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Interference effects on indium tin oxide enhanced Raman scattering

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Optical interference is known to alter the intensity of Raman scattering signals. Its effect on enhanced Raman scattering from embedded indium tin oxide (ITO) nano-island arrays prepared by pulsed laser deposition of ITO films with different thicknesses on Si templates with nano-scale roughness are studied. Optical self-interference of the incident, scattered, and emitted light is observed to modulate the intensity and shape of the Raman signals as well as fluorescence background. The fluctuations in the Raman signals and fluorescence background can be explained by a theoretical model considering multiple reflections at the surface and interface. This interference effect must be taken into account in the investigation of enhanced Raman scattering from ITO. © *2012 American Institute of Physics*. [doi:10.1063/1.3684965]

I. INTRODUCTION

Transparent conductive oxides such as indium tin oxide (ITO) have attracted significant interest in recent years for potential applications in surface plasmon resonance (SPR) based sensing and surface-enhanced spectroscopy.[1–4] It has been reported that the SPR from ITO resembles that of noble metals and is free from interference from interband transitions.[5,6] However, fabrication of nanostructured ITO surfaces with evenly distributed plasmonic fields and reliable SPR properties is still challenging, and more research is needed to enable wider use of ITO in chemical and biological sensing.

We have recently reported surface-enhanced Raman scattering (SERS) from embedded ITO nanoisland arrays prepared by pulsed laser deposition of ITO films on Si templates with a roughened surface.[4] Because of the optical transparency and chemical stability, the functional ITO layer is protected at the interface and not prone to contamination and other undesirable surface activities. Considerable Raman enhancement is observed during Ar^+ laser irradiation, and the effect is modulated by the thickness of the ITO film due to the exponentially decaying field of the localized SPR at the interface. The interference phenomenon observed from ITO/Si substrates, however, influences the intensity of the Raman signals, but this topic has not been studied systematically. This interference phenomenon usually occurs between the surface and interface of a transparent film with a thickness between several nanometers and micrometers.[7,8] In fact, in previous studies pertaining to the enhancement of Raman signals using the interference phenomenon, an enhancement factor of up to 30 was observed.[9–11] In this work, the influence of the interference phenomenon is investigated on ITO films having thicknesses in the range of 40-480 nm. Periodical fluctuations in the intensity of Raman signals and fluorescence background are observed, and a theoretical model is proposed to elucidate the mechanism.

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II. EXPERIMENTAL

Si templates with nano-scale roughness were formed on *p*-type (100) Si wafers (1-60 Ω-cm) by wet etching in a 15 wt. % NaOH solution at 30 °C for 8 min. High-density and randomly distributed Si islands can be observed from the Si surface after etching according to the AFM (Veeco Multimode) image depicted in Fig. 1 and our previous work.[4] The embedded ITO (In_2O_3 92 wt. %, SnO_2 8 wt. %) nano-island arrays on the Si templates were prepared by pulsed laser deposition (248 nm KrF laser, 300 mJ/pulse, 3.0 Pa oxygen) at room temperature. To improve crystallization and conductivity, the samples were annealed at 550 °C in vacuum (2×10^{-3} Pa) for 30 min. The crystal structure of the ITO film was characterized by x-ray diffraction (XRD, Bruker) on a 350 nm thick ITO film. The result (not shown here) indicates that the annealed ITO films retain the cubic crystal structure of In_2O_3 and the ITO grains with an average size of 40 nm (Scherrer equation) are randomly distributed.

A 10^{-5} M aqueous rhodamine 6 G (R6 G) solution was used to evaluate the Raman enhancement effect, and the samples were kept in the R6 G solution for 40 min before measurement. The SERS measurements were performed at room temperature on a Horiba Jobin-Yvon LabRAM HR800 micro-Raman spectrometer with a 514 nm laser focused to a diameter of 1 μm. The incident power was 0.55 mW and acquisition time was 10 s. Koehler illumination was adopted to acquire on-site reflective optical images of the ITO/Si samples.

