Large-area metal-coated dielectric nanopillar array for excitation of surface plasmon resonance

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Abstract

Many of current techniques are not suitable for the fabrication of metallic nanostructure on the scale of usual optical coatings at reasonable fabrication cost and time. A fabrication process for producing large-area metal-coated periodic nanopillars is presented. A hybrid metallic nanostructure array was obtained by depositing a silver film with a thickness of ~40 nm on the fused silica nanopillars with an in-plane diameter of ~140 nm and out-of-plane height of ~130 nm, which was fabricated by a combination of interference lithography, metal deposition and etching. There are two peaks in the extinction spectrum of the p-polarized incident light, one at 585.3 nm and the other 493.6 nm. The shift of the higher peak is 32.9 nm (a red-shift), while that of the lower peak is 42.3 nm (a blue-shift) with the addition of absolute ethanol on the sample surface. Such structure was used to monitor the evaporation process of the absolute ethanol on the sample surface. It was found that narrowest extinction peak appears at normal incidence, while the polarization of the incident light does not affect the experimental result due to the symmetrical distribution of the nanostructures. The fabrication process and unique optical properties of the structure array are expected to be suitable for the development of high-throughput ultrasensitive chemical sensor arrays.

Keywords: Large-area, Hybrid metallic nanostructure, Interference lithography, Surface plasmon resonance.

1. Introduction

Localized surface plasmon resonance (LSPR) refers to the ability of the conduction electrons in the nanoparticle to oscillate collectively, which can concentrate and enhance electromagnetic energy surrounding the nanoparticle. Recent technical developments in nanolithography and the chemical synthesis of metal nanostructures have allowed the production of metallic nanostructures with various shapes such as dots, triangles[1-4], shells [5,6], rings [7], rods [8], disks [9] and cups [10]. Unfortunately, many of these techniques are not suitable for the fabrication of metallic nanostructure on the scale of usual optical coatings (i.e., on a cm² scale) at reasonable fabrication cost and time. Nanosphere lithography is a powerful technique and has been used to inexpensively produce nanoparticle arrays with controlled shape, size and interparticle spacing, but the typical defect-free domain sizes are in the 10-100 µm range [1,2,4]. Wang et al.[11] reported a one-step electron-beam lithography process to fabricate a nanopillar array, in which each nanopillar is constituted by a metal-capped dielectric pillar sitting on a ring-shaped metallic disc. However, the exposure dose they used is much higher than normal dose to enable the centre cross-linked PMMA to survive during the subsequent lift-off process. Interference lithography, as an inexpensive and versatile technique, has already successfully been used on the fabrication of 1D metallic photonic crystal slabs [12], of magnetic metamaterials [13], and of negative-index metamaterials at infrared range [14]. Here an interference lithography based fabrication technique is presented, which is capable of producing large-area hybrid metallic nanostructure array for excitation of surface plasmon resonance [15]. The structure consists of a metal capped dielectric nanopillar array and a metallic hole array.

2. Experimental details

The large-area periodic metallic nanostructures were fabricated by a combination of interference lithography, metal deposition and etching. Fused silica substrates with a size of 2 cm by 2 cm were cleaned in isopropyl alcohol for 10 minutes, assisted with an ultrasonic processor, to remove dust and then prepared by washing in running deionised water for 1 minute, dipping in a 1:1 mixture of concentrated sulfuric acid and hydrogen peroxide for 10 minutes to remove organic contaminants, and washing again for 1 minute in running deionised water. Finally substrates were dried with a nitrogen gun and baked on a hotplate for 1 hour at 170 °C. A chromium film with a thickness of ~20 nm was deposited on the newly cleaned substrate by thermal evaporation. On top of the chromium, a layer of AZ3100MI(20cp) (positive resist) with a thickness of 120nm was spun, followed by a post application bake of 100 °C for 15 minutes. The resist was patterned by IL and periodic resist nanostructures were obtained after development in Microposit 303A (Shipley Co.). Oxygen reactive ion etching (RIE) was used to remove resist residual in the patterned regions (O₂ gas flow=10 sccm, pressure=1 Pa, power=30 W). Chromium patterns were obtained by dipping the substrate into a chromium etchant. The resist on chromium was removed by sonication in acetone. CHF₃ RIE was used to etch the newly exposed fused silica (CHF₃ gas flow=30 sccm, O₂ gas flow=1 sccm, pressure=1 Pa, power=80 W), transferring the patterns to the oxide layer. After the remaining chromium is removed in chromium etchant, a new chromium film with a thickness of 5 nm (to improve
adhesion) and a silver film with a thickness of \(\sim 40\) nm are deposited onto the periodic oxide nanopillars. Finally a hybrid metallic nanostructure array was obtained.

