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A Novel Route to Fabricate Patterned Film of Silver Nanoparticles Using Electron Irradiation

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1. Introduction

Silver nanoparticles (Ag NPs) have superior properties like antibacterial effects, high electrical conductivity, and novel optical properties in comparison with other metal nanoparticles [1]. Since the properties of Ag NPs are closely related to size and shape, lots of methods to control the morphology of Ag NPs exist including chemical reduction, thermal decomposition, electroless deposition [2]. Although Ag NPs have been studied intensively and used widely, however, the fabrication of patterned or well-controlled Ag nanostructures is still remained as a knotty challenge.

Recently, a novel method to synthesize various nanomaterials and nanostructures using electron irradiation has been reported [3,4]. The chemical structure of materials can be changed only by irradiating an electron onto materials. The electron irradiation method has extraordinary advantages such as high purity of final products since no reductants are needed, simple process to fabricate patterned structures.

In this work, we present a new and facile way to fabricate patterned Ag NP films, which has the potential for applications in bio-sensing [5], micro/nano electronics, and optical devices, based on electron irradiation technique.

2. Experimental Methods

2.1 Materials and Substrates

Silver acetate (99%), ethanol (95%), nitric acid (63%) were used without further purification. Silicon wafers (1 cm × 1 cm) were cleaned in a piranha solution (a 3:1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide) for 1 h in ultrasonic conditions, and then thoroughly rinsed with distilled water. All substrates were kept in distilled water before use to maintain the hydrophilicity of surface.

2.2 Sample Preparation

Silver precursor solution was prepared by dissolving silver acetate (AgAc) 100 mg in 2.2 ml ethanol with the assistance of 100 μl nitric acid. As-prepared silver precursor solution was quickly spin-coated on silicon substrates at 1000 rpm for 1 min and the average thickness of consequent film was ~300 nm.

2.3 Electron Irradiation Experiments

The silver precursor films were irradiated with an electron beam (EB) produced from a thermionic electron gun with a tantalum filament cathode. Copper TEM grids successfully stuck onto the as-prepared samples and were used as a mask. Consequently, the silver precursor coated Si substrates were directly attached on a sample stage and cooled down by water to prevent from unexpected heating. All the experiments were carried out at ambient temperature, particularly in vacuum of less than 2×10^{-5} torr [2-4]. The beam energy was 30 keV and the current density was 35 $\mu A/cm^2$, respectively. The beam diameter was 12 mm and the total electron fluence was varied from 3×10^{18} cm^{-2} to 6.5×10^{18} cm^{-2}.

2.4 Characterization

The morphology and structure of the samples were characterized by a field-emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan). The crystalloid of the samples was analyzed with X-ray diffractometer (XRD, D/MAX-RC, Rigaku, Japan) using Cu-K_α radiation.

3. Experimental Results

A schematic representation of the process for the fabrication of patterned Ag NP film is shown in figure 1.

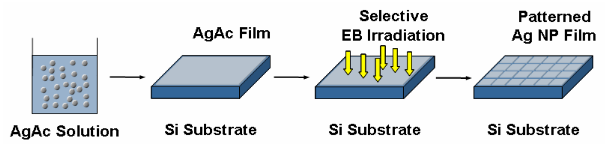

Figure 1. Schematic representation of the process for the fabrication of patterned Ag NP film

Figure 2 shows the FESEM images of the precursor film before irradiation and the electron-irradiated sample at the fluence of 6.3×10^{18} cm^{-2}. As shown in the figure 2(a), the spin-coated silver precursor film consists of uniform AgAc with large area. Figure 2(b) shows patterned silver nanoparticle films using 200 mesh TEM grids. Bright parts are composed of Ag NPs and dark parts are composed of AgAc. Although there are several cracks, square patterns can be easily distinguished by contrast.

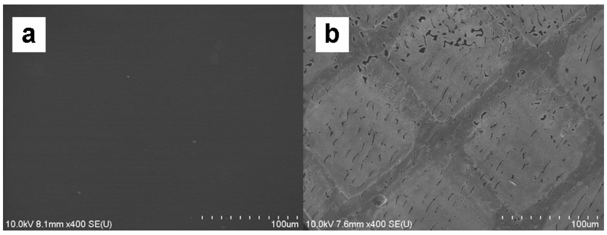

Figure 2. FESEM images of (a) pristine film and (b) patterned Ag NP film using 200 mesh TEM grid.

Figure 3 show the XRD spectra of the samples after the irradiation at the fluence of 6.3×10^{18} cm^{-2}. The four strong diffraction peaks located at 38.2°, 44.4°, 64.7°, 77.6° correspond to the silver peaks which are Ag(111), Ag(200), Ag(220), Ag(311), respectively. Inset in figure 3 shows Ag NPs with 15 ~ 40 nm of size which compose the patterned Ag NP films.

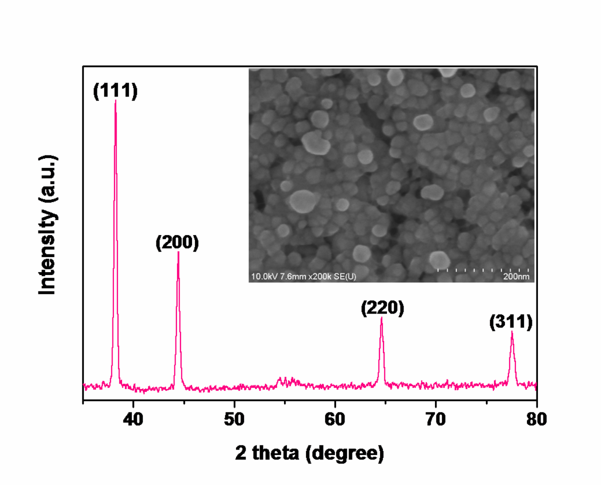

Figure 3. XRD results of the Ag NPs comprising the patterned Ag NP films (Inset: Ag NPs).

The mechanism of transformation from AgAc to Ag can be briefly explained by electron induced decomposition. Electron irradiation decomposes the silver precursors into crystalline silver nanoparticles, particularly in vacuum. The detailed explanation can be found in our previous reports [2]. Hence, a selective exposure of electron beam to the precursor films coated on Si substrates using a mask can fabricate patterned Ag NP films consequently.

4. Conclusion

In conclusion, a novel and facile synthetic route to fabricate patterned Ag NP films using electron irradiation has been presented. The size of pattern and particles can be controlled and the purity of final products is very high. Patterned Ag NP films can be useful to analyze samples, especially bio-molecules, using surface enhanced Raman scattering (SERS) since the enhancement factor of SERS by Ag NPs are approximately $10^6 - 10^{15}$ [5].

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