Research Letter

Surface Plasmons and Surface Enhanced Raman Spectra of Aggregated and Alloyed Gold-Silver Nanoparticles

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Received 17 February 2009; Accepted 10 May 2009

Recommended by Roberto Morandotti

Effects of size, morphology, and composition of gold and silver nanoparticles on surface plasmon resonance (SPR) and surface enhanced Raman spectroscopy (SERS) are studied with the purpose of optimizing SERS substrates. Various gold and silver films made by evaporation and subsequent annealing give different morphologies and compositions of nanoparticles and thus different position of the SPR peak. SERS measurements of 4-mercaptobenzoic acid obtained from these films reveal that the proximity of the SPR peak to the exciting laser wavelength is not the only factor leading to the highest Raman enhancement. Silver nanoparticles evaporated on top of larger gold nanoparticles show higher SERS than gold-silver alloyed nanoparticles, in spite of the fact that the SPR peak of alloyed nanoparticles is narrower and closer to the excitation wavelength. The highest Raman enhancement was obtained for substrates with a two-peak particle size distribution for excitation wavelengths close to the SPR.

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1. Introduction

Since the discovery of SERS many variations of the technique have been explored using different substrates and metals (gold, silver, and copper [1–5]), metal film morphologies and patterning methods aimed at creating maximally enhancing SERS surfaces. SERS, as many experiments have shown [6, 7], occurs due to the presence of a metal surface in proximity to the scattering molecule and contains two components; electromagnetic [8, 9] and chemical [10–12]. Electromagnetic enhancement, the primary contribution to SERS is due to the excitation of a surface plasmon [8] (SP) which generates a strong, localized, secondary field, that Raman scatters from the molecules together with the incident field. These phenomena have been modeled for a single metal sphere [9] and a small illuminated metal particle [13, 14] and have also been extended to an array of spheres with varying sizes [15–17]. Experiments have revealed correlations between the SERS enhancement and the excited surface plasmon including works on tuning the surface plasmon resonance by different nanoparticles structures, sizes, and dielectric constants [18–23]. The

models predict a Raman enhancement on gold or silver spheres of six to seven orders of magnitude and have been confirmed in experiments [24–27]. Specifically, the influence of gold and silver nanoparticle size in colloids [3, 4] and core shells [28] on the surface plasmon resonance and SERS enhancement have also been reported. It follows from the experiments and theoretical models [29] that the maximum SERS enhancements are observed when the SP resonance wavelength is equal to $\lambda_{sp} = (\lambda_{exc} + \lambda_{Rs})/2$, where λ_{sp} , λ_{exc} , and λ_{Rs} are the surface plasmon, excitation, and Raman wavelength respectively. Furthermore, it was predicted that using different size of nanoparticles influences not only the surface plasmon wavelength but also the intensity of the electromagnetic field created in between the nanoparticles leading to higher SERS enhancements [15–17]. Differences between various metals were also discussed, revealing that the SERS enhancement of silver exceeds that of gold, which exceeds that of copper. The explanation for this lies in the parameter ϵ_b (the contribution of interband transition to the dielectric function), when ϵ_b is large, the width of the resonance increases and the SERS enhancement decreases [30].

FIGURE 1: Absorption spectra of Ag (a) and Au (b) films of ~ 10 nm thick annealed at different temperatures.

In this paper we examine the influence of different parameters (nanoparticle size, morphology, and composition as well as SP resonance wavelength) on SERS. We present an experimental study of SERS substrates consisting of gold, silver, and alloyed gold-silver nanoparticles of various sizes and compositions with the aim of finding the optimal conditions for fabricating substrates with maximum SERS enhancement factors. We have developed a simple technique of tuning the SP resonance frequency by a combination of vacuum deposition of silver and gold films with subsequent annealing of the deposited layers. We find that tuning by Ag-Au alloying results in much smaller enhancement factors compared to tuning by deposition of small Ag nanoparticles over larger Au nanoparticles although the SP of Ag-Au alloy coincides better with the excitation wavelength. We show that a maximum Raman enhancement in the Ag-Au films can be obtained from an island film composed of Ag nanoparticles over Au particles, tuned to an SP resonance close to the excitation wavelength and possessing a double-peak size distribution in the particle ensemble.

