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Atomic layer deposition of platinum thin films on anodic aluminium oxide templates as surface-enhanced Raman scattering substrates

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ABSTRACT

Platinum thin films are deposited on anodic aluminium oxide (AAO) templates by atomic layer deposition (ALD). The highly ordered island-like platinum nanostructures formed on the AAO template produce a high Raman scattering signal because of the periodical hexagonal arrangement. As an illustration, dramatic enhancement is achieved using Rhodamine 6G (R6G) as a molecular probe.Field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) show that the gap between the island-like structures is below 10 nm. Owing to activation by the incident laser beam, the localized electromagnetic field on the platinum island surface can be dramatically enhanced by the sub-10 nm regime subsequently amplifying the Raman signal. Finite-difference time-domain (FDTD) calculation matches the experimental phenomena suggesting that the excellent surface-enhanced Raman scattering (SERS) characteristics of the platinum structure arise from the high density and abundance of hot spots. Because the platinum film is inert in air, the SERS enhancing substrate can be used reliably in many trace chemical and biological detection applications.

1. Introduction

Surface-enhanced Raman scattering (SERS) is one of the most powerful spectroscopic techniques [1,2] for high-sensitivity and nondestructive chemical and biological sensing [3,4]. The SERS effect is dominated by the localized plasmon modes created by strong electromagnetic coupling between two adjacent metallic objects in a nano-array [5,6], and the effective Raman cross section of a molecule placed between two metallic nanoparticles can be enhanced dramatically [7]. Hence, preparation of ordered nanostructures with even plasmonic field distribution and ideal enhacement factors are the key issues [8]. We have recently developed a facile technique to obtain high-density hot-spots on SERS substrates using anodic aluminum oxide (AAO) as the template [9,10].A continuous silver thin film is deposited on the self-organized AAO membrane by conventional direct-current (DC) magnetron sputtering to form ordered hexagonal island-like structures which possess excellent Raman-enhancing performance and high enhacement factors. However, nanostructured silver is easily oxidized and unstable in air thereby hampering wider applications. As an alternative, more stable noble metals such as gold and platinum can be a substitute. Considering our motivation of biological detection, platinum may be a good option [11] due to its almost total inertness to the chemical groups of biological matters. Among the various fabrication techniques, atomic layer deposition (ALD) is mature and suitable [12,13], especially with respect to the production of high-quality platinum thin films on an oxide surface [14].

ALD is a vapor phase method for thin films making use of sequential self-limiting surface reactions. As the gaseous precursor molecules reach the sample surface, a gas–solid chemical reaction occurs and ceases when reactants are exhausted, thereby allowing layer-by-layer deposition and precise thickness control of the atomic layer level. Owing to the independent reactions and inert gas saturation on the sample surface, films produced by ALD are usually conformal to the initial surface even on nanoporous materials [14]. Unfortunately, metals produced on an oxide surface tend to form clusters in lieu of a continuous film because of the higher surface energy of the metal film relative to the oxide surface. Consequently, many ALD cycles are needed to fabricate a continuous metal film and film conformality cannot be guaranteed [15]. Furthermore, the steric hindrance effect caused by ligands of the organometallic precursor binding to oxide surface can exacerbate the situation [16]. Recently, plasma platinum ALD using

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(methylcyclopentadienyl)-trimethyl platinum ($MeCpPtMe_3$) and oxygen plasma has been developed to produce coutinous platinum thin films [17]. In this work, continuous platinum thin films with highly ordered nano-islands are deposited on AAO templates by the plasma ALD technique.Theoretical calculation and experiments are conducted to elucidate the enhancement mechanism and determine the actual enhancement factor. The long-term reliability of the materials is also assessed.

2. Experimental details

All chemicals including (methylcyclopentadienyl)-trimethyl platinum ($MeCpPtMe_3$), rhodamine 6G (R6G), adenine, and adenosine were analytical grade purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without any further purification. All the solutions were prepared with demineralized and filtered water.

The AAO templates were fabricated by anodic oxdation by varing the DC voltage at 10 °C. An ordered nanopore structure was produced by a two-step anodizing process using optimzed parameters reported previously [9,18]. The Pt films were deposited on an ALD instrument with an inductively-coupled plasma (ICP) source at 300 °C. The reactor was evacuated to less than 10^{-3} Pa by a turbomolecular pump backed by a mechanical one. The Pt precursor (98% pure $MeCpPtMe_3$) was vaporized at 70 °C and introduced into the reactor.Deposition was carried out at an oxygen flow rate of 20 sccm (working pressure of about 10^{-2} Pa) for 300 cycles (100 W plasma power for 1 s for each cycle).