The refractive index (n), extinction coefficient (κ), and thickness (d) of the ITO films were measured from the *s*-polarization reflective spectra of the ITO/Si samples and Si wafer on a spectrometer equipped with a Xe lamp and Iceland spar polarizer at an incident angle of 45°. Figure 2 shows the representative *s*-polarization reflectivity ratio $R_{ITO/Si}/R_{Si}$

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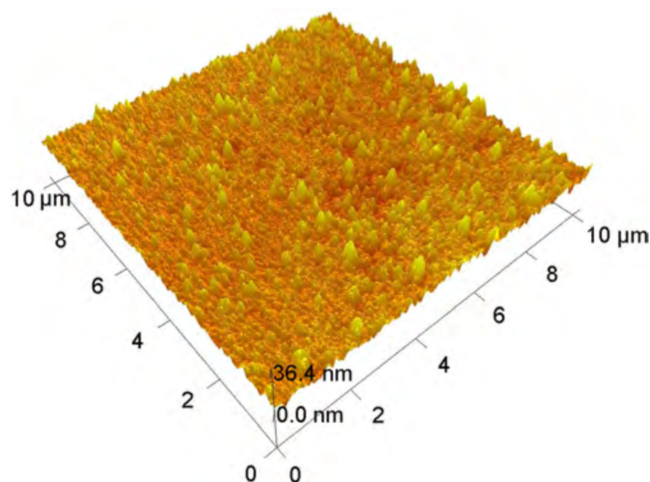

FIG. 1. (Color online) AFM image of the etched Si surface.

spectrum of a ITO(650 nm)/Si sample and Si wafer. The refractive index and extinction coefficient of the ITO film were obtained based on the optical interference theory.[12] The thickness distribution of ITO films was determined from the *s*-polarization reflective spectra and the obtained refractive index curve in Fig. 2.

III. RESULTS AND DISCUSSION

Figure 3 shows the enhanced Raman spectra of R6 G (10^{-5} M) molecules absorbed on the ITO films with six different thicknesses with an average spacing of 65 nm together with the corresponding reflected white-light optical images of the films. The Raman intensity varies substantially with ITO film thicknesses. Strong Raman signals and fluorescence background can be observed from the spectra obtained from the 70, 200, and 330 nm thick ITO films, but very weak Raman signals and fluorescence background are observed from the spectra obtained from the 150 and 270 nm thick ITO films. Because no visible R6 G Raman signals and fluorescence background can be observed from the spectrum (marked by 0 nm) of R6 G mol-

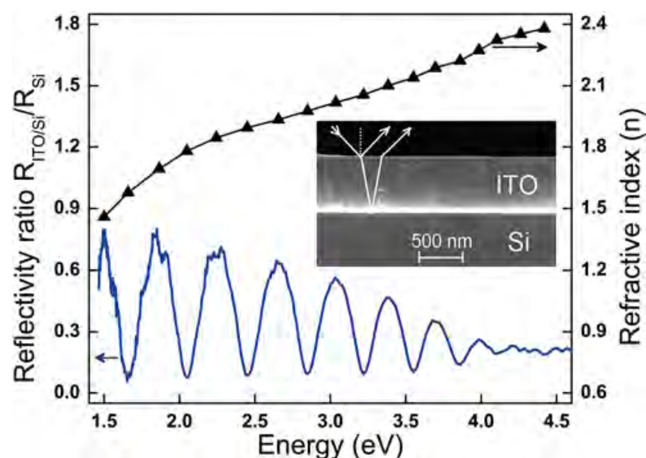

FIG. 2. (Color online) Ratio of *s*-polarization reflectivity spectrum of a ITO(650 nm)/Si sample to that of Si wafer (left) and calculated refractive index of ITO film (right). The insert is a cross-sectional scanning electron microscopy image of the ITO/Si sample and the lines with arrowheads denote the optical interference at an incident angle 45°.