An IL system based on Lloyd’s mirror configuration \([16, 17]\) was built up, in which a mirror is placed normal to the substrate and illuminated with an s-polarized laser beam with a wavelength of 442 nm. A part of the incident laser beam is reflected by the mirror and interferes with the un-reflected part of the beam to form interference patterns. Nanopillar arrays were fabricated by rotating the sample and double exposure. In order to obtain a two-dimensional nanopillar array in the resist, the exposure dose must be high enough otherwise that the resist only at the crossings of the grid lines (after first and second exposure) receives enough energy to be removed after development. The intensity of the incoming light in the exposed area was measured to be 0.65 mW/cm\(^2\) for normal incidence. The resist was exposed to the interference line pattern for 8 seconds. After rotating the substrate to 90\(^\circ\) the exposure was repeated. The resist was developed in Microposit 303A (Shipley Co.) for \(\sim 30\) seconds and rinsed in deionized water.

The extinction spectra of the structure were measured to study the optical characteristics of this structure. A beam of white light (300nm-800nm) was sent to a collimating lens via an input fibre. The well-collimated light beam was incident to the sample surface at an angle, which is controlled by a rotating stage. The probe diameter was approximately 3 mm, which is controlled by a diaphragm. The output fibre carried the light from the sample to the spectrometer (Ocean Optics USB4000) connected to a computer. All spectra in this study are the results of macroscopic measurements performed with polarized light. The measurement was performed at room temperature with a relative humidity of 47%. A drop of absolute ethanol was added on the surface of the metallic nanostructures to change the surrounding refractive index. The difference between the extinction maximum before and after the addition of absolute ethanol is the wavelength shift response. To measure the evaporation process of this drop of absolute ethanol on the surface of this structure, a series of extinction spectra were collected every 1 minute. Effects of the incident angle and light polarization on extinction spectra were studied by independently changing the rotating stage and the polarizer.

3. Results and discussion

Figure 1(a) shows SEM images of fused silica nanopillar array with a pitch of 321 nm, an in-plane diameter of \(\sim 140\) nm and out-of-plane height of \(\sim 130\) nm. Although some residues are observed in the nanostructures, they may originate from the chemical reactions in pattern transfer from chromium to fused silica by RIE and could be eliminated by prolonged sonication in acetone. Figure 1(b) is the SEM image showing the final hybrid metallic nanostructure array obtained through this approach. In comparison with figures 1(a), it can be observed that there is some silver extending from the top of the oxide pillar and partly down the side wall. The variation of oxide pillar size between its top and bottom and evaporative edge effects due to the minor change of evaporation direction are the possible causes. The metallic structure can be improved with sharper oxide nanopillars by optimizing etching conditions during the pattern transfer processes.

![SEM image of pillars](image1)

![SEM image of metallic nanostructure](image2)

![Extinction spectra with p-polarized light](image3)
A well-collimated white light beam was incident normally to the surface of the hybrid metallic nanostructure array. Figures 2(a) and 2(b) show the extinction spectra for the periodic nanostructures. There are two peaks in the extinction spectrum of the p-polarized incident light, one at 585.3 nm and the other 493.6 nm. The peaks are shifted to 451.3 nm and 618.2 nm with the addition of absolute ethanol on the sample surface. The shift of the higher peak is 32.9 nm (a red-shift), while that of the lower peak is 42.3 nm (a blue-shift). Such structure was used to monitor the evaporation process of the ethanol on the sample surface. Fig. 2(b) shows the extinction spectrum change during the evaporation process. The initial spectrum in the experiment was obtained without absolute ethanol. The spectrum turned into a plot very much similar to the spectrum shown in Fig. 2(a) shortly after the addition of absolute ethanol. This spectrum lasted for 3 minutes. One further minute later, the curve turned back to the initial spectrum, indicating that the whole evaporation process took 3-4 minutes.

Effects of the incident angle and light polarization on extinction spectra were studied in further experiments. Figure 3(a) shows the experiment configuration where the incident angle and polarization can be independently adjusted by selecting different exposure doses and by changing the incident angle of the laser beam in the IL step, respectively. The height of the dielectric pillar can be controlled by modifying the RIE etching condition during the pattern transfer step. The plasmon response of the hybrid metallic nanostructures can be viewed as the collection of plasmons arising from two geometries to form an interacting system, which makes it possible for the structure to possess unique optical properties. Hence, it is possible to tune the optical properties by tailoring the geometries of the hybrid metallic nanostructures in order to achieve specific extinction spectra on demand. The large-area fabrication process, unique optical properties, and further improvement of the hybrid metallic structure array are expected to be suitable for the development of high-throughput ultrasensitive chemical sensor arrays, nanobiosensor array etc.

4. Conclusions

A low-cost, high-throughput fabrication process has been developed to produce hybrid metallic nanostructure array over large areas without the need for e-beam lithography. The pillar size and pitch of the nanostructures can be independently adjusted by selecting different exposure doses and by changing the incident angle of the laser beam in the IL step, respectively. The height of the dielectric pillar can be controlled by modifying the RIE etching condition during the pattern transfer step. The plasmon response of the hybrid metallic nanostructures can be viewed as the collection of plasmons arising from two geometries to form an interacting system, which makes it possible for the structure to possess unique optical properties. Hence, it is possible to tune the optical properties by tailoring the geometries of the hybrid metallic nanostructures in order to achieve specific extinction spectra on demand. The large-area fabrication process, unique optical properties, and further improvement of the hybrid metallic structure array are expected to be suitable for the development of high-throughput ultrasensitive chemical sensor arrays, nanobiosensor array etc.

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References

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