Synthesis of Gold Nanopattern using Electron Irradiation and Post-pyrolysis

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1. Introduction

Synthesis of noble metal nanoparticles (NPs) such as gold (Au) and silver attracted great interest for various applications to optics, biochemical sensors, catalysis, and surface-enhanced Raman scattering (SERS) [1] because of their size- and shape-dependent surface plasmonic properties. Especially, SERS is a powerful tool for the detection of tiny amount of biochemical molecules adsorbed on noble metal surfaces.

While considerable effort for SERS-active substrates has been directed toward the size- and shape-controlled synthesis of noble metal NP arrays, fabrication of a position-controlled assembly or patterning of metal NPs on a solid substrate is still challenging. However, such patterned noble metal NPs are indispensable for the applications to lab-on-a-chip devices that allow to detect different molecules simultaneously using one substrate.

Here, we report a facile and straightforward approach to synthesize Au nanopattern by selective electron irradiation and postpyrolysis of a precursor material.

2. Experimental Methods

2.1 Chemicals

Hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4 \cdot nH_2O$, n = 3.5), poly(diallyldimethyl ammonium chloride) (PDDA; 20 wt % aqueous, M_w = 400000-500000 $g \cdot mol^{-1}$), ethylene glycol (EG; 99%), thiophenol (TP, or benzenethiol; 98%), and methanol (>99.9%) were used without further purification.

2.2 Precursor Film Preparation

Polished p-type Si(100) cut in 1 × 1 cm were piranha treated to derive a hydroxyl surface, and were then used as substrates after thoroughly rinsed with pure water. All substrates were kept in pure water prior to use.

To prepare precursor solution, an aliquot of 10 μL $HAuCl_4$ (500 mM) aqueous solution was added into a mixture of 1 mL of EG and 20 μL of PDDA with stirring. The as-prepared Au precursor solution was spin-coated on Si substrates at 600 rpm for 60 s. The drop amount of Au precursor solution was varied to prepare a film with a different thickness. After spin-coating, all the samples were immediately dried in vacuum ambient ($\sim 10^{-3}$ Torr) for 15 min.

2.3 Electron Irradiation and Pyrolysis

The precursor films were irradiated with an electron beam produced from a thermionic electron gun. All the experiments were carried out at ambient temperature, particularly in vacuum of less than 2×10^{-5} Torr. The beam energy was 20 keV and the total electron fluence was 8.29×10^{16} cm^{-2} [2]. A 200 mesh copper TEM grid was used as a mask for the pattern formation. After the irradiation, the samples were developed with pure water to remove unexposed parts. Finally, the samples were pyrolyzed in air at 600 °C for 30 min. A schematic representation of the process for the synthesis of the Au nanopattern is shown in Figure 1.

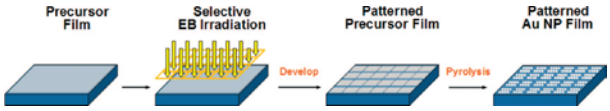

Figure 1. Schematic representation of the process for the synthesis of Au nanopattern

2.4 Characterization

The morphology and structure of the samples were characterized by a field-emission scanning electron microscope (FESEM, S4800, Hitachi). The crystalloid of the samples was analyzed with an X-ray diffractometer (XRD, D/MAX-RC, Rigaku) using Cu K_α radiation. The chemical composition of the samples was characterized with an X-ray photoelectron spectrometer (XPS, AXIS NOVA, Kratos) equipped with a monochromatic Al KR X-ray source. All the XPS spectra were referenced to C 1s at 285 eV.

3. Experimental Results

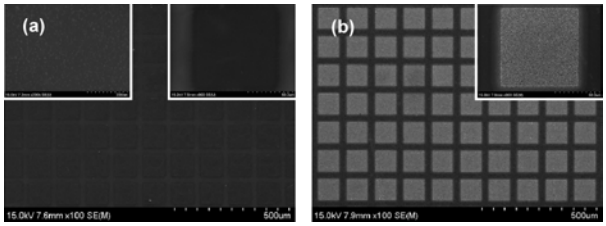

Figure 2. FESEM images of (a) the irradiated film using a 200 mesh TEM grid as a mask, and (b) the post-pyrolyzed film. Inset in parts a and b are magnified images of each pattern.

