Local surface plasmons and resonant mechanism for surface-enhanced second-harmonic generation

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A method involving a direct variation of the parameters of a collective electron resonance of a system of small metal particles upon a change in the dielectric properties of the surrounding medium has been used to establish that an electromagnetic mechanism contributes to the surface enhancement of second-harmonic generation in island films.

Two basic types of surface-enhancement mechanisms have been proposed in attempts to explain surface-enhanced Raman scattering and surface-enhanced second-harmonic generation in ultradisperse metal systems. First is the electromagnetic ("classical") mechanism, which involves an increase in the electric field of a pump during the excitation of local surface plasmons in metal granules.[1] The mechanisms of the other type are the molecular-adsorption mechanisms, which link the surface enhancement with a roughness at the atomic scale and the appearance of additional bands in the electron spectrum of the adsorbate-metal system.[2]

Both the electromagnetic and molecular-absorption mechanisms are of a resonant nature, so a study of the excitation spectra of the surface-enhanced Raman scattering and the surface-enhanced-harmonic generation could not by itself distinguish the contributions of these mechanisms to the enhancement. Substantially more information can be found from the experimental variations in the resonant properties of the ampli-

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fying structure itself. The resonant frequency and the quality factor of a molecular-adsorption resonance are determined primarily by the chemical properties of the molecule-metal system and are difficult to vary by means of external agents. The situation is different for a resonance of local surface plasmons: By varying the complex dielectric constant of the surrounding medium one can vary the parameters of a collective electron resonance of a system of small metal particles and thus determine the contribution of the electromagnetic mechanism to the surface enhancement.

With this goal in mind we have studied the process of surface-enhanced-harmonic generation for silver island films synthesized by vacuum deposition in high vacuum on a semiconductor substrate with a large dielectric constant in the visible range (germanium or silicon). In order to arrange a controllable effect of the substrate on the frequency and quality factor of the surface-plasmon resonance, we first deposited a dielectric layer with a variable thickness $d \sim 0$–1000 Å of silicon monoxide, in the form of a stepped wedge, between the island film and the semiconductor single crystal (see the inset in Fig. 1). The layout for observing the surface-enhanced-harmonic generation was similar to that used in Ref. 3.

Figure 1 shows the experimental results on the intensity of the surface-enhanced-harmonic generation, $I_2\omega$ as a function of d. At thicknesses $d > 500$ Å of the dielectric wedge, the dependence $I_{2\omega},(d)$ reaches saturation. The value of the intensity at saturation, $I_{2\omega}(\infty)$ to which the values of $I_{2\omega}(d)$ are normalized, is different for the germanium and silicon substrates; $I^{Si}_{2\omega}(\infty)/I^{Ge}_{2\epsilon}(\infty) \sim (1.5 \pm 0.3)$. As d is reduced to zero (more precisely, to the thickness of the film of the natural surface oxide of the semiconductor, ~ 20 Å), the intensity of the second harmonic falls off by a factor of 1.5×10^2 from $I_{2\omega}(\infty)$. An important point is that for some of the island-film samples

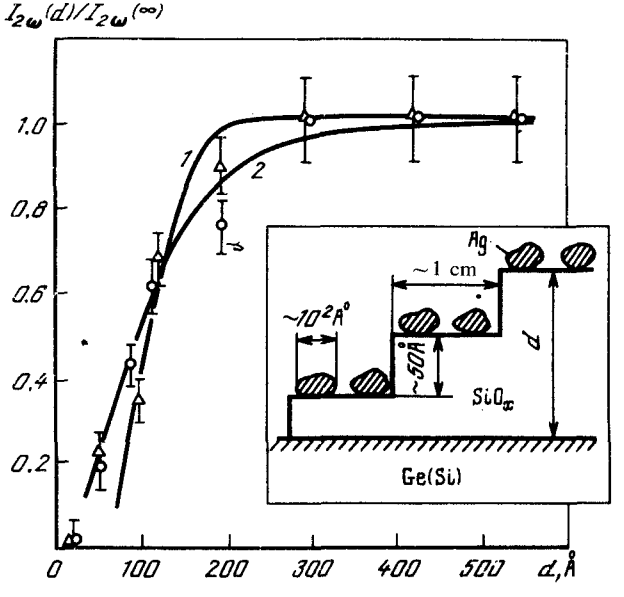

FIG. 1. Experimental results on the intensity of the surface-enhanced-harmonic generation versus the thickness of the dielectric wedge for (△) germanium and (○) silicon substrates. The solid lines are theoretical results for the following sets of parameter values: $\epsilon_0(2\omega) = -11.8 + i\ 0.37$; $\epsilon_2 = 2$; line 1 (germanium)—$\epsilon_1(2\omega) = 19.3 + i21$, $x = 4.08$, $n = 10^{10}$ cm^{-2}; line 2 (silicon)—$\epsilon_1(2\omega) = 17 + i0.4$, $x = 6.67$, $n = 10^{11}$ cm^{-2}. The geometric parameters of the samples are shown in the inset.