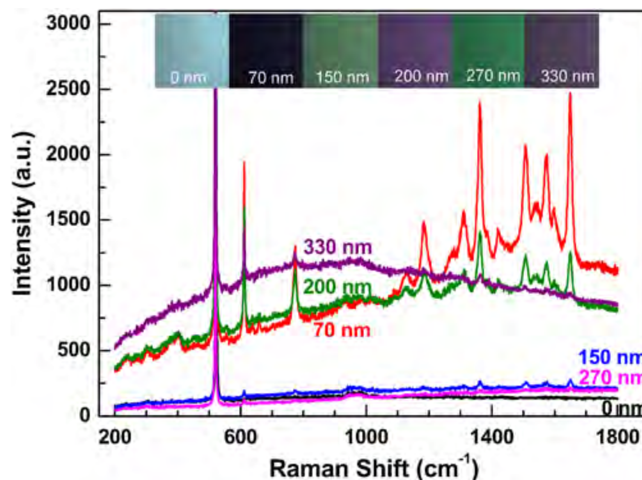

FIG. 3. (Color online) SERS spectra acquired from R6 G molecules adsorbed on ITO films with different thicknesses on nanoroughened Si templates. The insert shows the corresponding optical images of the samples by reflective white-light interference. The size of each image is 50 μm.

ecules on the etched Si template, the strong Raman signals and fluorescence background in some of the spectra are due to the enhancement by ITO films on rough Si templates.[4]

The large fluctuations in the Raman signals and fluorescence background with film thickness are in accordance with the color variation in the optical images (see the insert of Fig. 3). It is well known that the observed color is caused by optical interference between the surface and interface of a transparent film. The color corresponds to the wavelength at which the light shows the maximum reflection. Here, the color of the optical images is green for the 150 and 270 nm thick ITO films, black for the 70 nm thick ITO film, and deep purple for the 200 and 330 nm thick ITO films. The refractive index distribution (see Fig. 2) shows that the refractive index of the ITO film for green light is about 1.88. It can be deduced that green light forms the first order and second order reflection maximum at film thicknesses of around 150 nm and 270 nm, respectively. Similarly, green light forms the first, second, and third order reflection minimum at film thicknesses of around 70, 200, and 330 nm, respectively.

The detailed variations in the intensity of the Raman signal and fluorescence background are shown in Fig. 4(a) as a function of ITO film thickness [intensity at 612 cm^{-1} (531 nm) is used]. The changes in the Raman signal and fluorescence background with film thicknesses exhibit a monotonic trend although the intensity ratios are not constant. The period is about 130 nm, which is consistent with the spacing of the green reflective interference fringes. The in-step variations in the Raman spectra and optical interference images indicate that the observed periodical fluctuations in the Raman signals and fluorescence background arise from optical interference as well.

To investigate the mechanism, the multi-reflection model is adopted.[13] As shown in Fig. 5, three self-interference terms including the incident light, scattered light, and emitted light are considered and treated separately. The fluctuations in the Raman spectra are the final result of the three self-interference terms. Self-interference of the incident light modulates the electromagnetic intensity on the surface of the ITO film. The lowest electromagnetic field corresponds to the lowest

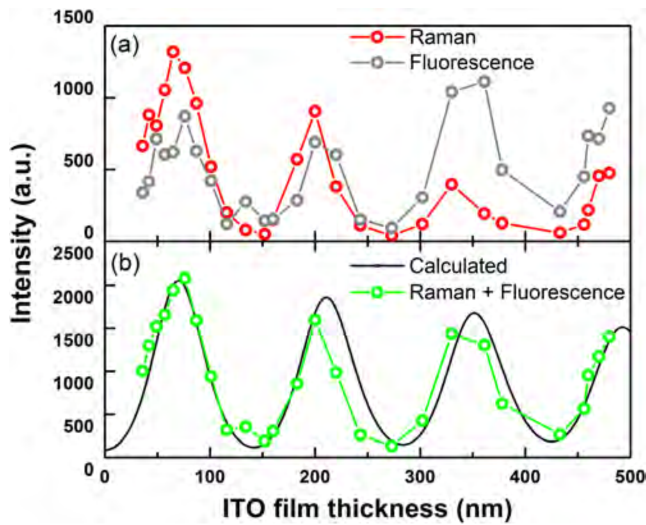

FIG. 4. (Color online) ITO film thickness dependence: (a) Raman signal and fluorescence background and (b) Sum at $612\,\text{cm}^{-1}$. The curve in (b) is the fitted result using the modification factor $F(d, \lambda_1, \lambda_2)$ where $a = 3$.

