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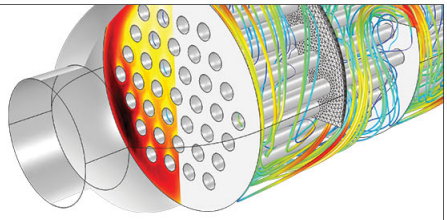

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Spoof-like plasmonic behavior of plasma enhanced atomic layer deposition grown Ag thin films

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The plasmonic behavior of Ag thin films produced by plasma enhanced atomic layer deposition (PEALD) has been investigated. We show that as-deposited flat PEALD Ag films exhibit unexpected plasmonic properties, and the plasmonic enhancement can differ markedly, depending on the microstructure of the Ag film. Electromagnetic field simulations indicate that this plasmonic behavior is due to air gaps that are an inherent property of the mosaic-like microstructure of the PEALD-grown Ag film, suggesting that this is a metamaterial with behavior very similar to what would be expected in spoof plasmonics where gaps are fabricated in films to create plasmonic-like resonances. © *2012 American Institute of Physics*. [doi:10.1063/1.3679106]

A technique that depends exclusively on plasmonics is surface enhanced Raman scattering (SERS), in which the Raman signal can be enhanced by many orders of magnitude by the use of metal nanoparticles[1] and metal shell/dielectric core nano particle composites.[2] This enhancement is due to the local electromagnetic fields that are created by the laser excitation of localized surface plasmons. Current research with metallic nanoparticles suggests that the size, geometry, shape, and alignment are important parameters for this enhancement.[3–6] The metal which exhibits the highest SERS in the visible is silver (Ag), and many SERS enhancement studies have been reported for Ag-based nanoparticles.

Since Ag-based nanoparticles are required to elicit the SERS effect, one would not expect that a flat Ag film would exhibit such localized plasmonic properties. However, Pendry *et al.*[7] has suggested that plasmons can be localized at gaps that are created by corrugating flat metallic films, which need not be plasmonic. This effect is known as spoof plasmonics, and high fields exist in the vicinity of these corrugations. Up to now, lithography or deliberate fabrication has been required to produce these structures.

Here, we present the results on the unexpected plasmonic behavior of Ag thin films produced by plasma enhanced atomic layer deposition (PEALD). We show that as-deposited, flat PEALD Ag films exhibit plasmonic properties, and the enhancement can differ markedly, depending on the microstructure and thickness of the Ag film. Unlike ordinary Gaussian roughness, PEALD-grown Ag films exhibit spoof like corrugations that are created at the boundaries between neighboring grains. The PEALD films are two-dimensional (2D) with a cylindrical grain structure, resulting in a film that is mosaic in nature. We show that in these PEALD Ag films, the plasmonic fields originate from the air gaps located between the Ag islands, and the strength of the enhancement correlates with the film thickness and gap density (2D island size). We also show that the SERS from self-assembled monolayers of benzene thiol (BZT) can be very strong on these PEALD films. Furthermore, the SERS from PEALD-coated ZnO or Ga_2O_3 nanowires is 100× more intense than from nanowires[6] coated by any other Ag deposition technique, implying the presence of the spoof-plasmon modes. Theoretical simulations of the electric field enhancements from the gaps in PEALD Ag support the experimental results.

The growth of the Ag films was performed by remote PEALD,[8,9] using Ag(fod)(PEt_3) (fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctade-3,5-dionato) and hydrogen plasma as the precursors.[8] The Ag films were grown at 125 °C on Si(100). The thicknesses of the Ag films ranged from 9.7 nm to 49.1 nm and were obtained by a n,k spectrometer. All PEALD Ag films were examined using a Leica Cambridge Stereoscan 360FE scanning electron microscope (SEM) with energy dispersive x-ray (EDX) capabilities. SERS spectra were obtained using two micro-Raman systems, one operating at 514.5 nm and the other at 785 nm. The former was a home built system described previously, and the latter was a DeltaNu Reporter 785. The spectra were collected with a laser power of less than 3 mW.

