Synthesis of Al–Si nano-template substrates for surface-enhanced Raman scattering application

A. Bendavid *, P.J. Martin, C. Comte, L.K. Randeniya, D. Weller

CSIRO Manufacturing Flagship, PO Box 218, Lindfield, NSW 2070, Australia

ABSTRACT

Al–Si nano-porous templates were prepared using filtered cathodic vacuum arc deposition and investigated as surface-enhanced Raman scattering (SERS) active substrates. Al–Si thin films were deposited onto silicon substrates followed by immersion in ammonia solution to remove the aluminium columns to form a nano-porous structure. The pore size and density were controlled mainly by the deposition bias voltage applied to the substrate. Gold particles were deposited onto the nano-porous Al–Si templates by displacement deposition in a solution containing $HAuCl_4$ (0.1 mM). The size and dispersion of the deposited Au particles were controlled by the concentration of Au ions, the immersion time and morphology of the Al–Si template. The SERS-activity was measured with Cresyl Violet ($C_{25}N_3H_{30}Cl$) dye as the target molecule, and the enhancement was influenced by the morphology of the nano-porous Al–Si templates. As the pore size decreased a higher density of nucleation sites for the growth of Au nanoparticles was formed resulting in a shorter inter-particle spacing of Au particles, and an enhancement of the Raman signal.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

There is wide interest in using nanomaterials for a range of potential applications. Nano-porous materials are a family of nanostructured materials that possess unique surface, structural, and bulk properties that underline their important uses in various fields such as separation, catalysis, sensors and biological molecular isolation. The use of nano-porous materials also offers opportunities in areas of molecular manipulation, for making nanoparticles, nanowires and other quantum nano-structures. Nano-porous materials are important due to their enhanced capability to adsorb and interact with atoms and molecules on their large interior surfaces and in the nanometre sized pore space. There are a number of techniques for fabricating nano-porous templates such as porous-Si; where anodization of highly doped Si in hydrofluoric acid solution is the most widespread technique. Other approaches mainly include lithographic dry etching and electrochemical HF wet etch [1]. In some cases the structures (pores) are too small to be fabricated by conventional lithographic techniques.

There have been a range of reports regarding the applications of porous Si. Canham *et al.* [2] reported the visible emission of porous Si at room temperature and this resulted in many studies on the application for visible light-emitting devices. The modification of porous substrates by applying nanoparticles onto the surface and into the pores is a method by which these porous templates can be used for surface-enhanced Raman scattering (SERS) applications. Wet processes, such as displacement deposition and electro-deposition, are appropriate techniques for metal deposition inside small pores because of controllability and low cost [3]. Gold particles with nanometre-sizes could be deposited by immersing the nano-porous Si into a solution containing Au ions such as $HAuCl_4$. The application of noble metal nanostructures on nano-porous Si studies on SERS has been reported [4]. It is well known that the presence of Ag or Au particles induces particularly high enhancement of Raman scattering, which permits the detection of molecules of low concentration.

However, there is a necessity for further development of fabrication techniques for more effective SERS substrates. The most widely used SERS-active materials are colloids of Ag and Au aggregates, and also substrates made of noble metals with surfaces containing nanosized asperities. However, the stability and difficulties in the fabrication of colloidal solutions, and also the low enhancement of the Raman signal on the electrodes impede their application [5].

Here, we report on the fabrication of nano-porous Al–Si templates using filtered cathodic vacuum arc deposition (FCVAD) [6]. One of the attractive features of the FCVAD technique is the generation of a flux of positively charged ions which may be delivered to the substrate with the energies that may be controlled by applying a negative voltage to the substrate. FCVAD is an excellent technique for the deposition of phase separated Al–Si films [6]. Phase separated Al–Si films consist of Al cylinders which align vertical to the substrate surface embedded in an amorphous Si matrix [6–9]. The porous structure is obtained after removal of the Al cylinders resulting in a nano-scale template. The pore diameters are in the range of 3–13 nm [6,9]. In the phase separation process of Al–Si films, one of the important growth parameters that determine the final structure is the surface diffusion length of depositing

* Corresponding author. Tel.: +61 2 9413 7109.
E-mail address: avi.bendavid@csiro.au (A. Bendavid).

species [10], which is controlled by the substrate bias voltage. This is a relatively simple technique for fabricating nano-porous structures without the use of conventional lithographic techniques.

The main focus of this study is to demonstrate the simplicity and re-producibility of a fabrication method for robust Al–Si nano-porous templates with regular nano-pores that could be used for SERS applications. The potential for using these materials for research and detection of complex organic compounds at low concentrations has been demonstrated, for the example of Cresyl Violet dye molecules. The relation between the surface morphology of Al–Si nano-porous films and the SERS activity of these substrates is discussed.

2. Experimental details

2.1. The synthesis of nano-porous templates by phase separation of Al–Si thin films

The FCVAD system used in this study is described elsewhere [6]. The diameter of the cathode was 58 mm and mounted onto a water cooled copper hearth. The base pressure of the deposition system was 1.0×10^{-4} Pa. In this study, we used high purity AlSi composite (AlSi 50:50) cathodes (purity, 99.99%). The arc current was set at 90 A direct current (DC) and the positive ion beam current measured at the position of the substrate was 0.1 A. The substrates used were high purity silicon wafers (<0.015 Ωcm, n-type). The substrate bias voltage was varied from −0 V to −200 V. The AlSi films were deposited onto the substrates at normal incidence. The thickness of the films was controlled by the de-position time and was measured by a Dektak 3030 surface profiler. The film thickness was typically 100 nm. The deposition rate of the films was 30 nm/min. In order to form a nano-porous structure, the Al cylinders were etched from the AlSi films in a 2.8 wt.% ammonia solution for about 15 min at room temperature. The surface morphologies of AlSi films were imaged using a HITACHI S-5000H field-emission scanning electron microscope (SEM) and Quanta 200 FEI. The average pore size, density and average area were estimated using the Scion Image (version 4.0.3.1, Scion Corporation).

