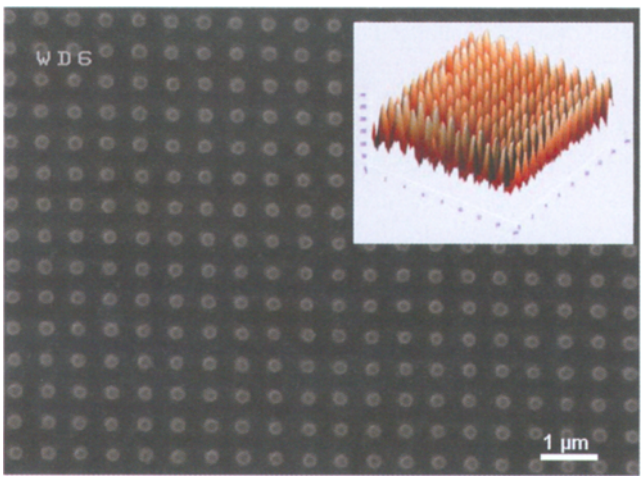

Fig. 2 SEM and AFM images of gold nano-dot array on top of the quartz substrate. The period of the structures ranges from 450 to 560 nm and the diameter of the gold nano-dots ranges from 100 to 260 nm

continuous film to get the same patterns, and the photoresist was then removed by acetone, with the nano-structured gold film left. The whole process flow for the structure fabrication is illustrated in Fig. 1 and SEM and AFM images of typical gold nano-dot features are shown in Fig. 2. For a constant period, the grating structure in the photoresist depends mainly on the exposure dose [11]. Therefore, the gold nano-dot array with the period reduced down to 450 nm was achieved. The homogeneous area of the gold nano-dot array

has reached 15 × 15 mm^2, and larger areas can be fabricated with larger laser spot size and higher laser power. After the nano-structure fabrication, the samples were annealed at 800°C in nitrogen ambient for an hour to further investigate the SPR tuning by thermal effect.

3 Results and discussion

Figure 3 shows the UV–Vis transmission spectra of Au thin film with and without periodic nano-patterns. The incident light ranges from 300 to 800 nm and is normal to the Au thin film. The solid line represents the spectrum of continuous Au film without patterns, while the dashed line represents the Au film with periodic nano-patterns. It is common to observe granular structures at the surface of deposited metal films, so the typical resonance peak of metal materials also exists on films without regular nano-structures. The peak at 504 nm (solid line) has good reproducibility and is attributed to the normal SPR of gold material [12, 13]. After laser nano-patterning of the film, it shows that this characteristic peak has red-shifted to 552 nm, which is due to the significant change of the surface topography. It implies the difference between the interactions of light with periodic Au nano-dot arrays and random Au grains of a continuous film. It is interesting to note that a typical peak at 698 nm appeared after the Au thin film was nano-structured. The experimental results show that this peak is more dominated by structure parameters, such as period, shape and dimension, rather than material properties. Annealing of the Au nano-structures was then carried out by thermal annealing to investigate the role of tuning the nano-structure in SPR mode.

Figures 4a and b show the SEM images of Au nano-chain array before and after high temperature annealing, respectively. Before the annealing, Au nano-dots were linked to form a nano-chain-like aggregated (called nano-chain) array, and the length of such a nano-chain was random because it depends on the experimental parameters during a series of process steps including coating, exposure, developing, and etching. It has been reported by Yang et al. that the tuning of optical properties and SPR frequency could be attained by controlling the length of such nano-chains [14]. After 800°C annealing in nitrogen ambient for an hour, the gold coalesced nano-dots separated and became more ball-like. Meanwhile, the diameters of nano-dots were reduced with the array period remaining the same. This is because the spherical shape has the minimum surface free energy and thus is more stable [3].

Figure 5 shows the UV–Vis transmission spectra of an Au nano-dot array before and after the thermal annealing. The light source of the UV–Vis spectroscope is a white light lamp without polarization. Obvious multi-peaks can be observed at 490, 564 and 678 nm in the pre-annealing curve. The peak around 500 nm is the characteristic peak of gold material, with the maximum intensity. Towards longer wavelengths, the intensities of the peaks become weaker and the widths of the peak bands become larger. In addition, the whole pre-annealing curve is not so smooth but consists

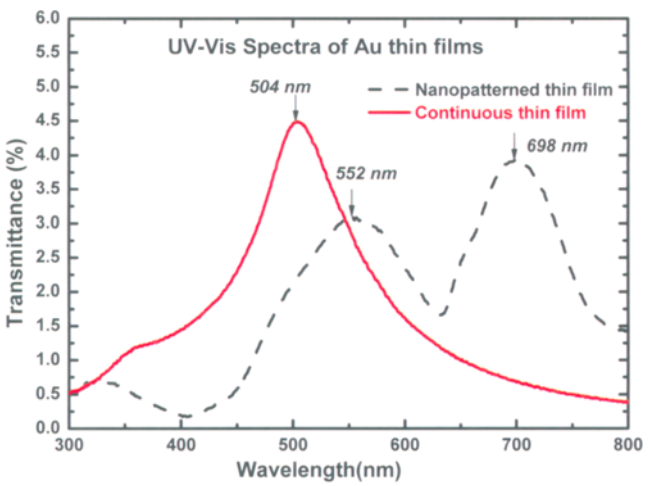

Fig. 3 UV–Vis transmission spectra of the Au thin films with and without periodic nano-patterns

