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Fabrication and surface-enhanced Raman scattering (SERS) of Ag/Au bimetallic films on Si substrates

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ABSTRACT

Ag films on Si substrates were fabricated by immersion plating and served as sacrificial materials for preparation of Ag/Au bimetallic films by galvanic replacement reaction. The formation procedure of films on the surface of Si was studied by scanning electron microscopy (SEM), which revealed Ag films with island and dendritic morphologies experienced novel structural evolution process during galvanic replacement reaction, and nanostructures with holes were produced within the resultant Ag/Au bimetallic films. SERS activity both of sacrificial Ag films and resultant Ag/Au bimetallic films was investigated by using crystal violet as an analyte. It has been shown that SERS signals increased with the process of galvanic substitution and reached intensity significantly stronger than that obtained from pure Ag films.

1. Introduction

When the molecules are adsorbed to metallic surfaces exhibiting atomic scale roughness, the Raman signal intensity could be enhanced by 10^4–10^6 times through amplifying the local electromagnetic field incident on an adsorbed molecule (electromagnetic enhancement [1]) or promoting electronic resonance/charge transfer between the molecule and the metal surface (chemical enhancement [2]), which is called surface-enhanced Raman scattering (SERS). In some cases, the enhancement is large enough to allow single molecule detection [3,4]. Since the Raman spectrum yields structural information, SERS is widely used as a powerful analytical tool in a wide range of applications, including biomolecular recognition, macromolecular characterization and ultra-sensitive detection [5]. For example, the ability to detect and distinguish single DNA bases by SERS could be used for rapid DNA sequencing [6].

The most critical aspect of SERS is the development of efficient SERS-active substrates that can provide sensitive Raman signals. Generally, Ag and Au nanoparticles based substrates are regarded as one of the best candidates for SERS studies. Ag nanostructures can provide large enhancement in Raman intensity, but they are not preferred for in vivo studies of biological system. In contrast, Au nanostructures are biocompatible, but they provide moderate enhancement in SERS experiments [7]. Therefore, Ag/Au bimetallic nanostructures, combining the optical enhancing properties of Ag and the benefits of the surface properties of Au, are fascinating materials for the study of SERS. In addition, Ag/Au bimetallic nanostructures are attractive due to their particular structural and optical properties, which are distinct from those of corresponding single metal nanostructures [8,9].

Herein, we report a simple method for fabricating Ag/Au bimetallic nanostructures on Si wafers. The growth process of the bimetallic film on Si substrate was carefully monitored by scanning electron microscopy (SEM) and the SERS properties of the films were characterized by using crystal violet as an analyte.

2. Experimental

Silver nitrate ($AgNO_3$), hydrofluoric acid (HF), crystal violet and $KAuCl_4$ were purchased from Shanghai Reagents Co. and used as received. The Si wafers used in this study were p-type, boron-doped and ⟨1 0 0⟩ orientation. The wafers were cut into squares and cleaned by sonicating sequentially for 20 min each in acetone, ethanol and deionized water. After dried under N_2 stream, the wafers were ready for further use.

2.1. Preparation of Ag films on Si wafers

In a typical synthesis, solution of 5 M HF and that of 0.02 M $AgNO_3$ were blended uniformly. The mixed solution was then heated on a water bath at 60°C. Si wafers were immersed into the solution for different periods of time. When taken out, the surface of the wafers turned gray, indicating the formation of Ag films.