absorption of molecules and occurs when reflection from the ITO surface is maximum. This is why the minimum of the Raman signals and florescence background is always observed at the green reflective fringes when a green laser is the excitation source. Self-interference of the incident light has a uniform influence on the entire Raman spectrum. However, self-interference of the scattered and emitted light depends on the wavelength. Hence, the intensities at different wavelengths reach maximum values at different film thicknesses. That is to say, the spectral shape varies with the film thickness.[8,14] Figure 3 shows that the most intense region in the Raman spectrum shifts from the right to the left when the film thickness is increased from 70 nm to 330 nm.

Numerical calculation and theoretical derivation are carried out to investigate the combined effects of the three interference terms. Here we only discuss the *s*-polarization component because the interferences arising from *s*-polarization and *p*-polarization are the same in this backscattering geometry. The *s*-polarization reflectance (r) and reflectivity (R) of the three-phase media are:[12]

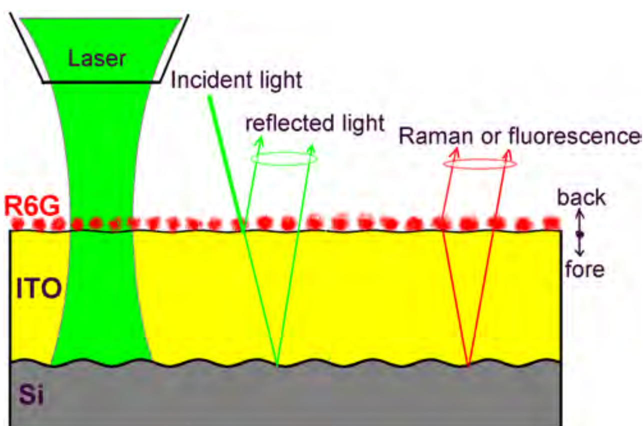

FIG. 5. (Color online) Schematic diagram of the optical self-interference of incident light, scattered light, and emitted light. Although the backscattering geometry is adopted in the experiments, a small angle deviating from the normal of the surface is used to avoid line overlapping.

$$r_{123} = \frac{r_{12} + r_{23}e^{2i\beta}}{1 + r_{12}r_{23}e^{2i\beta}}, \quad R = |r_{123}|^2$$

for light incident from phase 1 and $\beta = 2\pi(d/\lambda)N_2\cos\theta_2$ and r_{jk} are the reflectance at interface of phase j and k:

$$r_{jk} = \frac{N_j\cos\theta_j - N_k\cos\theta_k}{N_j\cos\theta_j + N_k\cos\theta_k}$$

for light incident from phase j. $N_j = n_j + i\kappa_j$ is the complex refractive index of phase j and θ_j is the incident or refractive angle of phase j.

For the air (phase 1)/ITO (phase 2)/Si (phase 3) system, the complex refractive indexes are set as $N_1 = 1 + i0$, $N_2 = 1.886 + i0.032$ (514.5 nm) and $1.868 + i0.032$ (531 nm), and $N_3 = 4.232 + i0.062$ (514.5 nm) and $4.160 + i0.053$ (531 nm).[15] The modification factor $f_1(d, \lambda_1)$ of the excitation intensity due to self-interference of the incident light (λ_1) is $f_1(d, \lambda_1) = 1 - R$.

