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Surface and interference co-enhanced Raman scattering from indium tin oxide nanocap arrays

Yimin Yang[a,*], Teng Qiu[a,b,**], Zhichang Liu[a], Qi Hao[a], Xianzhong Lang[a,b], Qingyu Xu[a], Gaoshan Huang[c], Paul K. Chu[b]

[a] Department of Physics and Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 211189, People's Republic of China
[b] Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China
[c] Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China

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ABSTRACT

Large-area indium tin oxide (ITO) nanocap arrays are fabricated on porous anodic alumina (PAA) templates to produce robust and cost-effective surface-enhanced Raman scattering (SERS) substrates. The electromagnetic enhancement mechanism is believed to be the main reason for the enhancement. The topography of the ITO nanocap arrays can be adjusted to optimize the enhancement factor by varying the anode voltage applied to the PAA templates. The optical interference in enhanced Raman scattering from the ITO nanocap arrays with different thicknesses are systematically studied and optical self-interference from the incident, scattered, and emitted light is observed to modulate the intensity and shape of the Raman signals.

1. Introduction

Indium tin oxide (ITO) is one of the most widely used transparent conducting oxides because of its electrical conductivity and optical transparency and it can be deposited as a thin film. Recently, experimental observation of the surface plasmon resonance (SPR) effects from ITO has implications to solid state and surface science as well as optical applications to sensing and analysis [1–3]. It has been reported that SPR from ITO is similar to that observed from noble metals and free from interferences from interband transitions [4]. Compared to noble-metal nanostructures, ITO has the following additional advantages. First of all, ITO has no inter- and intra-band transitions in the vis-NIR region permitting systematic studies of the origin of the optical effects arising from SPR of conduction electrons [4]. Secondly, ITO can have a range of compositions resulting from different metal doping and oxygen content. The SPR frequency can thus be tuned by changing the thin film preparation technique or changing the In/Sn molar ratio [3]. Thirdly, ITO is often used to make transparent conductive coatings in displays. SPR thus has a positive impact on the performance of integrated optical devices such as organic light-emitting diodes and solar cells that make use of ITO as a transparent electrode [5]. Fourthly, ITO is chemically and thermally stable. No protective layers are needed in long-time measurements to monitor biological interactions [2].

One of the attractive aspects of SPR is that subwavelength structures can be used to concentrate and channel light and produce electric field enhancement that can be utilized to manipulate light–matter interactions and boost non-linear phenomena [6]. In particular, the enhanced localized electromagnetic (EM) field near the nanostructured surface gives rise to surface-enhanced Raman scattering (SERS) [7]. SERS has been observed from embedded ITO prepared by pulsed laser deposition of ITO films on Si templates with a roughened surface [8] and recent work by Zhao et al. shows that the Raman enhancement from ITO nanorods is comparable to that observed from Au nanorods [9]. Nevertheless, fabrication of ITO nanostructures with evenly distributed plasmonic fields and reliable SPR properties is still challenging and more research is needed to spur wider use of ITO in chemical and biological sensing. In this work, periodically patterned ITO nanocap arrays are fabricated on porous anodic alumina (PAA) templates to produce robust and cost-effective SERS substrates with significant Raman enhancement. The use of PAA templates to fabricate SERS-active substrates is promising considering the easy fabrication, excellent reproducibility, modest cost, and large area production [10]. Moreover, this technique can create long-range uniform plasmonic structures up to the cm dimensions [11]. Because of the optical transparency, the influence of the interference phenomenon in ITO nanocap arrays is investigated and our results demonstrate that the interference effect is substantial.

* Corresponding author. Tel.: +86 25 52090600.
** Co-corresponding author.
E-mail addresses: yangyimin@seu.edu.cn, 101010713@seu.edu.cn (Y. Yang), tqiu@seu.edu.cn (T. Qiu).

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2. Experimental details

High-purity aluminum (Al) foils (99.99%) were degreased by acetone and then electropolished using a mixture of ethanol and perchloric acid with a volume ratio of 5:1 at a constant DC voltage of 15 V for 3 min to further remove surface impurities. After rinsing in distilled water and drying, the Al foils were anodized separately in a 0.3 M oxalic acid solution at a DC voltage of 30 V, 40 V, 50 V, or 60 V at 5 °C. In order to obtain an ordered nanopore array, a two-step anodizing process was adopted. The Al foils were first anodized for 2 h (30 V, 40 V, and 50 V) and 30 min (60 V) followed by immersion in a mixture of chromic acid (1.8 wt.%) and phosphoric acid (6 wt.%) at 75 °C (1:1 in volume). The anodization time in the second step was 15 min (30 V), 6.5 min (40 V), 2 min (50 V) and 40 s (60 V), respectively and the PAA templates were obtained.

The ITO nanocap arrays were prepared on the PAA templates by pulsed laser ablation (248 nm KrF laser, 300 mJ/pulse, 3.0 Pa oxygen, 10 Hz) of an ITO target (In_2O_3 92 wt.%, SnO_2 8 wt.%) at room temperature. Uniform ITO films were deposited by rotating the PAA substrates during ITO deposition. Thickness-continue ITO films were deposited by immobilizing the PAA substrates during ITO deposition. Similar films were deposited on Si substrates to determine the film thickness or thickness-distribution more accurately. To improve crystallization and conductivity, the samples were annealed at 500 °C in vacuum (2×10^{-4} Pa) for 30 min.

