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Fabrication of plasmonic nanopillar arrays based on nanoforming

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ABSTRACT

A new fabrication method for realizing ordered nanopillar array is reported in this paper. First, a metallic nanodot array is prepared by combining two techniques, viz., nano-grid patterning by Nanoplastic Forming (NPF) and dot agglomeration by thermal dewetting. These processes do not include complicated and expensive procedures such as electron beam lithography. Then Au-capped nanopillar arrays are produced by reactive ion etching (RIE). In the refractive index sensing application, it is shown that the sensitivity of the Au-capped nanopillar array is higher than that of the Au nanodot array. The plasmonic nanopillar arrays with Ag coating are used as SERS-active substrates, which exhibit good performance.

1. Introduction

Nanoplasmonic structures have been extensively studied in the last decade due to its notable optical properties, its remarkable capability of controlling light at nanoscale and its important role in combining photonics with electronics. Among them, plasmonic nanopillar arrays have attracted great attention due to its broad applications in antireflection [1–3], localized surface plasmon resonance (LSPR) biosensor [4–8], surface-enhanced fluorescence (SEF) [9,10], surface-enhanced Raman scattering (SERS) [11–18], photodetectors [19] and photovoltaic devices [20]. For example, by lifting the metallic nanoparticle above the substrate using a dielectric nanopillar, the refractive index sensitivity of a LSPR sensor was enhanced, and the biosensing capability was improved [4–8]. Another important application of plasmonic nanopillar arrays is for the fabrication of SERS-active substrates. SERS-based sensing technique has been developed as a powerful high-throughput tool for detecting molecules. It has been demonstrated that using metal-coated nanopillar arrays as SERS substrate can greatly increase the sensitivity due to its strong interaction with incident light in three-dimensional (3D) configuration, which has high surface area and high density of hot-spots [11,13,14,17]. Recently, ultrasensitive and specific detection of biomolecules at picomolar levels was achieved by combining an aptamer-functionalized nanopillar substrate with SERS mapping analysis [18].

To bring the nanodevices such as SERS substrate to practical applications, it is desirable to develop an efficient fabrication method for highly ordered nanostructures with reproducible and controllable morphologies. Abundant of nanofabrication techniques have been studied to produce nanopillar arrays. Nanosphere lithography [3,7,16,21] and porous anodic alumina (PAA) [5,22] are widely used based on the nanosphere or PAA template. The limitation is the geometric constraints of the templates. As for the conventional lithographic approaches, focused ion beam lithography and electron beam lithography (EBL) are disadvantageous because of their high facility cost, time-consuming process and low productivity. Nanoimprint lithography (NIL) was developed as an efficient method for nano-patterning [23,24]. The lithographic processes such as resist coating, etching and lift-off processes are used in the same way as in the conventional lithography method. Resistless nanoimprinting in metal was recently reported to fabricate plasmonic nanostructures with high-resolution and low-cost [25]. However, the nanostructure mold used in the NIL process is usually produced by EBL and etching processes. Thus, NIL method cannot avoid the drawback of conventional lithographic procedures. Lithography-free fabrication method using thermal dewetting induced metallic nanodots mask is another approach for realization of large area nanostructures [2,12,26,27]. The limitation is that the agglomerated nanodots are randomly distributed.

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To overcome limitations of current fabrication methods, authors have reported a new strategy for two dimensional (2D) nanostructure arrays by using Nanoplastic Forming (NPF) in conjunction with thermal dewetting process [28–30]. This approach shows several advantages such as low-cost, high-throughput, without any resist coating or adhesion layer deposition. Based on the 2D nanodot arrays, ordered Dot-on-Plate (DoP) nano-sandwich arrays were developed [31]. In our previous report, single nanodot array was used as a template and the DoP nanostructure was fabricated based on multilayer deposition technique [30]. In this research, single nanodot array is utilized as an etching mask, and plasmonic nanopillar arrays are produced by the dry etching technique. The performance of dual LSPR/SERS sensor based on the nanopillar array is studied. The SERS enhancement mechanism is also investigated by numerical simulations.

2. Experimental method

Fig. 1 illustrates the fabrication processes used to produce the nanopillar arrays. The process mainly involves five steps. First, (1) a metal film (Au) was coated on a substrate by sputtering. Next, (2) a square nano-groove lattice was patterned on the coated metal layer using NPF. Subsequently, (3) the patterned specimen was annealed for inducing layer deleting and dot formation. Then, (4) reactive ion etching (RIE) was employed. The self-organized metallic nanodot array was utilized as a mask during the dry etching process. Ordered Au-capped nanopillar arrays are fabricated after selective etching of the glass substrate (SiO_2). Finally, (5) a metal film (Ag) was deposited on the nanopillar arrays. Experimental conditions of the nanopillar array fabrication are summarized in Table 1.

