Scanning tunnel microscopy of the surfaces of "cold" silver films and surface-enhanced second harmonic generation

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An investigation was made of surface enhancement and annealing of the enhancement properties in the generation of an enhanced second harmonic in cold silver films. A scanning tunnel microscope with a resolution of 0.1 Å × 2 Å was used to investigate the topography of the surface of annealed cold films and to establish the absence of a significant porosity in their structure, confirming the electromagnetic nature of the enhancement and of the annealing effect in the observation of an enhanced second harmonic.

In recent investigations of surface-enhanced Raman scattering a considerable attention has been paid to the problem of the mechanism of this effect "cold" silver films, i.e., of films evaporated in high vacuum on a metal substrate cooled down to $T \lesssim 120$ K. Adsorption of organic molecules on such films increases the Raman scattering cross section by four or five orders of magnitude.[1] Enhancement of second harmonic generation (SHG) as a result of reflection of laser radiation from the surface of a cold film can reach two or three orders of magnitude.[2] The surface-enhanced Raman scattering and enhanced SHG in cold films are accompanied by an annealing effect: the enhancement disappears when films are heated to $T \gtrsim 200$ K.

Initially the phenomenon of surface-enhanced Raman scattering by cold films was attributed to enhanced Raman-active centers formed on the surface of a cold film in the course of evaporation; the adsorption at these centers was assumed to be responsible for the resonant increase in the Raman polarizability of the adsorbed molecules because of the appearance of a charge-transfer band.[3] However, there is no agreement about the nature of these hypothetical active centers. Some authors are of the opinion that these are adsorbed silver atoms (adatoms), the others attribute these effects to clusters of atoms, atomic steps on the surface, vacancies, and other inhomogeneities on the atomic scale. The annealing effect is closely related to the mechanism of the surface enhancement and has been initially attributed to the thermal destruction of the surface-enhanced Raman-active adsorption centers.

However, a study reported in Ref. 4 revealed an inhomogeneity on a larger scale in the structure of cold films: this was associated with the formation of pores between grains during film growth. Such pores may give rise to resonant localization of surface electromagnetic modes increasing the intensity of a local pump radiation field.[5] Therefore, at least some of the surface enhancement effect is due to an electromagnetic mechanism of an increase in the intensity of the local field $E_{\text{loc}}(\omega)$ in the pores between grains. In fact, for the simplest model of a spherical vacuum void in a metal the local field inside the void is related to the external pump radiation field $E_0(\omega)$ by the following expression:

$$E_{loc}(\omega)=L(\omega)E_0(\omega)=3\varepsilon_m(\omega)E_0(\omega)/[1+2\varepsilon_m(\omega)], \qquad (1)$$

where $\varepsilon_m(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$ is the permittivity of the metal. The local field factor $L(\omega)$ has a resonance structure and it may increase considerably at a frequency ω_r, at which we have $\mathrm{Re}[1+2\varepsilon_m(\omega_r)]=0$. For a spherical void the resonance frequency ω_r lies in the ultraviolet range, whereas in the case of disk-shaped pores the resonance shifts to the visible range[4] and causes enhancement of nonlinear optical processes in the case of visible and infrared radiation. Heating of cold films to room temperature may fill the pores because of the self-diffusion of silver and can therefore result in irreversible annealing in studies of surface-enhanced Raman scattering and enhanced SHG.

Up to now this surface enhancement and annealing in the case of cold films have been investigated by the surface-enhanced Raman scattering method. However, this approach cannot give an unambiguous answer to the question of the nature of these effects because the intensity of light scattered by this process

$$I_{\text{RS}} \propto \alpha_{\text{eff}}^2 N_{\text{ad}} L^4(\omega) E_0^2(\omega) \qquad (2)$$

always contains a combination of the effective Raman scattering polarizability α_{eff}, which allows for the appearance of a charge-transfer band on adsorption of a molecule at an enhanced Raman-active center, and the local field factor $L(\omega)$ related to the electromagnetic enhancement mechanism. In the absence of an adsorbate, when the surface density of adsorbed molecules is $N_{\text{ad}}=0$ the intensity of surface-enhanced Raman scattering vanishes. Under similar conditions the intensity of SHG for a clean surface with a cold film (CF) of silver does not vanish, but is given by the expression

$$I_{2\omega}^{\text{CF}} \propto [\chi_m^{(2)} S_p L(2\omega) L^2(\omega) E_0^2(\omega)]^2, \qquad (3)$$

