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Nano-patterning of gold thin film by thermal annealing combined with laser interference techniques

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Abstract We present an efficient method for fabrication of desired periodic metallic structures. By using the magnetron sputtering technique, the gold nano-layer was isotropically deposited onto a photoresist template, which had been previously fabricated by an interference technique. During a subsequent thermal annealing process, the gold coating layer melted and split allowing the photoresist core-template to evaporate and consequently leave a desired metal structure on the substrate surface. The proposed method exhibits advantages such as simplicity and low cost, which allows one to realize large-area plasmonic structures that are very promising for numerous applications, especially plasmonic-based photonic devices.

1 Introduction

The noble metal nanoparticles exhibit special optical properties attributed to the oscillation of conduction electrons excited by the electromagnetic field of incident light, namely localized surface plasmon resonance (LSPR) [1, 2]. The LSPR leads to resonant absorption and scattering of the incident light and high electric field enhancements on the surface of such metal particles [3]. These resulting phenomena have been experimentally and theoretically reported to be strongly enhanced in the nano-structured array as opposed to the isolated particles [4, 6]. Consequently, metal plasmonic nano-structures have been extensively researched and have become promising candidates in many applications such as biosensing [6–8], optical devices [9–11], and clean energy production [12, 13].

Numerous fabrication methods of plasmonic structures have been proposed. Focused ion beam milling is well known as the most conventional technique used to make hole-structured arrays in thin metal films by using an ion beam with kinetic energy high enough to pierce through the film, resulting in a structure with controllable lattice parameters (period and/or filling factor) with a reasonable precision at the nanoscale [14–17]. However, a small fabrication area (several hundred μm), low speed, and high costs are obvious disadvantages of this method which limit it in some specific applications such as fabricating masks with high-resolution features. Another common approach for fabricating metal nano-structures is the template lithography-based technique. The desired metal is initially deposited onto the top of the resist templates that have been previously made by standard lithography techniques such as optical lithography [18, 19], electron beam lithography [20, 21], and nano-sphere assembly lithography [22, 23]. The resist lift-off and/or etching steps are then employed to remove the template, leaving a final desired metal structure. This approach is interesting due to its low cost and high speed, but the involving lift-off and etching processes are difficult to control at the nanoscale for large-area fabrication.

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It has been known that the melting temperature of the gold nano-platforms decreases remarkably at the nanoscale [24, 25]. As a consequence, high-temperature annealing has been reported as a simple and high-throughput technique, called dewetting method, to fabricate large-area plasmonic gold nano-island structures from thin metal films [26–30]. However, previous research using such an annealing process only successfully achieved gold nanoparticles with different sizes and random distribution on a flat substrate. Recently, by combining the thermal annealing with structured substrates, which are fabricated by some lithography processes, such as nano-imprint and microspheres-based method, several groups demonstrated that it was possible to fabricate metal structures [31, 32]. This method needs involving a series of consecutive steps to induce the dewetting effect of the metal precursors and transfer them into the ordered structures. However, the templates are still existed after the formation of metal structures, which remains as a drawback of this method. An alternative method based on femto-second laser-based direct laser writing technique has been also proposed to realize different kinds of metallic nano-structures [33, 34]. The advantage of this technique is that it is template-free, and it allows to realize arbitrary nano-structures. However, this technique is expensive, time-consuming and the size of fabricated structures is limited to hundred micrometers.

In this work, we demonstrate an alternative method for fabricating various periodic gold nano-structures by thermally annealing the gold layer deposited onto the photoresist core-template structures, which are fabricated by interference technique. By integrating such a thermally removable matter template structure as an interlayer between the gold layer and the substrate, we were able to manage the melting and coalescence of the gold material at high temperature, causing them to form into the desired periodic structures after the annealing process. The structured templates have been removed due to the annealing without using any additional processes, leaving the metal structures on the glass substrate. We also present a formation mechanism of the metal structures, which has not been previously reported.