The interference effects of the scattered and emitted light are quite complicated because the radiation is anisotropic in three-dimensional space. To simplify the treatment, we only consider the initial scattered or emitted intensity for the backward direction $I_{back} = \frac{1}{2}N_1E_{10}^2$ and forward direction $I_{fore} = \frac{1}{2}N_1E_{20}^2$. To properly interpret the data, the two components are assumed to interfere with each other. By setting a new parameter $a = I_{fore}/I_{back}$, the modification factor $f_2(d)$ of the detected Raman or fluorescence intensity caused by self-interference of the scattered or emitted light (λ_2) is:

$$f_2(d, \lambda_2) = \frac{1}{1+a}\left|1 + \sqrt{a}\frac{2\sqrt{N_1N_2}}{N_1 + N_2}\frac{r_{23}e^{2i\beta}}{1 + r_{12}r_{23}e^{2i\beta}}\right|^2.$$

The combined modification factor of the interference effects are given by $F(d, \lambda_1, \lambda_2) = f_1(d, \lambda_1) \cdot f_2(d, \lambda_2)$. Figure 4(b) shows the calculated result of $F(d, \lambda_1, \lambda_2)$ as a function of film thicknesses, where $\lambda_1 = 514.5\text{nm}$, $\lambda_2 = 531\text{nm}$, and $a = 3$. The calculated results agree well with the total intensity of the Raman signal and fluorescence background, thereby verifying the validity of this theoretical method in the study of interference phenomena.

Under interference modulation, Raman scattering and fluorescence are enhanced by the high electric field near the surface of the ITO film due to excitation of local SP polaritons too. By considering the influence of optical interference and film absorption, the Raman intensity degrades as the film thickness is increased, but the fluorescence background shows an opposite change in this thickness range. Besides the thickness-dependent plasmonic intensity, there are several factors such as surface roughness, absorption capability, and surface conductance that are possibly thickness dependent thereby influence the degree of enhancement. Experiments focusing on these factors are being carried on, and related results will be reported in due course.

IV. CONCLUSION

Strong dependence of the SERS spectra of adsorbed R6 G molecules on the thickness of ITO films produced on Si templates with nano-scale roughness is observed and

analyzed in terms of multiple reflection interference. The results provide strong evidence that the interference effect cannot be ignored in enhanced Raman scattering from ITO and provide insight to the origin and mechanism.

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[1]S. Szunerits, X. Castel, and R. Boukherroub, J. Phys. Chem. C **112**, 15813 (2008).
[2]M. Kanehara, H. Koike, T. Yoshinaga, and T. Teranishi, J. Am. Chem. Soc. **131**, 17736 (2009).
[3]C. R. Zamarreno, M. Hernaez, I. D. Villar, I. R. Matias, and F. J. Arregui, IEEE Sens. J. **10**, 365 (2010).
[4]Y. M. Yang, T. Qiu, H. L. Ou, X. Z. Lang, Q. Y. Xu, F. Kong, W. J. Zhang, and P. K. Chu, J. Phys. D **44**, 215305 (2011).
[5]S. Franzen, J. Phys. Chem. C **112**, 6027 (2008).
[6]C. Rhodes, M. Cerruti, A. Efremenko, M. Losego, D. E. Aspnes, J. P. Maria, and S. Franzen, J. Appl. Phys. **103**, 093108 (2008).
[7]S. Gupta, G. Morell, R. S. Katiyar, J. R. Abelson, H. C. Jin, and I. Balbert, J. Raman Spectrosc. **32**, 23 (2001).
[8]Y. M. Yang, L. W. Yang, M. Q. Cai, and P. K. Chu, J. Appl. Phys. **101**, 093503 (2007).
[9]R. J. Nemanich, C. C. Tsai, and G. A. N. Connell, Phys. Rev. Lett. **44**, 273 (1980).
[10]Y. Y. Wang, Z. H. Ni, Z. X. Shen, H. M. Wang, and Y. H. Wu, Appl. Phys. Lett. **92**, 043121 (2008).
[11]X. Ling and J. Zhang, J. Phys. Chem. C **115**, 2835 (2011).
[12]W. N. Hansen, J. Opt. Soc. Am. **58**, 380 (1968).
[13]D. Yoon, H. Moon, Y. W. Son, J. S. Choi, B. H. Park, Y. H. Cha, Y. D. Kim, and H. Cheong, Phys. Rev. B **80**, 125422 (2009).
[14]L. B. Gao, W. C. Ren, B. L. Liu, R. Saito, Z. S. Wu, S. S. Li, C. B. Jiang, F. Li, and H. M. Cheng, ACS Nano **3**, 933 (2009).
[15]D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).