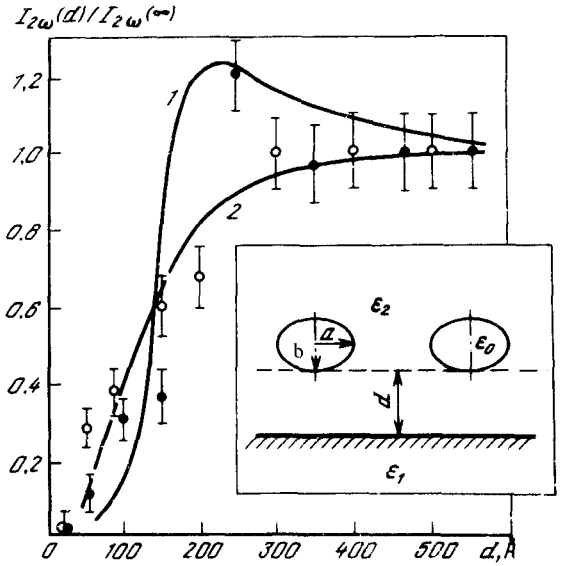

FIG. 2. Points: experimental results on the intensity of the surface-enhanced second-harmonic generation versus the thickness of the dielectric wedge for two types of island films on a silicon substrate. Solid lines: Calculated behavior for the following parameter values: ϵ_0, ϵ_1, and ϵ_2 are similar to the parameter values in Fig. 1. Line 1— $x = 4.04$, $n = 1.5 \times 10^{10}$ cm^{-2}; line 2— $x = 5.71$, $n = 10^{11}$ cm^{-2}. The inset shows the parameters of the model system.

the second-harmonic intensity $I_{2\omega}(d)$ goes through a maximum before reaching saturation (Fig. 2).

To explain this behavior, we consider the expression

$$I_{2\omega} \sim (nv)^2 c(2\omega) \langle |\chi^{(2)} L(2\omega) L^2(\omega)|^2 \rangle I_\omega^2 ,$$

where n, v, and $\chi^{(2)}$ are the surface density, average volume, and square susceptibility of the silver islands; I_ω is the pump energy density; L is the local-field factor, which is related to the intensification of the pump field during the resonant excitation of surface plasmons; the angle brackets mean an average over the random parameters (the size and shape of the particles, etc.); and $c(2\omega)$ is a nonresonant factor which reflects the contribution to the intensity of the second harmonic from the polarization of the substrate at twice the frequency which is induced by the image of the nonlinear dipoles of the islands. The resonant properties of the local-field factor are strongly influenced by the interaction of the islands with their surroundings, including the substrate. The $I_{2\omega}(d)$ dependence is thus determined by the $L(d)$ dependence.

As a model for use in calculating $c(2\omega)$ and $\langle L(d) \rangle$ we consider a plane layer of oblate ellipsoids of revolution with semiaxes a and b (the axis of cylindrical symmetry of the ellipsoids is oriented normal to the plane of the layer) in a homogeneous medium at a distance d from the semiconductor substrate (see the inset in Fig. 2). Allowing for the additional sources of second-harmonic light which arise because of the dipoles reflected in the substrate at the frequency 2ω, incorporating the interaction of the ellipsoids with each other and with the substrate on the basis of the Lorentz mean-field theory, and adopting the electrostatic approximation (a, $b \ll n^{-1/2} \ll \lambda$; a, $b \ll d \ll \lambda$), we find

$$\langle L_\alpha(\omega, d)\rangle = [L_{0\alpha}^{-1}(\omega) + P_\alpha(\omega) + Q_\alpha(\omega, d)]^{-1}, \quad (1)$$

$$c_\alpha(2\omega) = |1 + \sigma_\alpha(\epsilon_1(2\omega) - \epsilon_2)/(\epsilon_1(2\omega) + \epsilon_2)|^2, \quad (2)$$

where

$$L_{0\alpha}(\omega) = [\epsilon_2 + N_\alpha(x)/(\epsilon_0(\omega) - \epsilon_2)]^{-1}$$

is the local-field factor of an individual ellipsoid, and

$$P_\alpha(\omega) = \frac{\pi}{6}\Delta_\alpha nab(\epsilon_0(\omega) - \epsilon_2); \quad Q_\alpha(\omega, d) = \frac{\pi a^2 b}{6d}\left(\frac{-1}{d^2} + 4n\delta_\alpha\right)\frac{(\epsilon_1(\omega) - \epsilon_2)(\epsilon_0(\omega) - \epsilon_2)}{(\epsilon_1(\omega) + \epsilon_2)}$$