2 Fabrication process

Figure 1 shows schematically the fabrication procedure of large-area periodic gold structures which involves two stages: fabricating photoresist templates by a standard optical technique (Fig. 1a) and annealing the gold deposited onto such templates at a high temperature (Fig. 1b). Here,

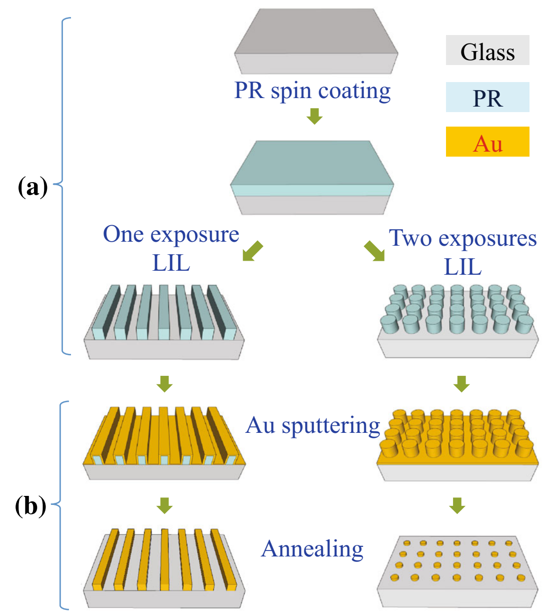

Fig. 1 Schematic of the fabrication process of plasmonic gold structures by thermally annealing the gold material deposited onto S1805 photoresist core-template structures. **a** Fabrication process of S1805 templates by multi-exposure two-beam LIL technique. **b** Subsequent sputtering and thermal annealing process to fabricate periodic gold structures

multi-exposure two-beam laser interference lithography (LIL) was used to produce desired one-dimensional (1D) and two-dimensional (2D)-structured photoresist templates due to its simple process and high-throughput fabrication. The working principle as well as the experimental setup of this technique has been described throughout our previous research [35–37]. In the present experiment, we used a 532-nm wavelength continuous laser source (Verdi G5 laser) to make S1805 photoresist patterns of either lines (1D) or pillars (2D) with a modulation depth of about 600 nm and a period ranging from 500 nm to 1.0 μm. The 1D and 2D structures were realized by controlling the number of exposures and the rotation angle between exposures (Fig. 1a), whereas their filling factors were adjusted by changing the exposure time [36]. A gold layer with well-controlled thickness was then deposited onto the photoresist structures by using the Emitech K650 magnetron sputtering technique. A subsequent annealing process at 500 °C for 30 minutes was carried out by a Nabertherm oven (accuracy = ±5°C) in order to melt the coated gold layer and remove the photoresist core-template, leading to periodic gold structures on the surface of the glass substrate. Thus, metal structures consisting of gold nano-lines or nano-dots on the glass substrate are produced after being cooled to room temperature, as demonstrated in the last step of Fig. 1b. The deposition step for all samples presented in this work was carried out with sputtering parameters which allow a 20-nm-thick layer to be formed on a flat glass substrate.

