Thickness-gradient dependent Raman enhancement in silver island films

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We show evidence of a dependence of the enhancement of the Raman scattering cross section on the length of the gradient in graded silver island films. A factor-of-three increase in the Raman signal is observed for gradients with length of the order of 0.5 mm when compared to gradients of the order of 9 mm. Scanning electron microscopy reveals the nanostructure of the two films to be statistically similar. We attribute the observation to differences in plasmon hybridization in the gradients arising from long range structural differences. © 2009 American Institute of Physics.

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The observation of remarkable enhancements in the Raman scattering cross section in the vicinity of metallic nanostructures is attributed to the concentration of electromagnetic energy by plasmonic resonances.\textsuperscript{1} Significant effort has focused on elucidating optimal nanostructures to maximize this surface-enhanced Raman scattering (SERS), which has gained extra impetus in the last decade since the demonstration of single molecule SERS.\textsuperscript{2,3} Optimizing the SERS effect requires two conditions to be fulfilled: a plasmonic resonance in the nanostructure at a frequency close to that of the laser used to probe the Raman scattering and a nanostructure which promotes a localized concentration of energy in a so-called “hot spot.”\textsuperscript{4} The majority of experimental SERS studies focus on optimizing only one of these requirements. Here we show that nanostructures which are identical at the local level may exhibit different SERS enhancement factors due to changes in the plasmonic resonance frequency determined by the differences in the structure on a much larger scale.

The observation of changes in the plasmonic resonances due to long range effects has been previously documented. Heinzie \textit{et al.}\textsuperscript{5} demonstrated that by changing the patterning of arrays of silver nanoparticles over many micrometers, the transmission spectrum was dramatically affected. The effect is attributed to hybridization of the plasmonic resonances; the electric field inside a metallic nanoparticle is determined not only by its conduction electrons but also by the fields produced in adjacent metallic structures.\textsuperscript{5} Since the effect is reciprocal, the plasmonic processes in nanostructured metallic arrays are a hybridization of individual local resonances over a large area. The implication for the SERS process is that the local nanostructure (i.e., a well defined hot spot) is affected by the long range nanostructure.

To investigate this effect we developed a SERS substrate based on the extensively investigated metal-island films (MIFs). Traditionally, MIFs are produced by physical vapor deposition and consist of an array of oblate spheroids, isotropic in the substrate plane, with the island size and density controlled by adjusting the deposition rate and substrate temperature. Here, we introduce a thickness gradient in the film resulting in a long range structural anisotropy, which is intended to influence the plasmonic resonances at the local level via hybridization. Since SERS enhancement factors are difficult to quantify we produced two gradients on a single substrate. This avoids disparities in the sample preparation, thus allowing qualitative comparison of the SERS enhancements arising solely from differences in the gradients.

MIFs were produced by magnetron sputtering a silver cathode onto a room temperature Si/SiO\textsubscript{2} (50 nm) substrate, precleaned in piranha solution and rinsed in H\textsubscript{2}O. A gradient in the film thickness was produced by depositing the film through a slits mask,\textsuperscript{7} with the distance from the slits determining the deposition rate and hence the thickness of the film [Fig. 1(a)]. The nominal thickness ranged from approximately 1 to 85 nm over a 9 mm distance. We define this gradient as “gradient A.” A second gradient (“gradient B”) was produced at the same time by partially covering the substrate with a 300 µm thick block under the slit mask, resulting in a narrow region (less than 1 mm) of the substrate being shadowed. The two film gradients, produced on the

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FIG. 1. (Color online) (a) Schematic of the thin film deposition. Two gradients (denoted A and B) with different lengths by depositing through a mask (“M”) and shadowing part of the substrate with a thin block (“S”), (b) shows a photographic image and (c) the thickness and deposition rates.
same substrate with the same deposition rates and temperature, are therefore identical in all respects except their length. A photographic image of the substrate is shown in Fig. 1(b). A color change across the sample due to plasmon resonance absorption is observed, which redshifts as the film thickness increases.8,9

A critical part of the experiment is to ensure that the SERS test molecule is evenly distributed over the substrate surface. The substrate was immersed in a 75 μM aqueous solution of Rhodamine 6G (R6G) for 60 s. This concentration was empirically chosen to be the lowest concentration, which displayed a low noise in the Raman scan, suggesting monolayer coverage of the adsorbed molecules. The sample was slowly removed from the solution in a direction perpendicular to the direction of the film gradient. The liquid remained attached via surface tension to the main reservoir, thereby avoiding the formation of droplets on the substrate. After removal no liquid was visible on the substrate, ensuring that all R6G adsorption occurred evenly during the immersion process. Raman spectra were recorded using a commercial Raman spectrometer (514 nm, 2 μW) with sample scanning capability. Repeated measurements at a single location gave stable results indicating that laser annealing did not occur. The laser was focused through a 50× (NA=0.75) objective lens (W.D.=0.38 mm), forming a diffraction limited optical spot approximately 1 μm in diameter. Scattered light was collected by the same objective and filtered through a holographic notch filter before spectroscopic sampling with a 300 line grating and charge coupled device. The spectral resolution was 4 cm⁻¹. Raman spectra were collected at 50 μm steps with an integration time of 1 s.