The images of four different thickness Ag films grown by PEALD are shown in Figure 1. Note the differences in microstructure, where the thickest film, D, exhibits the largest continuous 2D islands, separated by air gaps where the islands meet. Film C has a similar microstructure, with smaller islands. In film B, the microstructure has changed significantly, consisting of closely spaced, smaller, more spherical Ag islands. The thinnest film, A, also consists of small Ag islands, but they are spaced far apart.

The corresponding SERS spectra of BZT for the 514 and 785 nm laser lines are shown in Figure 2. Note that although film C and film D have very similar island shapes, they show very different SERS enhancements, where the SERS in D is much weaker than in C. Furthermore, although film B and film C show very different morphologies, they both exhibit strong and similar SERS enhancements. Finally,

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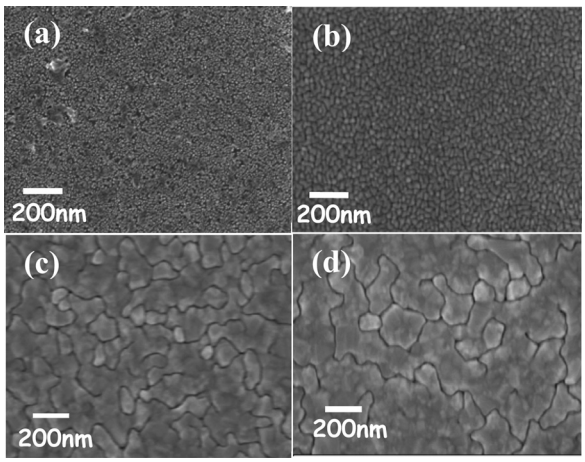

FIG. 1. SEM image of Ag films of different thicknesses produced by PEALD. (a) Film A, 9.7 nm; (b) film B, 31.2 nm; (c) film C, 43.4 nm; and (d) film D, 49 nm.

the thinnest film, A, exhibits a very weak SERS enhancement, similar to D, which is the thickest Ag film. These results were similar when SERS was obtained using the 514.5 nm Raman system, as shown in Figure 2.

In order to confirm that this effect is unique to the PEALD Ag film, we formed a Ag film using e-beam deposition and also coated it with BZT. The SEM microstructure and the SERS spectra from e-beam and PEALD Ag films are shown in Figure 3. Note the very different morphology of

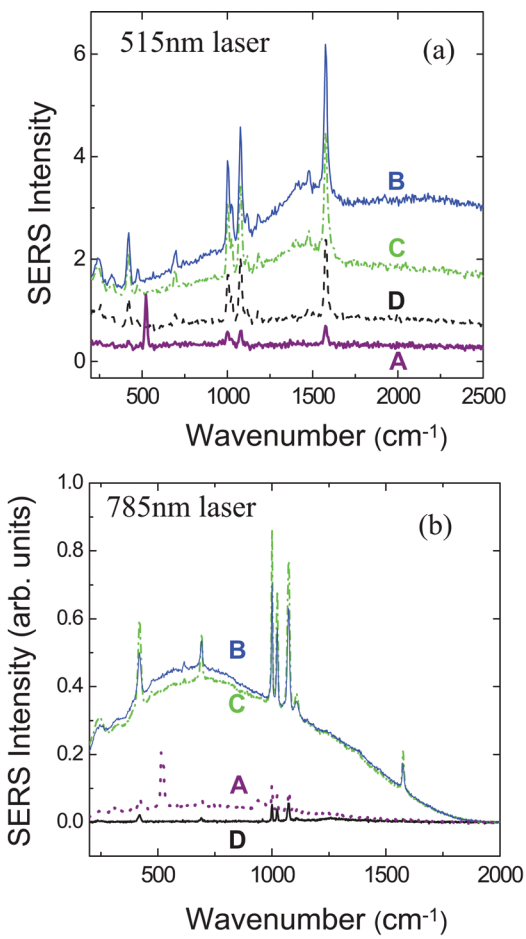

FIG. 2. (Color) SERS intensity for BZT for films A-D for 515 nm (a) and 785 nm (b) laser light excitation.

