

Surface-enhanced second-harmonic generation in “cooled” films; mechanism for surface enhancement

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Surface-enhanced second-harmonic generation has been observed in silver films deposited in high vacuum at a low temperature. The electromagnetic nature of the mechanism for surface enhancement in “cooled” films is discussed.

The thrust of the debate over the nature of the surface enhancement in surface-enhanced Raman scattering of light has recently moved on to a discussion of the particular features of this phenomenon for so-called “cooled” (cold) films.¹ When organic molecules are adsorbed on silver films which have been deposited in high vacuum on a cooled substrate ($T < 150$ K), one observes an increase by several orders of magnitude in the cross section for Raman scattering. The surface enhancement of Raman scattering disappears irreversibly when the films are heated to $T \sim 250$ – 270 K. A low-temperature adsorption of molecules on films deposited at room temperature does not result in the enhancement, and no surface-enhanced Raman scattering (SERS) is observed in such films.²

Since we are dealing with films with a rather large mass thickness, $d_m \sim 500$ – 2000 Å, cooled films do not have a clearly defined granular structure at their surface. This

circumstance sets these films apart from island films with $d_m \sim 10\text{--}100 \text{ \AA}$, which do have a granular structure. SERS is observed in island films at room temperature also. It is attributed in that case to a resonant strengthening of the local field upon the excitation of localized surface plasmons in the granules.³ The relative smoothness of the surface of cooled films and an irreversible annealing, which causes the amplifying properties to disappear, led to the concept of centers which are active in the SERS sense.¹ An adsorption of molecules at these centers results in an intensification of the Raman scattering because of a nonelectromagnetic short-range mechanism. Opinion in the literature is divided on the nature of these hypothetical SERS-active centers. Among the suggestions are adsorbed silver atoms (adatoms), clusters of atoms, surface vacancies, terraces, and other surface inhomogeneities of atomic scale.

Some pieces of experimental evidence which have recently appeared, however, indicate that the surface of a cooled film, while comparatively smooth in the sense that there are no granules, does contain deep, narrow fractures due to the boundaries of microscopic crystallites.⁴ Electromagnetic mechanisms for an increase in the local field and for the enhancement of Raman scattering upon the adsorption of molecules in such fractures were proposed in Ref. 5. The disappearance of SERS at room temperature in this case can be explained not as an annealing-out of point SERS-active adsorption centers but as a healing of cracks during heating due to self-diffusion of silver.

In general, a study of SERS cannot give us an unambiguous answer to the question of the nature of the surface enhancement, since the dipole moment of a molecule at the Stokes frequency, $d_{st} = \alpha L(\omega_L)E(\omega_L)$, depends on both the Raman polarizability of the molecule, α , which may increase in the case of adsorption at an SERS-active center (a molecular-chemical mechanism), and the local-field factor $L(\omega_L)$, which reflects the change in the electric field of the pump light, $E(\omega_L)$, due to electromagnetic mechanisms (the gap effect,⁵ the excitation of surface plasmons,³ and the lightning-rod effect⁶). In a study of the mechanisms for surface enhancement by generation of the reflected second harmonic, however, one can rule out an effect of adsorption, since the generation of the surface-enhanced second harmonic differs from the SERS in that it also occurs at a clean metal surface in the absence of an adsorbate.

We have observed second-harmonic generation upon the reflection of a p -polarized beam at a wavelength $\lambda = 1064 \text{ nm}$ from a Nd:YAG single-mode pulsed laser from the surface of a cooled film. The pulse length was $\tau \sim 20 \text{ ns}$, and the power density was $W_L \sim 1 \text{ W/cm}^2$. The system for detecting the second harmonic, with $\lambda = 532 \text{ nm}$, is described in Ref. 6. The cooled films are synthesized (and studied) in a high-vacuum chamber at a pressure $\sim < 10^{-9}$ torr throughout the deposition of pure (0.9999) silver on a polished copper substrate cooled with liquid nitrogen. The deposition rate is $0.5\text{--}1 \text{ \AA/s}$, and the film thickness is $\sim 500 \text{ \AA}$. The substrate temperature is measured with a Chromel-Alumel thermocouple.