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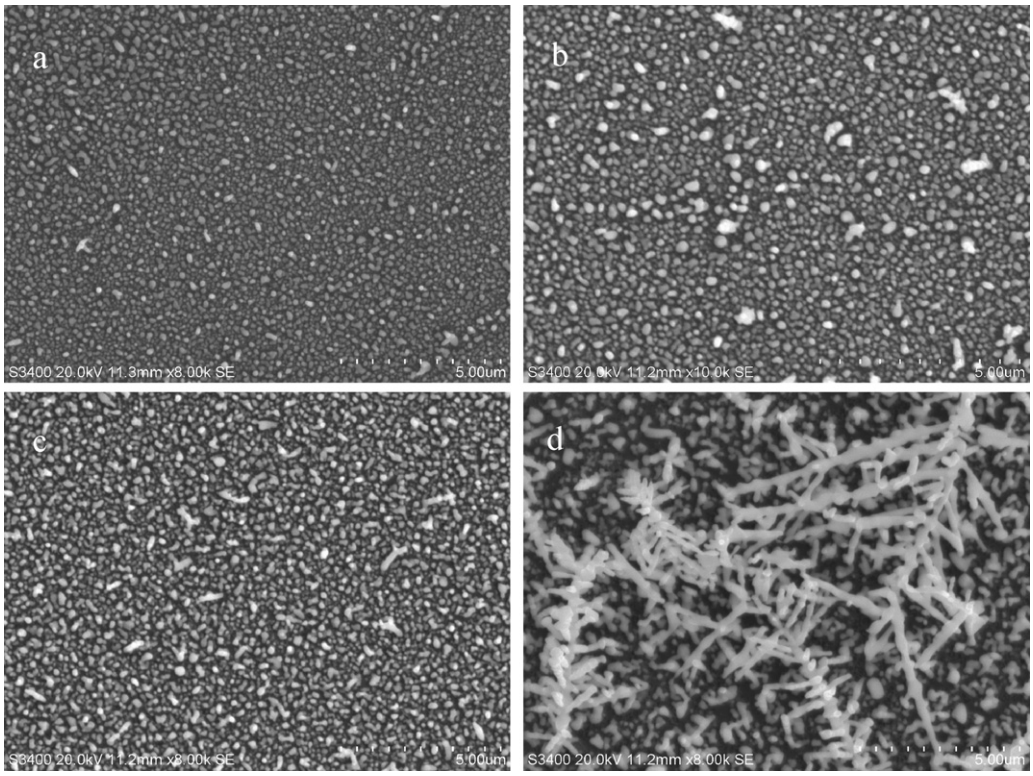

Fig. 1. SEM images of Ag films prepared by immersing silicon in HF and $AgNO_3$ mixed solution for (a) 10 s, (b) 20 s, (c) 30 s and (d) 1 min.

The resultant Ag films were rinsed with deionized water and dried under N_2 for standby.

2.2. Preparation of Ag/Au bimetallic films

The as-prepared Ag films were immersed into solution of $KAuCl_4$ (10^{-3} M) over different periods of time. After the galvanic replacement reaction, the samples were rinsed with deionized water and dried under N_2.

2.3. Characterization of Ag and Ag/Au films

SEM images were obtained with a S-3400NII scanning electron microscope (Hitachi, Japan). SERS measurements were performed by an Inspector Raman microscope (DeltaNu, America). Samples for SERS analysis were prepared by immersing the fabricated films in 10^{-4} M solution of crystal violet for 1 h. Radiation of 785 nm from a He–Ne laser was used for the SERS excitation. SERS spectra were collected in medium resolution mode with integration time of 1 s.

3. Results and discussion

3.1. Morphologies of Ag films

Electroless metal deposition in ionic metal (silver) and HF solution is based on a microelectrochemical redox reaction in which both anodic and cathodic processes occur simultaneously at the silicon surface [10]. At the start, silicon etching and silver deposition occur simultaneously at the Si wafer surface. The deposited silver atoms first form nuclei and then form nanoclusters, which are uniformly distributed on the surface of the silicon wafer. These silver nanoclusters and the Si areas surrounding these silver clusters could respectively act as local cathodes and anodes in the electrochemical redox reaction process, which can be formulated as two half-cell reactions (1) and (2):

$$Ag^+ + e^- \rightarrow Ag \quad (1)$$

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^- \quad (2)$$

SEM images in Fig. 1 display the morphologies of Ag films prepared by immersing Si wafers in HF and $AgNO_3$ mixed solution for time periods of 10 s, 20 s, 30 s and 1 min, respectively. It is reported that the deposition of metal onto semiconductor surface follows a 3-D island (Volmer–Weber) growth mechanism due to a weak interaction energy between the adsorbed metal atom and the semiconductor [11]. Apparently, this mechanism applies to the Si system using in this study as well. The SEM images show that when the Si wafer was immersed for only 10 s, the obtained Ag film is composed of nearly spherical particles with size around 120 nm. The deposited silver particles are uniformly distributed and have regular shapes. When the immersion time was prolonged to 20 s and 30 s, the particles grow bigger to about 170 nm and 200 nm, respectively. In addition, the larger particles in these two Ag films present clubbed shapes. From the bright and dark contrast of the pictures, it could also be concluded that particles grow higher and higher with increasing immersion time. Fig. 1d shows absolutely different morphology of Ag film prepared with immersion time of 1 min. Dendritic structures with trunks about several micron appear. However, these dendritic structures have not developed completely. There are still many Ag islands exhibiting branch features on the silicon surface and the dendrites are not so dense.

3.2. Morphologies of Ag/Au bimetallic films

Ag films prepared with immersion time of 20 s and 1 min, which will be referred as island Ag film and dendritic Ag film respectively hereinafter, were immersed in $KAuCl_4$ solution for 24 h, 48 h