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Modulation of surface-enhanced Raman spectra by depth selective excitation of embedded indium tin oxide nanoisland arrays

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Abstract
Embedded transparent conducting indium tin oxide (ITO) nanoisland arrays were prepared by pulsed laser deposition of ITO films on roughened Si templates and post-annealing to investigate the surface-enhanced Raman scattering activities. Considerable Raman enhancement of a rhodamine 6G probe during Ar⁺ laser excitation was observed and modulated by the thickness of the ITO film due to the exponentially decaying field of the localized surface plasmon polaritons at the interface. Because the Raman-enhancing functional layer is protected at the ITO/Si interface, this system is reusable and also believed to be immune to contamination and other surface activities.

1. Introduction
Surface-enhanced Raman scattering (SERS) is recognized as one of the most sensitive spectroscopic tools offering highly sensitive chemical and biological detection [1, 2]. The optical enhancement is commonly associated with the excitation of surface plasmon (SP) oscillations in most SERS systems and nanostructured surfaces often lead to SP resonance [3]. When a nanostructured metal is irradiated by a laser, coupling between the metal surface and electromagnetic (EM) radiation occurs and the coherent oscillations of free electrons are confined to the nanoscale metal surface giving rise to significantly enhanced local fields [4]. The enhanced fields consequently interact with near-field molecules and phosphors significantly enhancing the Raman scattering signals and fluorescence [5, 6]. The fact that particle plasmons allow direct coupling of light to resonant electron plasmon oscillations has spurred much effort in the design and fabrication of highly SERS-active substrates in nanostructured films and metallic nanoparticles [7, 8].

The frequency of the SP resonance depends on the dielectric constant of the metal which is responsible for the SERS effects observed mostly from metals such as gold and silver [3]. They are often stored in air and appreciable chemical and optical degradation occurs in a few days. In order to preserve the stability of these SP resonance interfaces, thin films with high imaginary refractive indices (typically conducting metal oxides) are deposited [9]. The advantages of the overlayers are the overall refractive index sensitivity and improvement in the SP resonance characteristics [9]. Some transparent conducting metal oxides such as conducting indium tin oxide (ITO), fluorine-doped tin oxide and aluminium-doped zinc oxide possess similar plasmonic characteristics to those of noble metals [10–12]. ITO possesses a tunable plasmon frequency that is free from...
interference from interband transitions [12, 13]. In this work, we report embedded ITO nanoisland arrays prepared by pulsed laser deposition. Because ITO is completely transparent in the visible region, the 514 nm line of the Ar+ excitation laser can penetrate the ITO film to excite localized SPs at the ITO/Si interface. Because the interface is protected, the longterm stability can be improved and the SERS activity is less prone to surface contamination. The parameters affecting the modulation of the SERS spectra induced by the exponentially decaying field of the localized SP polaritons at the interface are also presented and discussed.

2. Materials and methods

The material selection and conventional SERS measurement are outlined in figure 1(a). Si templates with roughened surfaces on the nanoscale were formed on p-type (1 0 0) Si wafers (1–60 Ω cm) by wet etching in a NaOH solution at room temperature. Figure 1(c) shows a typical atomic force microscopy (AFM) (Veeco Multimode V) image of the surface of etched Si. It can be observed that high-density Si islands formed on the surface of Si wafer after the etching treatment. The embedded ITO (In2O3 92 wt%, SnO2 8 wt%) nanoisland arrays were prepared by pulsed laser deposition (248 nm KrF laser with a power of 300 mW and frequency of 10 Hz) of ITO films onto the templates at room temperature. During deposition, oxygen (pressure of 3.0 Pa) was used to improve the conductance and transparency of the film [14]. To improve the crystallinity and increase the carrier concentration [15], the samples were annealed at 550 °C in vacuum (2 × 10^{-3} Pa) for 30 min. Figure 1(b) shows a typical AFM image of the surface of the deposited ITO film with a thickness of 200 nm. The maximum surface fluctuation was measured to be only 2 nm indicating that the surface of such an ITO film is really quite smooth. A 10^{-5}M aqueous rhodamine 6G (R6G) solution was used to evaluate the Raman-enhancing capability of the samples and the samples were kept in the R6G solution for 40 min before measurement. The SERS measurements were carried out on a Horiba Jobin-Yvon LabRAM HR800 micro-Raman spectrometer with the 514 nm laser focused to a diameter of 1 μm at room temperature. The incident power was 0.55 mW and the accumulation time was 10 s.