2.2. Immersion plating of Au on nano-porous Al–Si

The nano-porous Al–Si samples were rinsed in de-ionised water, followed by dipping in 5 wt.% HF to remove the native oxide layer. A mixture of 22 wt.% HF/ethanol solution was used for the solution. After the oxide removal, Au particles were deposited by dipping the Al–Si nano-templates in a solution consisting of HAuCl₄, 0.1 M for the displacement deposition. The duration of immersion was varied between 15 and 120 s.

2.3. SERS measurement of Au deposited nano-porous Al–Si

To investigate the activity of the Au-deposited nano-porous Si as a SERS-active substrate, Raman scattering of Cresyl Violet was used. Cresyl Violet (CV) was selected as the analyte for this initial investigation since it has a strong and narrow Raman peak at 590 cm^{-1}. The simplicity of the Cresyl Violet Raman spectrum enables unambiguous interpretation of the results [10]. SERS active templates were prepared by spin coating the Cresyl Violet solution onto nano-porous Si for 60 s at 4000 revolutions per minute (rpm). The concentration of Cresyl Violet solution was 20 mM. After depositing the dye-solution on the nano-porous layer, Raman scattering was measured in air, using a He–Ne laser (633 nm) as the excitation light at an incident power of 1 mW and with a spot diameter of 1 μm. The laser beam was focused onto the nano-porous Al–Si surface using a microscope objective lens (×20). The Raman spectroscopy was performed using a Renishaw In Via confocal Raman microscope system.

3. Results and discussion

3.1. The influence of substrate bias voltage on pore area and density

Top surface SEM images of nano-porous Al–Si films fabricated at different substrate bias voltages are shown in Fig. 1. The increase in the substrate bias voltage leads to an increase in the average pore diameter. The average pore diameters for films deposited at a. 0 V, b. − 50 V and c. − 200 V were estimated to be 3 nm, 8 nm and 13 nm, respectively. The calculated average pore area and density as a function of substrate voltage bias are also shown in Fig. 2a and b, respectively. This data corresponds to samples obtained using substrate bias voltages of 0 V, − 50 V, − 100 V, − 150 V and − 200 V. The average pore area increases quite markedly from 9.3 nm^2 to 70.0 nm^2 (we assume that the pores are circular) when the substrate bias voltage is increased from 0 V to − 200 V. The variation in average pore diameter with negative substrate bias is very similar to that reported by Horie et al. [8] for films deposited using RF magnetron deposition. In RF sputtering, the negative bias substrate voltage will affect only positive Ar ions generated in the magnetron discharge and the small ionized fraction of the sputtered particles. In the present work, the energy of the Al and Si ions is influenced by the substrate voltage bias and there is no contribution of positive argon ions as generated in a magnetron discharge. Fukutani et al. [10] have shown in their model (using the Cahn–Hilliard equation for phase-separated binary films) that the Al pore diameter and pore separation increase by about a factor 2 when the surface inter-diffusion length is increased by a factor 1.5. Saito [6] studied the effect of the substrate voltage bias on pore size. They [6] reported that a negative substrate bias enhances the pore coalescence, hence the pore size. The pore coalescence was attributed to an increase in the surface diffusion length of both Al and Si deposition species which leads to the structural changes. In Fig. 2b, the pore density decreases by a factor of 5 with increasing substrate voltage bias (from 0 V to − 200 V bias). The pore density is a critical parameter in fabricating suitable SERS substrates, since these pores act as a binding site for the deposition of Au or Ag nanoparticles. The increase in the number of binding sites is also likely to result in smaller inter particle spacing, i.e. increase of 'hot spot'. The pore separations were estimated to be 2, 6 and 10 nm for 0 V, − 50 V and − 200 V substrate biases, respectively.

3.2. SERS measurement

There are a number of studies [11,12] reported on SERS from Cresyl Violet adsorbed on Au or Ag structures deposited on porous substrates. It has been known that SERS depends strongly on the properties of the metallic surface, principally on the size and structure of metal and the surface plasmon resonance frequency [13]. The increase in roughness of Al–Si nano-porous templates and the Au nanoparticle deposits form a local electric-field caused by the localized surface plasmon. As the surface interacts with an incident laser beam, a locally enhanced electromagnetic field arises near the surface of the Au particles resulting in the enhancement of the intensity of the Raman spectrum. Electromagnetic mechanisms mainly contribute to the SERS [14]. The gap separating the Au nanoparticles is critical, since the optical-electric field is enhanced at the nano-gap. Therefore, controlling the separation of the metallic particles is critical for SERS-active substrates. Fig. 3 shows the effect of immersion time of the Al–Si nano-templates (fabricated at 0 V substrate voltage bias) in HAuCl₄, 0.1 M solution. The immersion times were; A. 15 s and B. 60 s. From Fig. 3 one can see that majority of the gold nanoparticles are in the nanopores, in some cases one can observe that the pores are fully covered.

Fig. 4 shows a comparison of the spectra of the CV dye on three types of Al–Si nano-porous templates fabricated at − 0 V, − 50 V and − 200 V substrate voltage biases and bare Si substrate (without Au). The plot shows that the magnitude of the SERS signal is about the same for all of the Al–Si nano-templates (the magnitude of the intensity of the