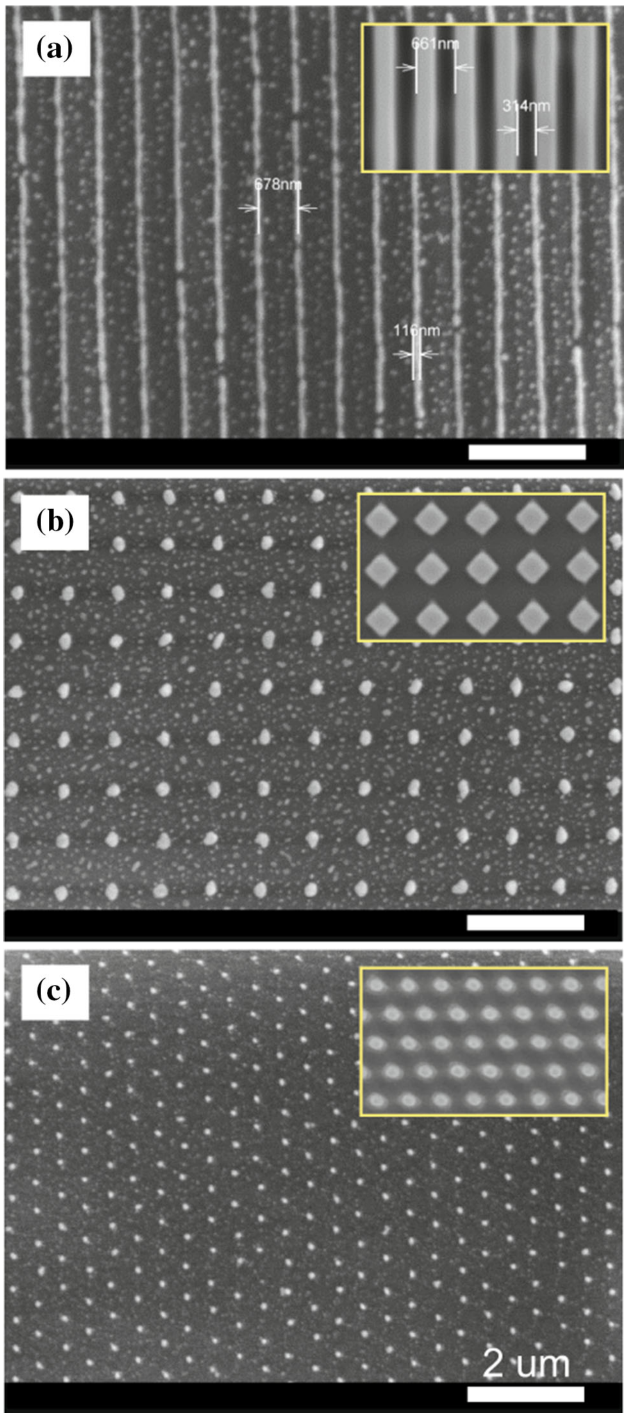

Fig. 2 SEM images of fabricated 1D (**a**), 2D-square (**b**), and 2D-isotropic hexagonal (**c**) plasmonic gold structures. The *insets* show the corresponding photoresist template structures. The calculated periods of the templates are 0.7 µm (**a**), 0.9 µm (**b**), and 0.5 µm (**c**), respectively

3 Experimental results and discussion

3.1 Structured morphology of gold structures

Figure 2 shows the scanning electron microscope (SEM, Hitachi-S3400) images of typical gold nano-structures fabricated by thermally annealing gold material coating on the S1805 core-templates. It can be seen clearly that the geometrical morphology of the resulting gold structure is directly determined by that of the photoresist core-template. In particular, the gold 1D structure containing continuous and homogeneous nano-lines with an average width of about 120 nm was obtained from the 1D-structured photoresist template. Similarly, from the 2D-structured templates, we obtained 2D gold structures with the same morphology and a highly qualified arrangement of metal nano-dots. For all samples, the period of the resulting gold structures is identical to those of the pre-annealing S1805 template structures. The gold dots in the hexagonal structure have an average diameter around 100 nm, which is smaller than those of the square structure with a diameter of approximately 220 nm. Considering the morphology of the templates corresponding to these structures, we hypothesize that the size of the resulting gold dots can be contributed by the size of the S1805 pillars. This will be presented and analyzed in more detail in the following section. In addition, all samples show small gold nanoparticles with a diameter of around 50 nm randomly formed outside the dominant periodic arrays. These random metal particles are more apparent in the 1D and 2D-square structures which have larger periods, but they did not influence the formation of the periodic lattice. Generally, all obtained gold structures exhibit a high uniformity for a large area (1.0×1.0 cm^2) similar to the area of the laser interference pattern, which can be easily extended to larger desired sizes [35]. Consequently, it can be concluded that by thermally annealing the gold material deposited on the photoresist template, we have successfully fabricated various large-area periodic gold structures with controllable structured morphologies.

In order to find the role of the resist template for the formation of the plasmonic structure, we have investigated the dependence of the structured morphology of resulting gold structures on the filling factor of the S1805 template structures. Figure 3 shows SEM images of square-2D gold structures with their corresponding S1805 templates from air-hole Fig. 3a to pillar structures Fig. 3b, c. It should be noted that, using the LIL technique, we easily produced the same S1805 structure with different filling factors by adjusting the exposure time. The well-organized 2D-square gold nano-dot lattices have only been obtained from the S1805 pillar-structure templates. Moreover, the average