Scanning electron microscopy (SEM, JEOL JSM-6335F) and atomic force microscopy (AFM, Vecco MultiMode V) were used to investigate the structures of ITO nanocap arrays. The Raman measurements were performed on a Jobin Yvon LabRAM HR800 micro-Raman spectrometer with the 514 nm laser line at room temperature. An area of ~2 μm in diameter was probed by a 50× objective lens (nominal aperture 0.45) and the incident power at the sample was 0.2 mW. The signal acquisition time was 10 s. To evaluate the Raman enhancing capability of the materials, a Rhodamine 6G (R6G) water solution was used. 8 μL of the R6G solution was added to the substrate and after the water was vaporized, a circular mark with a diameter of 3 mm remained on the substrate. The acquisition time and laser power were the same for all Raman spectra. The SERS spectra were recorded from multiple sites on the substrate to improve and confirm reproducibility. Similar SERS spectral characteristics such as enhancement, position, and relative intensity of the bands were determined from various locations to confirm large-area and uniform production.

3. Results and discussion

The use of the PAA templates in conjunction of the versatile coating technique allows flexible and rapid production of the nanocap arrays [10]. With the exception of the ordered hexagonal pore arrays on the PAA templates, there are small protrusions along the surface of the pore wall, and a dent exists between two neighboring protrusions. The open features of the pores caused by volume expansion when aluminum is converted into alumina can be used as templates to design and fabricate the nanostructured platform in which the areas exhibiting large gap-related enhancement are organized in a regular pattern. Fig. 1 shows a representative cross-sectional SEM image of the ITO nanocap array on the PAA template. The thickness of the ITO layer is 22 nm and that of PAA layer is 380 nm. Protrusions can be observed along the surface of the pore wall. There is a V-shape dent between two adjacent protrusions (see the inset) and the hot spots are believed to be located in these V-shape ortho-cap gaps. The ITO nanocaps separated by tunable gaps can be fabricated on the PAA templates with different nanopore diameters, which can be controlled by adjusting the anode voltage. Fig. 2 depicts a series of 3D AFM images of the ITO nanocap arrays

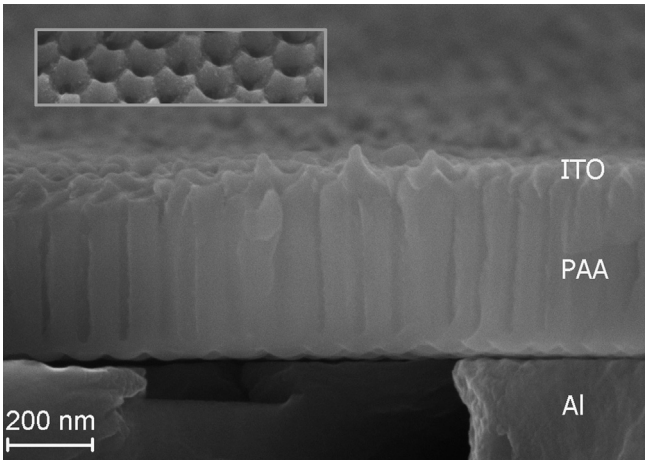

Fig. 1. Representative cross-sectional SEM image of the ITO nanocap array. The inset is a surface image at a 30° tilt.

formed at different anodic voltages. The thickness of the ITO layer is 22 nm. As shown in the AFM images in Fig. 2, these ITO nanocaps cover the alumina protrusions and exhibit a periodic hexagonal arrangement. It can be observed that perfect self-organized growth, which controls the nanopore arrangement, only occurs at a certain anodic voltage of 40 V. The detailed structural parameters of ITO nanocap arrays are shown in Table 1 and in general, a high SERS activity results from a high density of hot spots, high order, and large surface roughness.

To evaluate the Raman-enhancing capability of the ITO nanocap arrays, an R6G solution (3.3×10^{-6} M) is applied to the ITO/PAA/Al substrates. Fig. 3A shows a series of spectra illustrating the efficiency of SERS. Many salient Raman peaks can be observed from the R6G probe. The Raman intensity varies substantially with different nanopore diameters. The Raman enhancement observed from the ITO/PAA(40 or 50 V)/Al substrates is evident larger than from ITO/PAA(30 or 60 V)/Al substrates. The difference in spectral shape between the 40 and 50 V samples is result of different influence by interference effect which will be discussed later. The strong enhancement can be attributed to that the nanocap arrays are assembled with a favorable gap configuration and highly ordered

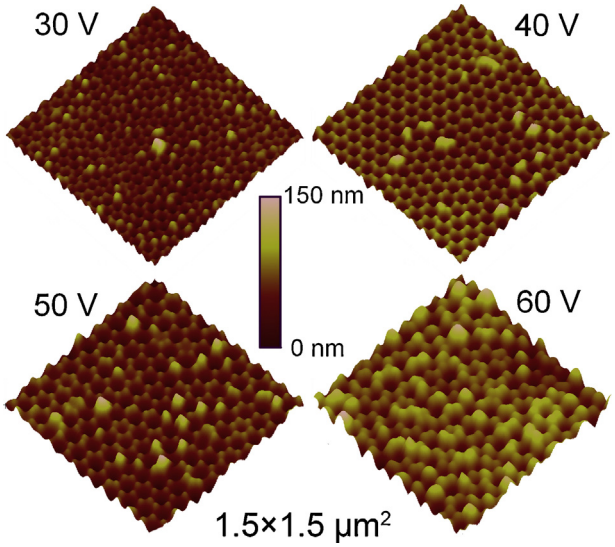

Fig. 2. 3D AFM image (1.5×1.5 μm^2) acquired from the ITO coated PAA membranes formed under different constant DC voltages: 30, 40, 50 and 60 V. The thicknesses of the ITO layer are all set to be 22 nm.