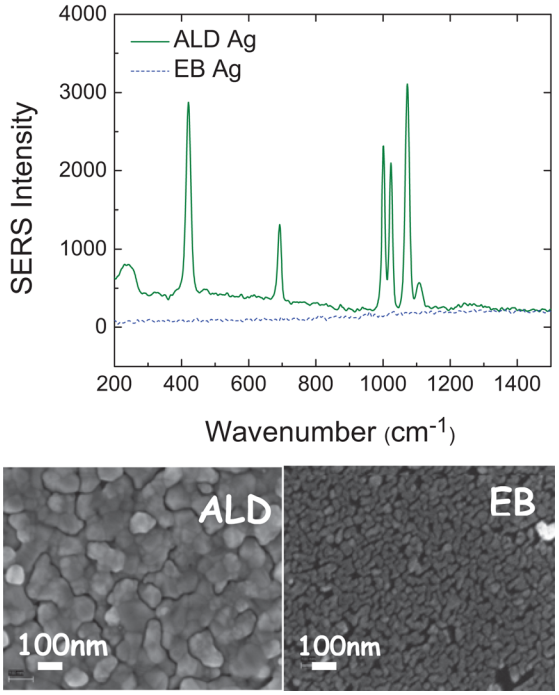

FIG. 3. (Color online) SEM images and comparison of the SERS signal of BZT of a PEALD Ag film (ALD) and e-beam evaporated Ag film (EB).

the two films. In the case of SERS, it is clear that no notable SERS signal is observed on the e-beam deposited Ag films, while the PEALD Ag film shows a strong SERS spectrum. This indicates that the microstructure of the PEALD film is the source of the plasmonic response.

In order to explain this unusual behavior, we performed 3D simulations of the electric fields of these microstructures using the COMSOL multiphysics finite-elements package.[10] The simulations were performed using the quasi-static approximation, which is appropriate for geometries smaller than the wavelength of light. In this case, the structures of interest in the PEALD films were 5 nm or smaller wide gaps that were 200 nm in length and coaxial structures of 200 nm or less. The polarization of light was circular to simulate random orientations of the structures. In addition, periodic boundary conditions were used to avoid spurious fields at the edges of the geometry. The sample microstructure and thickness were obtained from experimental results, and the plasmonic electric field enhancement was calculated for the structures modeled and was then compared to the SERS results obtained experimentally. The three geometric structures used to describe the shape of PEALD Ag film microstructure in the calculations are shown in Figure 4. They were linear air gaps of thickness 2 nm, coaxial cylinder air gaps, and "racetrack" air gaps, which are elongated oval structures. Each of the four PEALD Ag films was analyzed in terms of the percentage of each type of geometric structure that they were comprised of, and using this data, the plasmonic enhancement, $(E/E_0)^4$, and its spectral and spatial dependence were calculated. By changing the size of the unit cell, periodic boundaries allowed us to simulate the density of a given structure as determined from the SEM images.

The enhancements for all four films were obtained as a function of excitation wavelength and results are shown in Figure 4. Note that for our experimental results, there are