Figure 2 (inset) shows typical R6G scattering spectra from the sample from the points at 0.5 and 4 mm (roughly corresponding to the centers of gradients B and A). The spectra show sharp Raman peaks, which are ascribed to R6G molecular vibrations.10 To assess the enhancement of the substrate, we plot the integrated number of counts (baseline corrected) in the range from 1630 to 1670 cm⁻¹ incorporating the peak at 1650 cm⁻¹, as shown in Fig. 2. The plot indicates the relative enhancement of the substrate in units of s⁻¹ W⁻¹ cm². It does not show an enhancement factor, as it often shown in SERS studies, since we do not have knowledge of the unenhanced signal. In the absence of silver (0 mm), and when the silver film is continuous (1 mm), the Raman peaks are indistinguishable from the background noise. When the film is composed of large distinct nanoparticles the enhancement is strongest.

The striking characteristic of this plot is the significantly enhanced signal in the central region of gradient B with respect to gradient A, an enhancement of more than a factor of 3. We have consistently repeated this result and also observed it with gold films. The result is not a statistical anomaly; the noise in the data is small compared to the difference in enhancement. We propose that this is an all-optical effect; it is due to plasmon hybridization affecting the frequency of the plasmon resonance at the hot spots. There are two competing explanations that must be explored to test this hypothesis: homogeneity of the test molecule on the substrate and differences in the nanostructure of the two gradients.

The first alternative argument is that the concentration of the test molecule on the surface is inhomogeneous. We stress here that the effect is not due to the method of applying the R6G molecules. It is repeatedly observed whether the substrates were immersed for 1 or 10 min, rinsed or not rinsed, and dried with nitrogen gas or not. An important observation against the argument of molecular inhomogeneity is that the level of enhancement depends on the laser excitation frequency. At wavelengths of 488 and 633 nm the effect is observed, however the maximum difference in the enhancement factor was around a factor of 2 in both cases. Since Raman scattering intensity is linearly dependent on the concentration of the scattering molecule, we would expect the effect to be independent of the laser excitation frequency. We therefore dismiss the argument that the effect is due to a difference in the R6G concentration on the substrate.

The second alternative explanation is that the nanostructures in the two gradients are different. Since the angle of incidence of the atoms impinging on the substrate surface is different, the nucleation density and particle size may also differ as a function of the nominal film thickness. We investigated the film nanostructure using scanning electron microscopy (SEM). Figure 3 shows images of the film at 100 μm intervals in gradient B and at 500 μm intervals in gradient A. It is clear from the images that the nanoparticles on a local level are visually similar in size, shape, and density in the two gradients. A statistical analysis of the SEM images was performed for gradients A and B. The SEM images were converted to binary images and the area coverage, number of islands, and particle size were determined using a statistical software package. The number of islands and island size for a given surface area coverage are the same for both gradients [Figs. 3(a) and 3(b)] suggesting that there is no significant statistical difference in the film nanostructure. Since the resolution of the micrographs is limited we cannot completely rule out a statistical difference in the interparticle spacing below a few nanometers. The interparticle spacing is a crucial parameter affecting the electric field enhancement and this must be considered a possible origin of the effect. However, the evidence points to the nanostructure playing a negligible role in the effect under discussion. Considering once again the difference in the enhancement factors at different laser excitation frequencies, if the nanostructure of the two gradients were different, different laser excitation frequen-
frequencies should produce identical relative enhancements in the two gradients.

Since the effect is convincingly shown to be an optical phenomenon we may speculate as to the exact nature of the processes. Optimized SERS structures consist of both an ideal nanostructure and a maximized transfer of laser energy to such a hot spot. Since the gradient films consist of a large range of structurally different hot spots, a change in the plasmon hybridization due to the length of the gradient may shift the absorption maximum closer to the laser excitation wavelength at any given hot spot. Thus the nanostructure is optimized both structurally and "optically." This may manifest as either an increase in the number of hot spots or an improvement in the optimal nanogap distance, thereby increasing the excitation energy in the nanogap.

With respect to the design of SERS substrates, the results presented here provide some interesting possibilities. The demonstration of nanoparticle gradients with lengths scales of a few hundred nanometers will allow the exploitation of such an effect. Recent attempts have been made to investigate "nanolenses" composed of nanoparticles of decreasing size, which concentrate the photon energy to the smallest nanogap. In some respects the results presented here are similar; optimizing the plasmonic absorption of a nanogap. Recent interest in the transfer of photonic energy over many micrometers is now facing up to the realities of unacceptable losses due to electron scattering. In contrast, sensing changes in the plasmonic environment over many tens or hundreds of micrometers does not suffer from this drawback and provides exciting challenges.

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