Figure 1 shows the dynamic changes in the intensity of the reflected second harmonic during the deposition. During deposition on the cold substrate, the second-harmonic signal appears at a film thickness of a few angstroms, and it intensifies sharply at thickness $d_m \sim 150\text{--}200 \text{ \AA}$ (curve 1). With a further increase in the film

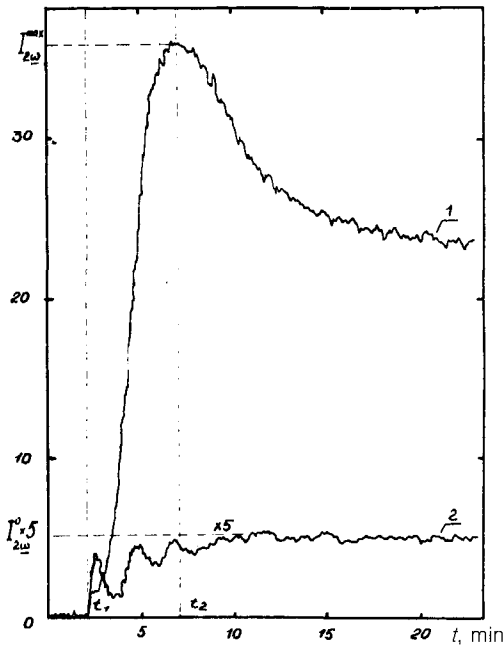


FIG. 1. Intensity of the p -polarized second harmonic for the case of a p -polarized pump versus the time during the deposition of silver on a copper substrate. 1—The substrate temperature is $T = 77$ K; 2— $T = 300$ K. The deposition is begun at t_1 and ended at t_2 . The interval of a steady-state behavior of the second-harmonic intensity, $I_{2\omega}^{\max}$, as the film thickness is varied from 150 \AA to 500 \AA on curve 1 is not shown (see the text proper). The scale is five times larger for curve 2.

thickness, there is no change in the intensity of the second harmonic. After the deposition, $I_{2\omega}$ decrease 20–30% in 1000 s, apparently due to the adsorption of a monomolecular layer of residual gasses, since at a pressure of 10^{-9} torr this time corresponds to an adsorbate exposure ~ 1 langmuir. Curve 2 shows $I_{2\omega}(t)$ during the deposition of silver on a substrate at room temperature. The steady-state value $I_{2\omega}^0$ for a warm substrate is 30–40 times lower than the second-harmonic intensity in a cooled film, $I_{2\omega}^{\max}$.

Figure 2 shows the temperature dependence $I_{2\omega}(T)$ for a cooled film during heating of the film to room temperature. The behavior of the second-harmonic intensity during the annealing is slightly different for cooled films deposited on a copper substrate (curve 1) and on an annealed silver film with a thickness $d_m \sim 2000 \text{ \AA}$ (curve 2). In the former case, there is a region of a slow decrease in $I_{2\omega}$, while at $T \sim 230$ K there is a sharp decay of $I_{2\omega}(T)$, with a transition to a steady-state value $\sim I_{2\omega}^0$, at room temperature. For the films of the second type, the sharp decrease is observed even in the initial region, $T \sim 80$ K. Upon a subsequent cooling to liquid-nitrogen temperature and a repeated heating to $T \sim 300$ K, the second-harmonic intensity does not change significantly; it has a value $\sim I_{2\omega}^0$.

To determine the critical temperature of the irreversibility of the annealing, we carried out heating-cooling cycles with a systematic increase in the heating temperature (curve 3). In the case of annealing to temperatures $T < 220$ K, a repeated cooling leads to a significant increase in $I_{2\omega}$. An annealing to $T > 220$ K causes an irreversible decrease in $I_{2\omega}$.