where $\chi_m^{(2)}$ is the quadratic susceptibility of silver and S_p is the area of the inner surfaces of pores per unit visible surface of the film. In contrast to Eq. (2), Eq. (3) applies only to the electromagnetic mechanism so that an investigation of enhanced SHG on a clean surface makes it possible to determine its contribution to the surface enhancement and to the annealing of the enhancement properties of cold films. The intensity of a second harmonic reflected from a film evaporated on a warm substrate, when the enhancement effect is no longer observed, is given by the expression

$$I_{2\omega}^{T} \propto [\chi_m^{(2)} S_0 E_0^2(\omega)]^2, \qquad (4)$$

where S_0 is the real area of the surface of the film per unit

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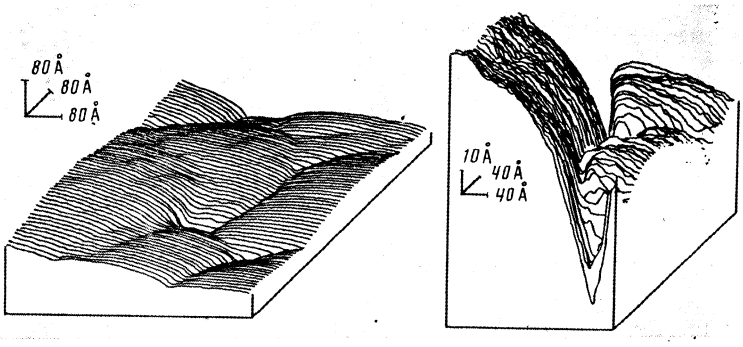

FIG. 1. Topograph of the surface of a cold silver film (shown on two scales) evaporated on a copper substrate and annealed in high vacuum at a residual pressure of $\sim 10^{-9}$ Torr.

area of its visible surface. Then, the coefficient describing enhancement of the intensity of the second harmonic is

$$\sigma_{\mathrm{SHG}} = I_{2\omega}^{\mathrm{CF}} / I_{2\omega}^{T} \propto [\delta L(2\omega) L^{2}(\omega)]^{2}, \qquad (5)$$

where $\delta = S_p / S_0$ is the porosity of a cold film. The surface enhancement coefficient related to the electromagnetic mechanism can then be defined by $\sigma_{\mathrm{EM}} \propto L^{2}(2\omega) L^{4}(\omega) \approx \sigma_{\mathrm{SHG}} / \delta^{2}$. It should be noted that in Eq. (3) it is assumed that the nonlinear sources induced by a local pump field in neighboring pores are coherent. In the case of dephasing of nonlinear dipole moments of the individual pores, the relationship between the surface enhancement coefficient and the porosity is more complex and initially depends on the statistical properties of the surface roughness.[6]

The existence of pores between grains in the cold phase of silver films at temperatures $T < 220$ K was established indirectly in Ref. 4 and confirmed by the appearance of enhanced SHG (Ref. 2) the mechanism of which in the absence of an adsorbate is of electromechanical origin, as pointed out already. The observation of irreversible changes in the intensity in the course of generation of an enhanced second harmonic on a clean surface of heated cold films[2] confirms indirectly the electromagnetic nature of the annealing effect: the porosity of the film decreases and there is a reduction in the associated change of the local field given by Eq. (1). However, in Ref. 7 a study of the structure of cold films annealed after the adsorption of a pyridine monolayer revealed unexpectedly a considerable residual porosity and this made unclear the nature of the enhancement process and of the annealing. This situation required nonlinear optical investigations of the electromagnetic enhancement in cold films followed by a study of the topography of their surface in the annealed state.

The samples of cold films were prepared in high vacuum (residual pressure $p \lesssim 10^{-9}$ Torr) by evaporation of pure (0.9999) silver on the surface of a substrate cooled to $T \approx 77$ K, which was either a polished copper plate or a layered SiO_2/Cr/Pd structure with its outer surface coated by a gold film of ≈ 700 Å thickness. The thickness of the cold films evaporated at a rate of ≈ 0.5 Å/s was ≈ 600 Å.

A method described in Ref. 4 and high-vacuum apparatus were used in a study of enhanced SHG. The pump radiation was provided by a YAG:Nd^{3+} laser emitting at a wavelength $\lambda = 1064$ nm. The enhancement of the reflected second harmonic σ_{SHG} was determined. Before annealing it was found that $\sigma_{\mathrm{SHG}} \approx 40$ and ≈ 10 for cold films deposited on copper and smoother gold substrates, respectively. After heating of a cold film to room temperature, it was found that $\sigma_{\mathrm{SHG}} \approx 1$. In view of measurements of the porosity of cold films, the parameter δ found in Ref. 5 was ≈ 0.1, which in turn give an estimate for the electromagnet enhancement coefficient $\sigma_{\mathrm{EM}} \approx (1\text{–}5) \times 10^{3}$.