The FESEM images of the electron-irradiated film and the post-pyrolyzed film are shown in Figure 2. As can be seen in Figure 2a, electron irradiation induced square pattern corresponding to the mask shape on the precursor film, and then a clear pattern of the precursor film was created after the water washing. High

resolution FESEM image displayed that tiny NPs with mostly less than 10 nm in size were embedded in the irradiated region (left inset of Figure 2a). When the patterned precursor films were pyrolyzed, NPs of several tens nm were formed while keeping the square pattern (Figure 2b). The pattern has the same size and shape with the mask, suggesting that two-dimensional (2D) NP pattern with a desired shape and size can be fabricated by using a proper mask.

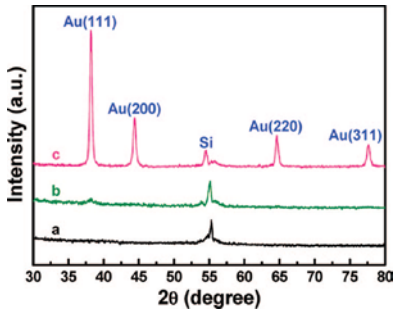

Figure 3. XRD patterns of (a) the pristine sample, (b) the irradiated sample, and (c) the post-pyrolyzed sample.

Figure 3 shows the XRD patterns of (a) the pristine sample, (b) the irradiated sample, and (c) the post-pyrolyzed sample. No Au peaks were observed for the pristine sample (Figure 3a). However, very weak and broad peak corresponding to Au(111) peak appeared in the irradiated sample (Figure 3b). Combining this result with the FESEM image shown in the left inset of Figure 2a, we can conclude that tiny Au crystals with the size of mostly less than 10 nm were produced inside the precursor materials by the electron irradiation. These small Au crystals might serve as seeds for further growth of Au NPs during the subsequent pyrolysis process [3]. For the pyrolyzed sample, clear diffraction peaks at 38.2°, 44.4°, 64.6°, and 77.6° were observed, which correspond to Au(111), Au(200), Au(220), and Au(311), respectively (Figure 3c).

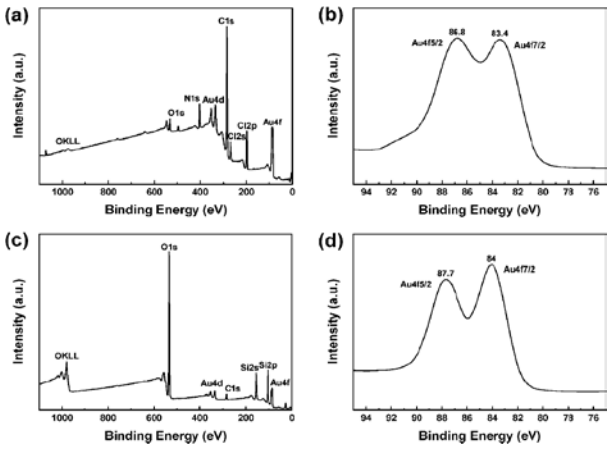

Figure 4. XPS spectra of (a) the pristine and (c) the post-pyrolyzed samples. (b and d) XPS spectra of Au 4f corresponding to parts a and c, respectively.

The chemical composition of the pristine and post-pyrolyzed films was characterized using XPS. The XPS spectrum of the pristine film displayed C, N, O, Cl, and Au peaks, which were originated from the precursor materials (Figure 4a). After the pyrolysis, however, N and Cl peaks disappeared and the intensity of C peak was remarkably decreased, while Si peak newly appeared and the intensity of O peak was greatly increased (Figure 4c). This suggests that PDDA polymer was almost completely decomposed by the pyrolysis process: C, N, and Cl are the elements comprising PDDA.

The peaks of Au 4f7/2 (83.4 eV) and Au 4f5/2 (86.8 eV) in the pristine film (Figure 4b) shifted by 0.6 and 0.9 eV, respectively, toward lower binding energies relative to pure Au atoms. However, the position of Au 4f spectrum for the post-pyrolyzed film showed the same as those of pure Au (84 and 87.7 eV), revealing that Au NPs were not covered with any materials (Figure 4d) [4]. Therefore, Au NPs of high purity were produced by the electron irradiation and post-pyrolysis process.

4. Conclusion

A strategy to synthesize Au nanopattern was presented based on electron irradiation and post-pyrolysis of a precursor film that consist of $HAuCl_4$, EG, and PDDA.

The presented technique, if proper precursor materials are chosen, can also be used to produce patterned monolayer arrays of other metal NPs, which are important for micro/nanoelectronics, photonic, and nanoelectromechanical devices as well as biological and chemical sensors, molecular sensor arrays, and transducers.

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