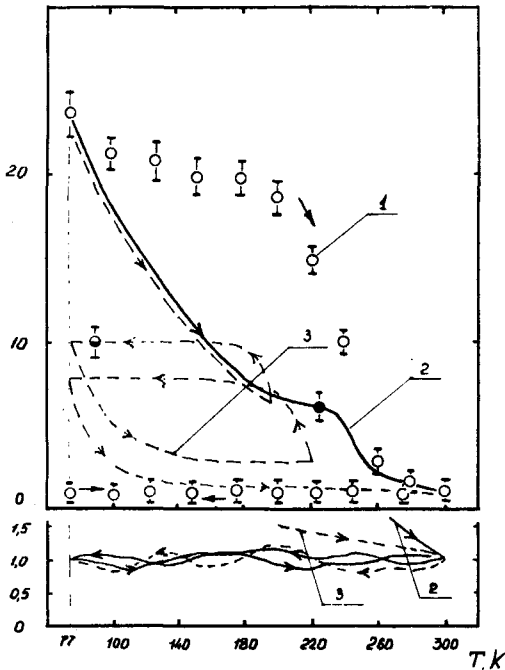


FIG. 2. Intensity of the second harmonic during temperature cycling. The arrows on the curves show the direction in which the temperature is varied. 1—Cooled film deposited on a copper substrate; 2—cooled film deposited on an annealed silver film; 3—partially reversible behavior of the intensity of the surface-enhanced second harmonic during annealing to $T \leq 220$ K. At $T \geq 220$ K the annealing is irreversible (similar comments apply to 1 and 2). The lower part of the figure shows curves 2 and 3 in larger scale after annealing to room temperature. The unit on the scale is $\sim I_{2\omega}^0$.

The reflected second harmonic is p -polarized. This result implies that there is no granular structure at the surface of the cooled film, since an s -polarized second harmonic should be observed at a rough surface, because of a disruption of the polarization selection rules.⁸

In summary, we can say that, by analogy with SERS, a generation of a surface-enhanced second harmonic is observed in cooled films. The surface-enhanced second-harmonic generation is observed at a clean silver surface in the absence of an adsorbate, so that there seems to be no need to appeal to the concept of SERS-active centers in order to explain the mechanism for the intensification of the reflected second harmonic. The mechanism for the intensification of the surface-enhanced second harmonic apparently does not involve nonlinear optical properties of formations on an atomic scale (at atoms, cluster, etc.), for two reasons. First, a high surface density of such formations is reached at thicknesses well below 200 Å, at which the surface-enhanced second-harmonic generation is observed. Second, the breakup of adatoms and clusters should be irreversible upon an arbitrary temperature increase, because of the vibration of silver atoms in the lattices of microscopic crystallites.⁴ The mechanism for the surface-enhanced second-harmonic generation in the cooled films is therefore of an electromagnetic nature and involves an intensification of the pump field in gaps between crystallites. To get a rough estimate of the amplification, we multiply the ratio $I_{2\omega}^{\max}/I_{2\omega}^0$ by the reciprocal of the porosity of the film, β (β is the ratio of the visible area of the film to the area of the gaps). Since no low-temperature measurements of β

for cooled films have been carried out, we use the data of Ref. 4, where the estimate $\beta \sim 10$ was given. The gain of the surface-enhanced second-harmonic generation is then found to be $\sigma_{SH} \sim 4 \times 10^2$. Measurements of β similar to those of Ref. 9, but carried out at low temperatures, might change our estimate of σ_{SH} substantially. For SERS, the gain σ_{SERS} reaches four or five orders of magnitude. An additional contribution to the SERS, ~ 10 – 100 , might involve a molecular-chemical mechanism for enhancement and a roughness of atomic scale.

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