An investigation of the surface microrelief of the annealed cold films was carried out using a scanning tunnel microscope with a resolution of $\delta z \approx 0.1$ Å along the normal to the surface and $\Delta \approx 2\text{–}3$ Å in the plane of the surface; the scanned region had the dimensions $2 \times 2 \times 2$ μm. A monotonic drift of the probe point relative to a sample (after approximately 1 h from the replacement of the sample) did not exceed ≈ 3 Å/min along the surface, which was an order of magnitude less than in the perpendicular direction. A probe point used in the tunnel microscope was a tungsten needle with an average radius of curvature $\lesssim 250$ Å prepared by the multistage etching method. Micropoints of atomic dimensions at the end of a probe were grown in an electric field after setting up a needle and a holder. An electron analog system for the control of the tunnel microscope stabilized

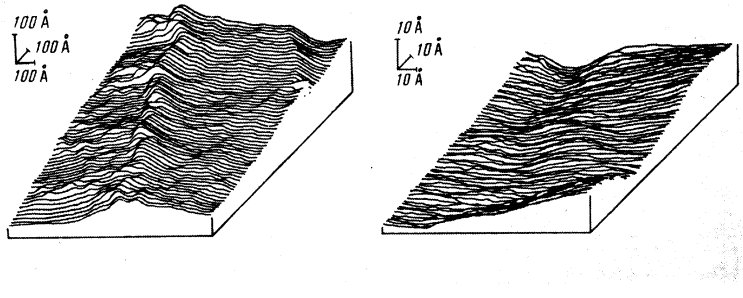

FIG. 2. Topograph of the surface of a cold silver film (two scales), evaporated on a gold substrate and annealed in high vacuum at a residual pressure of $\sim 10^{-9}$ Torr.

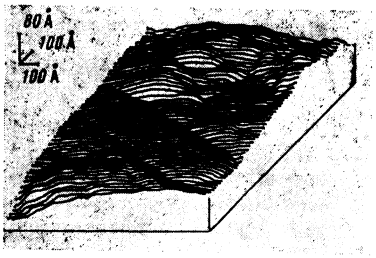

FIG. 3. Topography of the surface of a cold silver film evaporated on a copper substrate and annealed at a residual pressure of $\sim 10^{-7}$ Torr.

the tunnel current at a given value $J_T = \text{const}$ between 0.1 and 20 nA when the voltage between the point and the investigated sample did not exceed $|V_T| \leqslant 10$ V. A narrow band of frequencies within which stabilization of the current was possible because of a feedback loop, amounted to 0.5 kHz. The scanning tunnel microscope had a quartz base and it was set up to use a multilink antiseismic filter, which made it possible to carry out high-resolution measurements under ordinary laboratory conditions.[8]

Films annealed in a high-vacuum chamber were subjected to nonlinear optical measurements and were transferred through the atmosphere to the tunnel microscope chamber. Figure 1 shows a topograph of the surface of a cold film evaporated on a copper substrate and annealed at $p \lesssim 10^{-9}$ Torr. Over an area of ≈ 500 Å $\times 500$ Å there were between one and two grain-boundary breaks with a typical ratio of the pore width to that of $\beta \approx 0.5$. Porosity of this kind could not result in significant enhancement of the reflected second harmonic, because for these values of β the resonance frequency of localized surface plasmons was far outside the ultraviolet range. The shift of ω_r to the visible range would require $\beta \approx 0.01$ (Ref. 5). Equally good annealing results in high vacuum were obtained for a porous structure of cold films evaporated on a gold substrate: there was practically no porosity in the topograph (Fig. 2). The results obtained were in good agreement with those reported in Ref. 9.

In contrast to Ref. 7, where pores became fixed as a result of adsorption (before annealing) of organic molecules in our experiments we found no "fixation" of the porous structure as a result of adsorption of molecules of the residual gases. In fact, a topograph of the surface of a cold film annealed at a pressure of $\sim 10^{-7}$ Torr shown in Fig. 3 demonstrates the absence of breaks between grains.

Our investigation, with a high-resolution scanning tunnel microscope, of structural changes in cold silver films heated to room temperature established the mechanism of the temperature dependences of the electromechanical enhancement coefficient in the generation of SHG, involving annealing of the porous structure of the films.

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