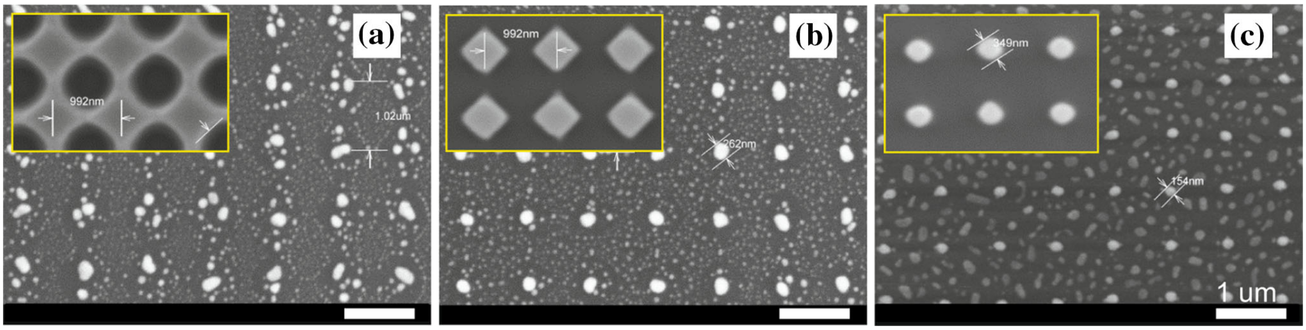

Fig. 3 SEM images of 2D-square gold structures and their corresponding S1805 templates, as shown in the *inset*, from air-hole structure (**a**) to pillar structures (**b–c**). The period of the structures is 1.0 µm

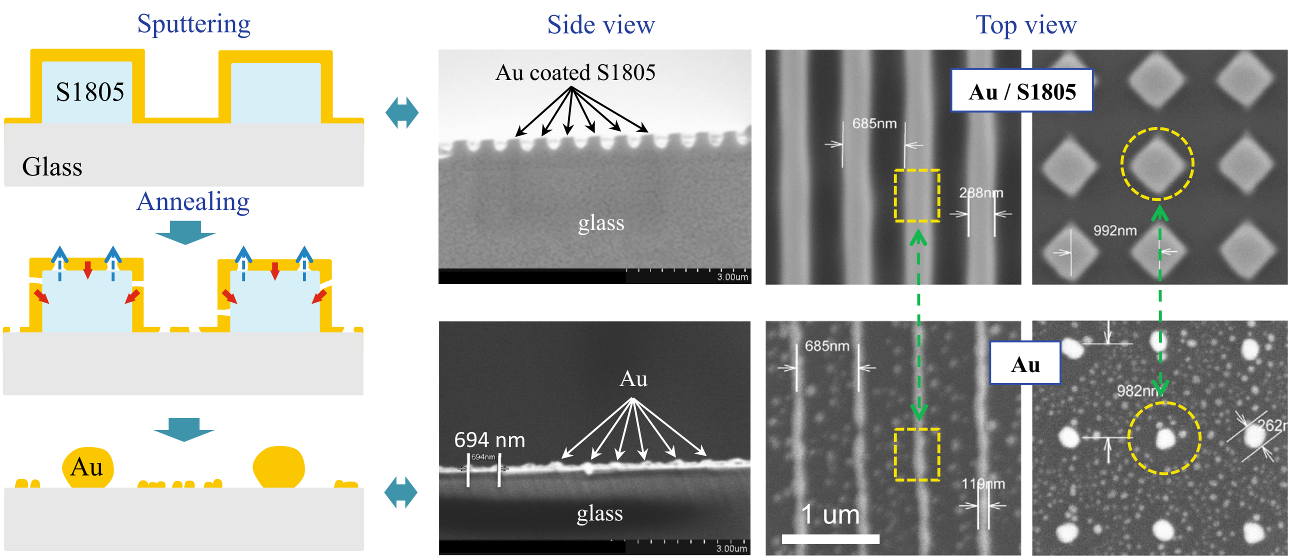

Fig. 4 Mechanism of the formation of periodic gold structures fabricated by thermally annealing a gold nano-layer deposited onto the S1805 templates. The *side-view* SEM images show the 1D-structured sample before and after annealing. The *top-view* SEM images indicate that the *gold nano-lines* or *nano-dots* were formed from the amount of gold coating on the top and side walls of S1805 periodic submicrostructure template

diameter of periodic gold dots decreases with smaller S1805 pillars, indicating again that the size of the template pillars directly determined the size of the resulting gold dots. For the air-hole S1805 template, the corresponding gold structure is still reasonably organized, but consists of periodic gold clusters instead of single dots. Furthermore, it is evident that the random gold nanoparticles appearing between the periodic lattice have larger average size and variable shape for the samples fabricated from the templates with a small filling factor.