2. Experimental

For substrates we use glass microscope slides, which were cleaned with soap and water, then rinsed with ethanol, and

FIGURE 2: SERS spectra of MBA on silver (solid line) and gold (dashed line) films with 633 nm excitation wavelength. The film thicknesses of both films were 10 nm; average particle sizes were 50 nm.

FIGURE 3: AFM scans and histograms of the two types of samples. (a) Annealed gold covered by annealed silver. (b) Gold covered by silver and annealed together. (c), (d) Histograms of the (a) and (b) samples, respectively.

dried with an air stream. Thin films of Ag and Au, as well as two-layer thin films consisting of Ag over Au or Au over Ag were deposited by thermal evaporation in a vacuum of about $1 \cdot 10^{-6}$ Torr. In the case of two-layered films, after the deposition of the first layer (Au or Ag of 5–15 nm thickness) some of the samples were annealed in hydrogen in the range 200–400°C for various times. Then the second layer of 2–10 nm thick was evaporated over the first layer (Ag over Au or Au over Ag). After deposition of the second layer the samples were annealed in hydrogen at 200–400°C for

FIGURE 4: Absorption spectra of the two types of samples, with various metal concentrations. (a) Annealed gold covered by annealed silver (samples A), 1, 2: various silver concentrations; ~ 80 , 20% , respectively. (b) Gold covered by silver and annealed together (samples B), 1–4: various silver concentrations; $\sim 20\%$, 40% , 50% , and 80% , respectively.

various times. The annealing process was done in hydrogen in order to avoid oxidation of the silver layer. The films were characterized by their optical absorption spectrum, and the film morphologies were examined using an atomic force microscope (AFM). For SERS measurements the substrates with the annealed films were spin coated with a homogenous layer of 6 mM of 4-mercaptobenzoic acid (4-MBA) dissolved in ethanol. According to our estimates, after the ethanol evaporation, the effective thickness of 4-MBA layer covering the nanoparticles was about 0.3 nm . SERS measurements were obtained in a Jobin Yvon HR800 Raman microscope with 514 nm and 633 nm excitation lasers with incident intensities of 1×10^5 and $2.5 \times 10^5 \text{ W/cm}^2$, respectively.

3. Results and Discussion

Examination by AFM showed that after deposition, both the Ag and Au films had a granular (island) structure. Annealing of the films causes a surface mass transfer between the

FIGURE 5: Absorption spectra of the two types of samples and pure gold and silver annealed at 400°C and 200°C , resp.

islands as well as alloying in two-layered films due to bulk interdiffusion at the annealing temperature. Surface mass transfer between the islands was noticeable at 200°C for Ag and at 400°C for Au and resulted in the formation of equilibrium nanoparticle shape close to a spherical segment with the wetting angle of about 80 degrees, both for Ag and Au. We also observed sintering and agglomeration of nanoparticles located near one another and diffusion coalescence of nanoparticles [31, 32] resulting in an increase of the average particle size. Due to the transformation of the random nanoparticle shapes to nearly spherical and the increase of the average particle size, SP resonance shifts to the blue and becomes narrower (Figure 1), in good agreement with previous studies [33].

Comparing the SERS enhancement from Ag and Au films (Figure 2) showed that the enhancement factor obtained with the Ag film was several times higher than that for the Au film, even for an excitation wavelength of 633 nm , which is closer to SP resonance of Au. This result is in a good agreement with theoretical predictions [30, 34] in which silver nanoparticles show a higher SERS enhancement than gold. On this basis we studied two-layered films, in which the Ag layer was deposited over the gold layer.

In the preparation of nanoclusters consisting of both Ag and Au we examined two different annealing procedures, by which we created two types of substrates. In the first (sample A) we created the two-layered films in two stages; deposition of Au, annealing at 400°C , and deposition of Ag and then annealing at 200°C . The particle size distributions of such samples, measured by AFM, show two peaks (Figure 3(c)). The additional peak at $R \approx 5 \text{ nm}$ is referred to the Ag nanoparticles formed after the second annealing (at 200°C) which are smaller than the gold particles formed during the first annealing at 400°C . The optical absorption spectra also shows two SP resonances: one is near the Au SP (with some shift to the blue) and the second near the Ag SP. The position of the SP resonances depends on the concentration of each metal and the annealing time at 200°C (Figure 4(a)). The fact that we observe two separate plasmon resonances implies