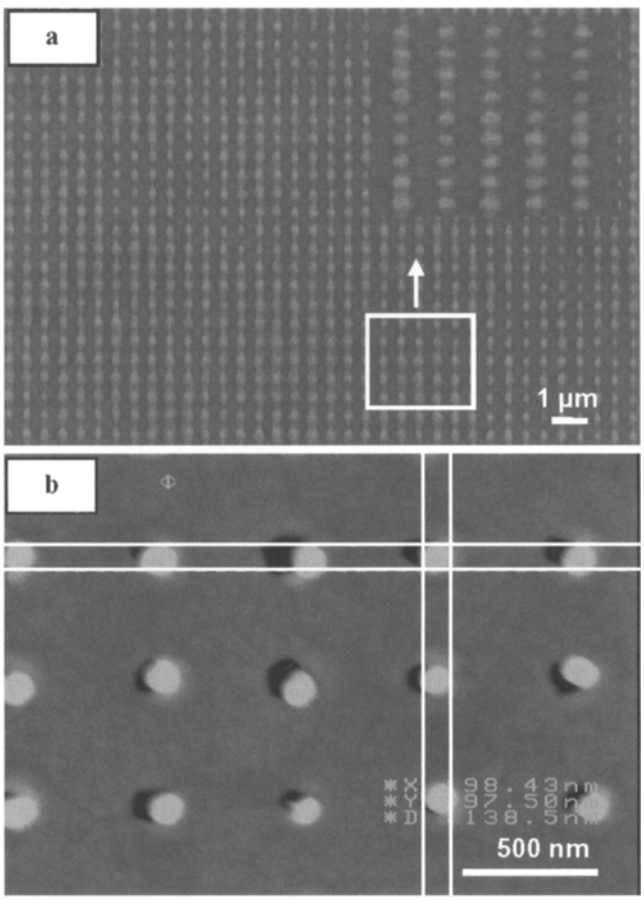

Fig. 4 SEM images of gold nano-chain array, (**a**) before annealing, and (**b**) after 800°C annealing in nitrogen ambient for an hour

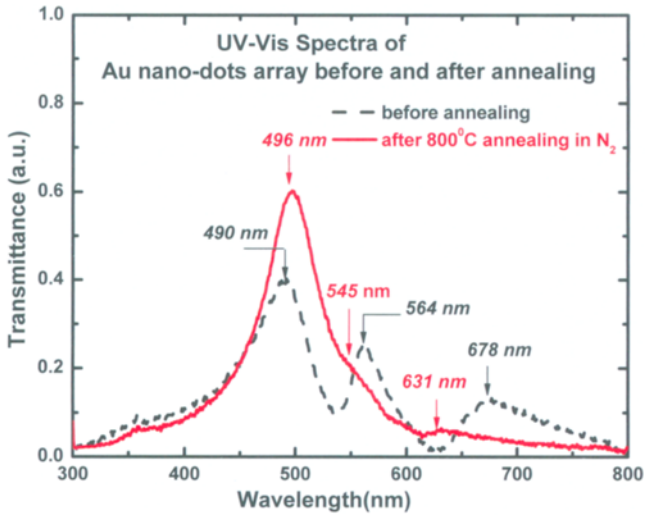

Fig. 5 UV–Vis transmission spectra of the Au nano-dot array before and after annealing at 800°C in nitrogen ambient for an hour

of many tiny peaks, especially in the longer wavelength regions. This observed broad SPR band is assumed to be the result of a broad size distribution and a morphological discrepancy among the Au nano-dots. After high temperature annealing, the linked nano-dots were separated and the roughness of the nano-dot surface reduced, thus leading to a smoother post-annealing curve. In addition, the shoulder peaks at 564 and 678 nm have a slight blue shift to 545 and 631 nm, respectively, which is in good agreement with previous reports that the wavelength of a surface plasmon resonance shifts to shorter wavelength regions when the particle size decreases and the shape anisotropy is reduced [15, 16]. While the intensities of the shoulder peaks drop dramatically, the intensity of the peak around 500 nm rises. This obeys the energy conservation law. The increase of the intensity is attributed to the reduced discrepancy of morphologies and dimensions of Au nano-dots after the annealing process. The results indicate that by laser nano-patterning and thermal annealing, it is feasible to tune the SPR in a wide visible region from 500 to 800 nm, which is the most desirable range for most applications, such as solar cells, nano-lithography and biosensing [17, 18].

While Figs. 2 and 4b have similar Au nano-dot array structures, they have different UV–Vis transmission spectra: the structure of Fig. 2 has two peaks, but the structure of Fig. 4b has only one peak. It is due to the difference in surface roughness and the diameter of the nano-dots in the two structures. The nano-dots of Fig. 4b have very smooth surfaces and the nano-dot sizes shrink a lot after thermal annealing, while the array period remains the same. Therefore, the light interactions among the nano-dots become weaker.

4 Conclusions

Utilizing laser interference lithography, large-area periodic nano-structures on gold thin films were fabricated with the period reduced to 450 nm and the diameter of gold nano-dot reduced to sub-100 nm. The UV–Vis transmission spectra have multiple resonance peaks at around 550 and 700 nm for the nano-patterned Au thin film, and peaks around 490, 560 and 675 nm for the Au nano-chain array. The characteristic peak near 500 nm is attributed to the gold material. Other typical peaks in the longer wavelength region are due to the SPR of the Au nano-chains. After the samples were annealed at 800°C in nitrogen ambient, the resonance peaks at longer wavelengths blue-shifted and their intensities decreased due to the reduced discrepancy of morphologies and dimensions among Au nano-dots after the annealing process. The intensity of the Au characteristic peak can be enhanced and tuned, which implies great potentials in plasmonic applications in solar cells, nano-lithography and biosensing.

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