are terms which reflect the interaction with neighboring particles and with the substrate, respectively. In addition, $x = a/b$; $N_\alpha(x)$ is a depolarization factor[4]; $\epsilon_0(\omega)$, $\epsilon_1(\omega)$, and $\epsilon_2 = \text{const}$ are the dielectric constants of the material of the ellipsoids, the semiconductor substrate, and the surrounding medium, respectively; $\alpha = \perp, \parallel$; $\Delta_\perp = 2$; $\sigma_\alpha = (1 + 2\delta_\alpha)$; $\Delta_\parallel = -1$; $\delta_\perp = 0$; and $\delta_\parallel = -1$. The index $\perp(\parallel)$ corresponds to an electric field which is perpendicular to (parallel to) the plane of the film. The d dependence of the local-field factor is strongest near the resonance. Numerical estimates for the samples studied ($x > 1$) and for the wavelengths $\lambda_\omega = 1.06\ \mu\text{m}$ and $\lambda_{2\omega} = 0.53\ \mu\text{m}$ show that a resonance is possible only for $L_\parallel(2\omega)$. At the resonance we have $c_\parallel|L_\parallel|^2 \sim c_\perp|L_\perp|^2$ despite the fact that for germanium and silicon the relations $c_\parallel(2\omega) \sim 10^{-2} \ll 1$ and $c_\perp(2\omega) \sim 1$. hold. In this case, regardless of the polarization of the pump light, we can use the approximation $I_{2\omega}(d)/I_{2\omega}(\infty) = |\langle L_\parallel(2\omega, d)\rangle|^2/|\langle L_\parallel(2\omega, d \to \infty)\rangle|^2$.

The solid lines in Figs. 1 and 2 show results calculated on the dependence $I_{2\omega}(d)/I_{2\omega}(\infty)$; here we fitted the values of the parameters x and n of the island films. The good agreement between the theoretical and experimental results shows that the enhancement is indeed determined by the resonance $L_\parallel(2\omega)$ and that the decrease in $I_{2\omega}$ as $d \to 0$ stems from a deviation of the local-field factor from resonance with the second-harmonic frequency because of an effect of the substrate. The two types of $I_2\omega(d)$ curves in Fig. 2 are determined by the different initial ($d \to {}_\infty$) positions of the resonance of the local-field factor with respect to the second-harmonic frequency. If the resonant frequency of the local-field factor is shifted in the red direction from 2ω before the interaction with the substrate, we observe a monotonic behavior; if the shift is instead in the blue direction, the $I_{2\omega}(d)$ curve has a maximum. For the resonant value of the local-field factor we find $L^2(2\omega) \approx 1.5 \times 10^2$. We might add that the calculated value of the ratio $I_{2\omega}^{\text{Si}}(\infty)/I_{2\omega}^{\text{Ge}}(\infty) = c_\parallel^{\text{Si}}/c_\parallel^{\text{Ge}} \approx 2$ agrees well with the experimental value, and the pronounced difference in the values of $\text{Im}\epsilon_1(2\omega)$ for germanium and silicon does not affect the curves of $I_{2\omega}(d)$, according to the measurements and the calculations.

The value found for $L(2\omega)$ can also be used to evaluate the contribution of the

electromagnetic mechanism to the surface enhancement of the Raman effect at island films. The intensity of the surface-enhanced Raman scattering is given by the expression $I^{RS} \sim c(2\omega)L^4(\omega_L)I_{\omega_L}$. Since the pump frequency usually satisfies the relation $\omega_L \approx 2\omega$ in experiments on surface-enhanced Raman scattering, it follows from our estimates of $L^2(2\omega)$ that the change in $I^{RS}(d)$ under similar conditions would be by a factor $\sim 2 \times 10^4$, or slightly more than in Ref. 5.

In summary, through a direct variation of the resonant properties of a collective electron resonance of an ultradisperse metal system, we have, for the first time, clearly identified the actual electromagnetic contribution to the surface enhancement of second-harmonic generation for silver island films.

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[1]M. Moscovits, J. Chem Phys. **69**, 4159 (1978).
[2]A. Otto, *Light Scattering in Solids*, Vol. IV, Springer, Berlin, 1984.
[3]O. A. Aktsipetrov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 505 (1985) [JETP Lett. **41**, 615 (1985)].
[4]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continous Media*, Pergamon, New York, 1986.
[5]S. A. Lyon and J. M. Worlock, Phys. Rev. Lett. **51**, 593 (1983).

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