3.2 Formation mechanism of the periodic gold structures

From the above analysis, we propose a mechanism to explain the formation of the gold periodic structures, as shown schematically in Fig. 4. Due to the nature of the magnetron sputtering technique, a gold nano-layer was deposited onto the top and the side wall of the resist template structures as well as the alternate blank areas of the glass surface [38]. During the annealing process, at temperatures around 140 °C, the S1805 material started melting but was confined by the sputtered gold layer. When the temperature increased over 200 °C, the gold layer started melting and being broken into segments allowing the S1805 to evaporated gradually as denoted by the dotted green arrows in the figure. Notably, the thickness of the deposited gold film was chosen to be 20 nm, at which the film could be melted at temperatures higher than 200 °C, as previously reported [39]. The loss of S1805 resist due to evaporation led to an aggregation of the coated molten gold segments following the direction of the bold red arrows. At the temperature around 500 °C, the S1805 evaporated completely and all of the gold coating the S1805 lines or pillars will be aggregated, forming localized and well-arranged gold nano-lines or dots. Therefore, after the annealing process, we have obtained gold structures with morphology features similarly to those of the initial resist templates. The SEM images on the right panel of Fig. 4 demonstrate in high magnification the gold samples and their corresponding pre-annealing S1805 templates coated with gold. The S1805 lines or pillars coated with a gold layer will transform into gold lines or dots after being thermally annealed. The geometrical size, both height and diameter, of the resist pillar or line template will contribute to the amount of coated sputtering material, determining the size of the resulting metal dot or line. In this experiment we maintained the height of the resist template. Therefore, when the diameter of the S1805 line or pillar decreases, the amount of gold coating also decreases, resulting in a smaller and thinner gold line or dot. Additionally, the deposited gold layer on the blank glass areas of the templates was melted and transformed into random nanoparticles after the annealing process as observed in all obtained gold structures. This result is highly consistent with previous reports on fabricating random gold nano-island structures on a glass substrate by thermal annealing [27, 29, 39]. Indeed, A. Serrano et al. [39] reported that the average size of the Au islands remarkably increases as the initial sputtered Au layer becomes thicker. It is also well known that in the sputtering technique, the Au atoms reach to the substrate from various directions [38]. Therefore, as the photoresist template has smaller filling factor, the Au amount reaching to the blank glass area will be more. Consequently, the random islands get larger in average size as observed in Fig. 3. Furthermore, it is also important to note that both density and average size of the random nanoparticles are remarkably decreased in the structures with smaller period, as shown in Fig. 2. However, according to our theoretical calculation, these disordered Au nanoparticles do not influence on the global features of the submicrometer-period Au structures.

All the mentioned results are insightfully explained and well understood by the proposed mechanism. In general, by using this technique, we are able to fabricate desired metal structures in periodic, quasi-periodic, or arbitrary networks. The optical response of such metal structures not only depends on the LSPR of the metal dots, but also varies significantly with their morphology. Hence, the resist template fabricated by optical lithography plays a vital role in determining the morphology and optical response as well as the consequent applicability of the resulting metal structures, which is currently being investigated.

4 Conclusion

In conclusion, we have proposed a facile method to produce desired periodic gold structures. The periodic photoresist templates were fabricated by the multi-exposure two-beam LIL technique. The sputtered gold nano-layers were then deposited onto the photoresist template; afterward, the whole system was thermally annealed at a high temperature. The formation mechanism of periodic metal structures has been described in which the photoresist core-template evaporates during the thermal annealing process, allowing the covering molten gold segments to merge into well-arranged structures. The mentioned results have demonstrated that the presented method is a reliable approach for fabricating plasmonic structures with various geometrical morphologies and adjustable lattice parameters. This method is especially promising for application purposes due to its simplicity, high processing speed, and low cost with respect to conventional techniques.

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