FE-SEM (JEOL, JSM-6335F) and AFM (Veeco, DI nanoscope IIIa) were conducted to invesitigate the structure of the AAO and prepared samples. Raman scattering was performed on a Renishaw inVia micro- Raman system using the 633 nm laser line at 20 °C. The laser spot was about 1 μm in diameter and there was a 100× objective lens. The performance of the SERS substrate was assessed by using R6G as the molecular probe at an incident power of 0.04 mW for a cumulative time of 50 s. The Raman signals from adenine (minimum 99% purity) and adenosine (minimum 99% purity) molecules were measured at under 0.2 mW for 40 s. The 10^{-5} M aqueous stock solution of R6G (99% pure) was prepared for SERS measurement. The substrates were immersed in the solution for 30 min to enable adsorption of molecules, taken out, and rinsed throughly with deioned water. The acquisition time and laser power used for the R6G Raman spectra were the same for both the silver and platinum films for the proper comparison and the platinum films were stored for 90 days to study the long term stability. The spectra were taken from differet sites on the surface and the average intensity and standard deviation (SD) were calcuated to ensure good statistics and reproducibility.

The local electromagnetic fields were calculated using the commercial FDTD software (FDTD Solutions 6.5, Lumerical Solutions Inc.). The model consisted of a perodical structure with six hexagonally arranged cones. The bottom radius of the cone is 30 nm and the top hemisphere has a radius of 20 nm. The 633 nm laser was assumed to impact the sample surface normally.

3. Results and discussion

The typical morphology of the AAO template prepared at 40 V is depicted in Fig. 1a. The FE-SEM image is taken at a 30° tilt to illustrate the hexagonal structure of the template. The perfect self-organized growth during anodic oxidation provides good control of

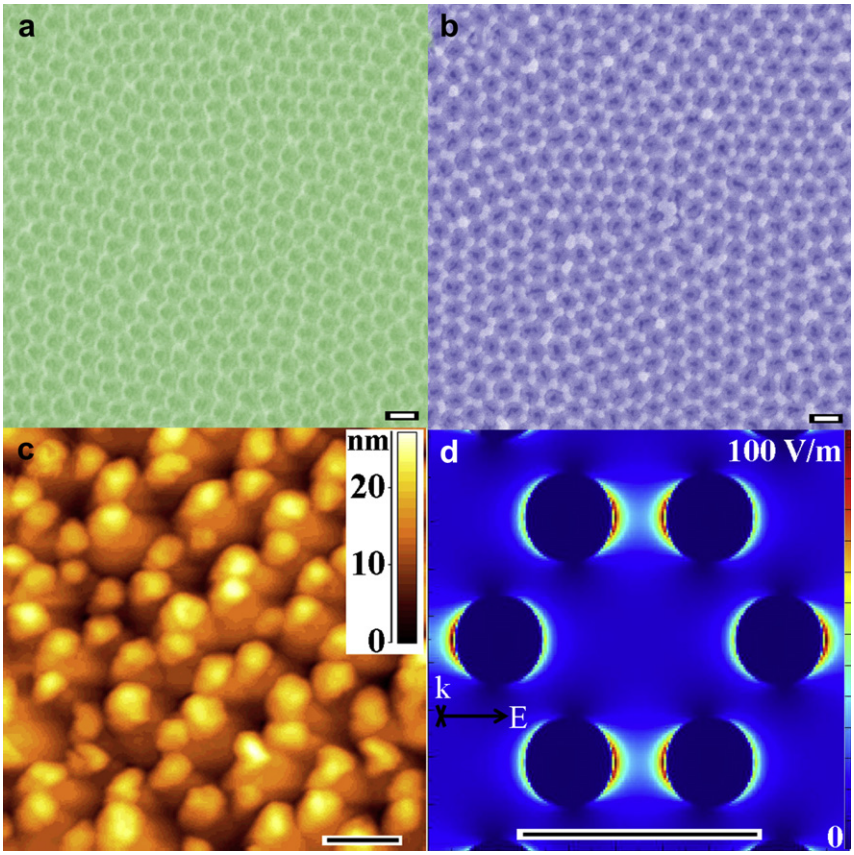

Fig. 1. (a) FE-SEM image of the representative AAO template at a 30° tilt, (b) FE-SEM image of the platinum-based SERS substrate, (c) AFM pattern of the as-prepared SERS substrate and (d) Contour of the near-field electromagnetic distribution of a model structure. The scale bar is 100 nm.