3. Results and discussion

Figure 2 shows a collection of spectra illustrating the Raman-enhancing capability. The Raman spectrum from a typical sample of embedded ITO nanoisland arrays is displayed in figure 2(a). The sample was prepared by etching Si in a 15 wt% NaOH solution for 8 min prior to deposition of a
200 nm thick ITO film. Many salient Raman peaks can be observed from the R6G probe [16]. On comparison, R6G adsorbed on the etched Si or ITO film deposited on unetched Si exhibits no visible R6G Raman bands (see the bottom of figure 2(a)). A comparison among the spectra reveals that Raman enhancement may be associated with the formation of the embedded ITO nanoisland arrays. This is confirmed by the AFM image of the etched Si surface depicted in figure 1(c) revealing the formation of randomly distributed Si islands after etching in NaOH. The Si islands have an average size of about 150 nm and height of about 10 nm. Consequently, embedded ITO nanoisland arrays can be easily prepared by pulsed laser deposition of an ITO film on etched Si. The junctions between the aggregated nanoparticles or nanoislands are believed to be SERS ‘hot spots’ where large field enhancements down to a single molecule are observed [5, 17]. This is the result of localized SP resonance coupled between the nanoparticles and enhanced EM field intensity localized at the nanoparticle interstitial sites in the nanoisland do not favour SERS with closely spaced features is quite short-ranged and large field enhancements down to the aggregated nanoparticles or nanoislands are believed to have a strong effect on the coupling between adjacent nanoislands in the SERS experiment.

Because the coupling between the nanostructured surfaces with closely spaced features is quite short-ranged and large interstitial sites in the nanoisland do not favour SERS [5, 18], the etching conditions are varied in order to evaluate the Raman-enhancing capability of different embedded ITO nanoisland arrays. All the ITO films have the same thickness of 200 nm. The variation in the SERS signal intensity at 612 cm$^{-1}$ is illustrated in figure 2(b). The strongest Raman line is observed from the Si substrate etched in 15 wt% NaOH for 8 min. The surface structure of the Si template is observed to have a strong effect on the coupling between adjacent nanoislands in the SERS experiment.

The SERS spectra can be modulated by the ITO layer thickness. This is because the EM field enhancement stems from the roughness-induced excitation of SP polaritons by the incoming light, resulting in large EM fields in the vicinity of the ITO interface that strongly polarize the adsorbed molecules in the interaction volume for evanescent waves. In response to the EM waves, the conduction electrons oscillate and create an electric field on the surface that has a limited penetration depth (skin depth). Since SPs can only occur within the skin depth of a conducting film and metals have different skin depths and optimum thicknesses [12, 19], the SERS spectra can thus be modulated by the ITO layer thickness which can be altered by varying the deposition parameters. With regard to Franzen’s calculation for ITO film thicknesses greater than 120 nm, the relevant excitation is the SP and the optimum thickness for the SP polaritons in ITO is 160 nm [20] and we did experiments to relate the ITO deposition parameters to the SERS spectra. Figure 2(c) shows the variation in the SERS signal intensity at 612 cm$^{-1}$ as a function of the ITO layer thickness deposited on a Si substrate etched in 15 wt% NaOH for 8 min. It can be observed that the Raman enhancement achieved from the sample with 200 nm of ITO layer is larger than that of others, which is in agreement with the theoretical study.

In routine trace analysis, SERS substrates must be stable with a high concentration of Raman cross-section hot spots, reproducible, inexpensive and easy to make. As aforementioned, metal-based SERS-active substrates are typically chemically unstable. We measured the SERS activity of the samples reported here and found no optical degradation after two months. Owing to the planar surface of the ITO film (see figure 1(b)), the adsorbed R6G molecules can be readily cleaned by heating in acetone or ethanol. Because the Raman-enhancing functional layer is protected at the ITO/Si interface, the SERS activity suffers no optical degradation when coupled to the R6G probe again. To evaluate the homogeneity of the sample, the 2D SERS map of the R6G molecules is shown in figure 3. The sample is prepared by etching Si in 15 wt% NaOH solution for 8 min before deposition of a 200 nm ITO film. The mapping area is 40 × 40 × 0.1 µm$^2$ and the scanning step is 1 µm. The spatial distribution of the Raman intensity is shown in the figure. The variation in the Raman signal intensity around 612 cm$^{-1}$ can be monitored by the brightness, with brighter spots representing higher intensities. The relative SERS peak intensity of the collection spots is centred in a narrow range, and the spot-to-spot relative standard deviation is calculated to be 7%. The data indicate that the substrate is quite homogeneous.

![Figure 3. SERS map (40.0 × 40.0 µm²) obtained from the sample prepared by etching Si in 15 wt% NaOH solution for 8 min prior to deposition of a 200 nm thick ITO film. The map is obtained from the integrated intensity of the 612 ± 5 cm$^{-1}$ band of 10$^{-3}$M R6G adsorbed on the sample. Each point in the map is acquired using 0.55 mW and 514 nm excitation with an integration time of 5 s.](image-url)
reported on ITO here can, in principle, be extended to other transparent metal oxides.

Acknowledgments

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