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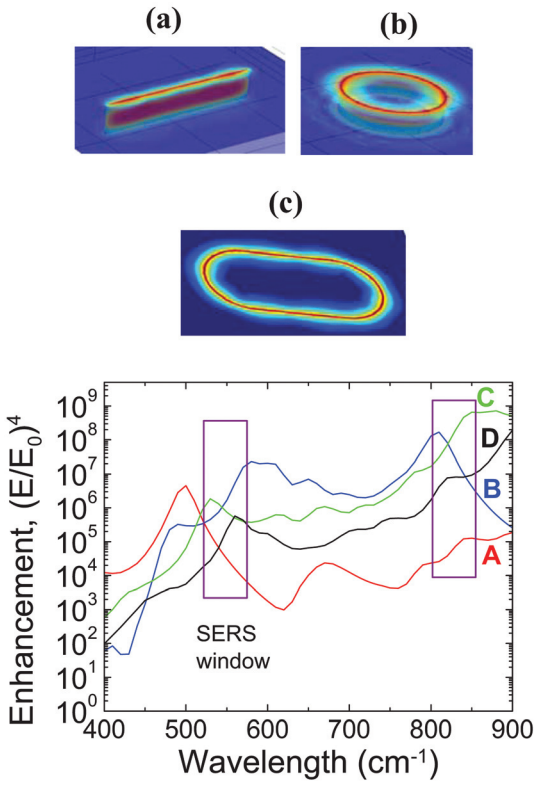

FIG. 4. (Color) The three geometric air gap shapes: (a) linear gap, (b) cylindrical gap, and (c) "racetrack" gap, used to obtain the COMSOL plasmonic enhancement for the four PEALD Ag thin films and the resulting predicted enhancement as a function of incident wavelength for each Ag film. The letters A, B, C, and D correspond to the films shown in Figure 1. Film A consists of non-interacting cylinders, 10 nm thick; film B consists of closely spaced cylinders, 30 nm thick; film C consists of slots, racetracks, and cylinders, 40 nm thick; film D consists of fewer slots, racetracks, and cylinders, 50 nm thick.

two "SERS windows," which correspond to the 514 nm laser line and the 785 nm line and were used in this experiment. The width of the window approximates the experimental spectral range of SERS from the BZT molecule. If one examines the predicted enhancements for the 514 nm line, theory would predict that films A and D would exhibit lower enhancements, while films B and C should show stronger enhancements, and they would be expected to be of similar magnitude. If one now examines the 785 nm window, the calculations would predict that films A and D would show the weakest signals, while the two strongest enhancements would be for B and C. Comparing this prediction to the experimental results shown in Figure 2, it is clear that the general trend is the same as predicted from the COMSOL simulations, in that the strongest comparable SERS exists in films B and C, while films A and D show weaker SERS. Note that although films C and D exhibit very similar 2D island morphologies, both experiment and theory show that C would exhibit stronger enhancement than D. Also, while films B and C have very different morphologies, both experiment and theory show these two films should have a similarly strong SERS enhancement.

From these results, it is clear that a strong plasmonic enhancement is observed from flat PEALD Ag thin films without the need for artificial lithographic patterning, nor does one have to form Ag based nanoparticles to take advantage of the plasmonic properties. This illustrates that as-deposited Ag PEALD films can provide appropriate enhancements for large-area SERS sensors. These PEALD SERS substrates differ markedly from the common SERS substrates based on roughened Ag surfaces in which the rough substrates work because the roughness is spherical in nature with a Gaussian distribution of sizes and it is only a surface effect. In our case, the situation is very different because our PEALD films are characterized by collections of coaxial type gaps that extend from the surface to the underlying substrate. This structure is not a typical roughened surface, and its optical response shows a well defined plasmonic resonance whose wavelength position depends on the thickness of the film. The reflectivity spectra cannot be modeled using a roughened Ag surface. In fact, the structure and the resultant resonances are the characteristic of coaxial hybrid spoof structure, which operate in the mid to far IR.

In conclusion, we have shown that PEALD Ag films exhibit plasmonic behavior which leads to localized surface plasmon modes from films not placed on plasmonic geometries. Simulations indicate that the plasmonic behavior is due to the gaps that are an inherent property of the PEALD growth of Ag and account for the trends observed between the strength of the SERS observed in the green and red. This suggests that using PEALD Ag on plasmonic geometries will produce enhancements that exceed those of non-textured Ag. This behavior is very similar to what would be expected in hybrid spoof plasmonics and suggests that PEALD Ag is a metamaterial.

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