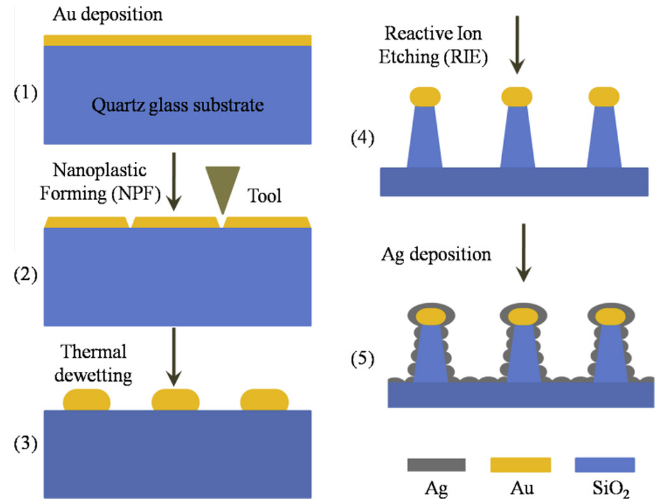

Fig. 1. Processing steps for the fabrication of plasmonic nanopillar arrays.

Table 1
Experimental conditions for nanopillar array fabrication.

Au film thickness (nm)	Lattice size (pitch) (nm)	Thermal dewetting temperature (°C)	Thermal dewetting time (min)	(RIE) Etching depth (nm)	Ag deposition (nm)
10	200	800	10	250	30, 40, 50

2.1. Fabrication details

Prior to the experiment, the quartz glass substrate was prepared from a finely finished slide glass and it was cleaned by an ultrasonic cleaner. The cleaning solution was acetone. In the step (1) and (5), metal deposition (Au or Ag) was conducted using a DC sputter coater. The pressure was set to 15 Pa and argon (Ar) was used as the sputter gas. The distance between the target and the sample was 35 mm. By varying the sputtering duration the metal film thickness could be controlled.

A NPF machine shown in Fig. 2(a) was utilized for the lattice patterning on a coated metal layer. A knife-edge diamond tool was utilized and the width of the tool was 1.5 mm. Details of the machine were explained in previous publications [28–30]. Fig. 2(b) schematically illustrates the NPF process. First, a series of parallel nano-grooves was indented on the Au layer by the diamond tool. Subsequently, the sample was rotated horizontally by 90 degree, and another series of parallel grooves were indented again on the prepatterned grooves. So that, a square groove lattice was created on the Au layer. The lattice size could be controlled in the experiment by adjusting the distance of the grooves. The total area of the produced array was 1.5 mm × 1.5 mm. The typical writing speed of the NPF process is 1000 grooves per hour. If the pitch setting is 200 nm, it takes 15 h to write the array. By incorporating other techniques such as roller imprinting process with NPF [32], the throughput of the fabrication process can be further increased. The NPF machine is fixed on a vibration isolation table. In order to prevent contamination, the entire equipment is placed inside a clean chamber.

Following NPF process, thermal dewetting was carried out by annealing the sample in an electric furnace under ambient atmosphere. Annealing time was 10 min. Annealing temperature was 800 °C. RIE was conducted using an ULVAC CE-300I high-density plasma etching system. Flow rate of CHF_3 was 15 Standard Cubic Centimeter per Minutes (sccm). Flow rate of O_2 was 25 sccm. The plasma power was 150 W. The bias power was set to 2 W. The pressure was held at 0.3 Pa. The etching duration could be adjusted to generate nanopillars with various heights.

2.2. Morphology observation and spectra analysis

The scanning electron micrographs of the nanostructure were obtained by a JSM-6301F JEOL or Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). The cross section of the sample was machined by a fine cutter followed by polishing and Ar ion beam etching. Then, it was characterized using a Hitachi SU8200 FE-SEM. After coating Pt for about 1 nm, element distribution of the nanostructure was analyzed by a BRUKER EDX system.

Au-capped nanopillar arrays without Ag coating were utilized for a LSPR sensor. In order to investigate the refractive index sensing properties, liquid chemical was spotted on the nanopillar and nanodot array specimen, and the ultraviolet–visible (UV–vis) extinction spectra were measured in a transmission configuration equipped with a light source of an Ocean Optics LS-1 tungsten and halogen lamp. The extinction spectra were recorded with a range of 500–800 nm using a BAS SEC2000 spectrometer. Sucrose solutions with three kinds of weight percentage were examined, i.e., 0%, 46% and 84%. The refractive indices (RI) of these solutions are 1.33, 1.41, and 1.50 respectively. Extinction spectrum of a nanodot array without solutions was also analyzed for comparison.

Au-capped nanopillar arrays with Ag coating were utilized for a SERS sensor. For the characterization of SERS properties, two kinds of probe molecules were used, Nile blue A (NBA) and Rhodamine 6G (R6G). A 20 μL droplet of NBA aqueous solution or R6G methanol solution was dispersed on the specimen and then they were dried in air to evaporate any moisture. Subsequently, Raman spectra measurements were performed on a WITec alpha-300 confocal