FIGURE 6: SERS measurements of 4-MBA on the two different substrates (sample A—black solid line, sample B—red dashed line) using two excitation lasers, 514 nm (ArL) and 633 nm (HeNe) left and right graph, resp.

that annealing at 200°C leaves the silver and gold nanoparticles compositionally separated, although each becomes sintered. Indeed, the Ag diffusion coefficient into gold at 200°C is $2.6 \times 10^{-24} \text{ m}^2/\text{s}$, and the interdiffusion of the two metals would require an incredibly long time to form even a very thin alloyed layer (about 670 hours to form a 5 nm layer).

In the second annealing procedure (sample B) we annealed two layered gold-silver films at 400°C. In this process we obtained bulk interdiffusion between the silver and gold and the annealing produced homogeneous islands (Figure 3(b)) with a normal size distribution (Figure 3(d)) and an SP resonance located between the SP of pure Ag and pure Au films (Figure 4(b)), with exact position depending on the concentration of each metal. Thus, annealing at 400°C results in formation of alloyed nanoparticles due to diffusion of silver into gold. The diffusion of silver into gold is faster than gold diffusion into silver [35], and at 400°C the diffusion coefficient is about $D = 8 \times 10^{-19} \text{ m}^2/\text{s}$, that is, the width of diffusion zone $2(Dt)^{1/2}$ (the thickness of the alloyed layer in Au nanoparticles) becomes equal to the particle radius ($R = 50 \text{ nm}$) for a time $t \sim 15$ minutes; several

times shorter than the annealing time in our experiments (1–2 hours depending on the film thickness).

To demonstrate how the morphology of Au-Ag films affects the SERS enhancement, we present SERS spectra obtained from both types A and B substrates.

Spectral absorption measurements of the type A and B substrates as well as pure silver (annealed at 200°C) and pure gold (annealed at 400°C) are shown in Figure 5 (the two vertical dashed lines mark the two laser excitation wavelengths (514 and 633 nm) used for SERS measurements). As shown in Figure 5 there are two absorption peaks for sample A, at 528 and 408 nm, while for sample B a single peak at 494 nm is observed. The pure gold and silver films have absorption peaks at 550 nm and 415 nm, resp.

Based only on the proximity of the laser excitation wavelength at 514 nm to the plasmon resonance we would expect both samples to provide good enhancement with a small advantage for substrate B which has a single strong plasmon resonance slightly blue shifted from the laser line [29]. The SERS measurements performed on 4-MBA, however, reveal that substrate A provides higher enhancement at both excitation wavelengths (514 nm and 633 nm) as shown in Figure 6.

These results clearly demonstrate that SERS enhancement depends not only on the proximity of the excitation wavelength to the plasmon peak position but also on the size distribution of the nanoparticles and the metal type. Since silver is known to be a better enhancing metal for SERS [29] and as we claimed above, in samples A, we have a silver layer on top of the SERS substrate while in samples B we have an alloy of gold and silver, it is reasonable that sample A should have the better performance. A further advantage of the two-layered samples (sample A) is that the method of preparation results in a wider cluster size distribution. Since it has been observed experimentally that the SERS enhancement occurs at specific “hot spots” on the surface, and based on theory [15–17] these “hot spots” are due to specifically sized cluster lying in close proximity to each other, a broader size distribution is expected to lead to a higher probability to find such cluster sizes near each other and thus to increased enhancement. Another advantage of the two-layered substrate is its broader, two-peaked plasmon resonance, which allows for a broader choice for the excitation wavelength.

4. Conclusion

We compare between two ways of creating Ag-Au SERS substrates, resulting in alloyed and two-layered films. We show that the surface plasmon resonance wavelength can be tuned by the alloying composition of the nanoparticles and the annealing process whereby we can create a film with one or two plasmon peaks. We demonstrate that the technique resulting in a two-layered film, in which small silver nanoparticles lie on top of larger gold nanoparticles, results in a better SERS surfaces that shows significantly higher Raman enhancements than alloyed gold-silver nanoparticles.

Acknowledgment

This work was supported by the Israel Ministry of Defense.

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