Interference effects on indium tin oxide enhanced Raman scattering

Yimin Yang, Teng Qiu, Fan Kong, Jiyang Fan, Huiling Ou et al.

Citation: J. Appl. Phys. 111, 033110 (2012); doi: 10.1063/1.3684965
View online: http://dx.doi.org/10.1063/1.3684965
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v111/i3
Published by the American Institute of Physics.

Related Articles
Optical characterization of ZnO nanopillars on Si and macroporous periodic Si structure
Radiative damping suppressing and refractive index sensing with elliptical split nanorings
Symmetrically tunable optical properties of InGaN/GaN multiple quantum disks by an external stress
Optical properties of a-plane (Al, Ga)N/GaN multiple quantum wells grown on strain engineered Zn1−xMgxO layers by molecular beam epitaxy
Spectrally and temporarily resolved luminescence study of short-range order in nanostructured amorphous ZrO2
J. Appl. Phys. 110, 103521 (2011)

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors
Interference effects on indium tin oxide enhanced Raman scattering

Yimin Yang,1,a) Teng Qiu,1,a) Fan Kong,2 Ji Yang Fan,1 Huiling Ou,1 Qingyu Xu,1 and Paul K. Chu3
1Department of Physics, Southeast University, Nanjing 211189, People’s Republic of China
2School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People’s Republic of China
3Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

(Received 21 October 2011; accepted 12 January 2012; published online 14 February 2012)

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.

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 (In2O3 92 wt. %, SnO2 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 In2O3 and the ITO grains with an average size of 40 nm (Scherrer equation) are randomly distributed.

A 10−3 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 (k), 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 $R_{ITO/Si}/R_{Si}$
spectrum of an 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. 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 molecules 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.

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. 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
The interferences arising from three-phase media are:12

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

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. \( N_j = n_j + ik_j \) is the complex refractive index of phase j and \( \theta_j \) 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). The modification factor \( f_1(d, \lambda_1) \) of the excitation intensity due to self-interference of the incident light (\( \lambda_1 \)) 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 \( I_{\text{back}} = \frac{1}{2}N_1E_{10}^2 \) and forward direction \( I_{\text{fore}} = \frac{1}{2}N_1E_{20}^2 \). To properly interpret the data, the two components are assumed to interfere with each other. By setting a new parameter \( a = I_{\text{fore}}/I_{\text{back}} \), the modification factor \( f_2(d) \) of the detected Raman or fluorescence intensity caused by self-interference of the scattered or emitted light (\( \lambda_2 \)) 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.

ACKNOWLEDGMENTS

This work was jointly supported by the National Natural Science Foundation of China under Grant Nos. 51071045 and 11074037, Specialized Research Fund for the Doctoral Program of Higher Education under Grant No. 20090092120032, Excellent Young Teachers Program of Southeast University, and Hong Kong Research Grants Council (RGC) General Research Funds (GRF) CityU 112510.