Role played by roughness in surface-enhanced Raman scattering in connection with scanning tunneling microscopy

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The formation of a roughness of superatomic scale during the removal of a monatomic surface layer of silver by electrochemical etching has been observed by scanning tunneling microscopy. This observation implies that an electromagnetic mechanism plays a key role in the enhancement of the nonlinear-optics processes under these conditions.

Although it has been more than decade since the experimental discovery of surface-enhanced Raman scattering (SERS), opinion in the literature regarding the nature of this phenomenon seems still divided;[1] Mechanisms of two types have been proposed to explain surface enhancement. First, there are the long-range electromagnetic mechanisms, which involve a modification of the incident field near a rough metal surface: The field of the pump light, $E_0(\omega)$, increases to values $E_{loc}(\omega) = L(\omega)E_0(\omega)$ as a result of the excitation of localized surface plasmons in

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roughness granules.[2] Alternatives are the molecular-adsorption mechanisms, which link the SERS enhancement with an increase in the Raman polarizability of adsorbed molecules as a result of the formation of metal-organic complexes on adsorbed atoms (adatoms) of the metal.[3]

In experiments on SERS, it has not been found possible to completely eliminate the effect of one of these alternative mechanisms, since the SERS intensity $I_{\text{SERS}} \sim N_{\text{ad}} \alpha_{\text{eff}}^2 L^4(\omega) E_0^2(\omega)$ always includes a combination of the surface density of adsorbate molecules, N_{ad}, their effective Raman polarizability α_{eff} (which incorporates the molecular-adsorption enhancement), and the local-field factor $L(\omega)$, which is related to the electromagnetic enhancement. The primary reason for the ambiguity of the results of such experiments is the ambiguity in the determination of the nature and extent of the roughness of the test surface, since the dimensions of the enhancing irregularities may lie beyond the resolution of scanning electron microscopes. A frequent consequence is an incorrect estimate of the relative contributions of the electromagnetic and molecular adsorption mechanisms to the surface enhancement.

In one of the pioneering studies of the role of the molecular-adsorption mechanism in SERS,[4] an enhancement $\sim 10^4$ was found for a "smooth" silver surface during the removal of monatomic and submonatomic surface layers by electrochemical etching. Pittinger *et al.*[4] believe that this type of surface preparation prevents the formation of the granular roughness which is necessary for the excitation of localized surface plasmons and that the observed SERS enhancement is of a molecular-adsorption nature, related to a roughness at the atomic scale: silver atoms, atomic steps, and so forth.

In this letter we are reporting a study by the method of the giant second harmonic and by direct studies of the surface topography in a scanning tunneling microscope. The results reveal the formation of a granular roughness during the electrochemical oxidation and subsequent reduction of a monatomic surface layer of silver. The results thus demonstrate that the SERS is of an electromagnetic nature under these conditions.

The surface of pure (0.9999) polycrystalline silver was first subjected to a two-step polishing. In the first step, the samples were polished with aluminum oxide with a grain size ~ 0.05 μm. The silver was then placed in an electrochemical cell holding an aqueous solution of potassium chloride and polarized for a long time at a high cathodic (negative) potential. This procedure made it possible to produce a surface with a roughness coefficient $\sigma = S_r/S_a \lesssim 1.1$, where S_r and S_a are the real and apparent surface areas of the sample.[5] For an etching of the surface with a submonolayer resolution, we carried out anodic oxidation-reduction cycles with a known charge density q (one monolayer of silver corresponds to $q \sim 0.3$ mC/cm^2).

The generation of the reflected second harmonic is extremely sensitive to surface irregularities. On a smooth surface of a centrally symmetric medium this process obeys polarization selection rules known as the "*p,s* and *s,s* exclusions."[6] These selection rules mean that there is no *s*-polarized second harmonic in the case of *p*- or *s*-polarized pump light. On a rough surface, however, the polarization exclusions are disrupted; the appearance of a "forbidden" second harmonic can be utilized as a roughness-

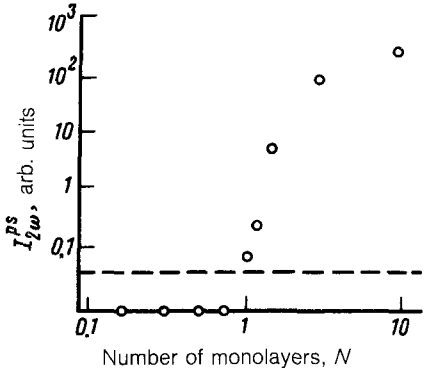

FIG. 1. Intensity of the giant *s*-polarized "forbidden" second harmonic versus the number of silver monolayers which have been etched away. The dashed line is the sensit. ity of the measurement system.

formation criterion. The nonlinear-optics method is particularly sensitive to a surface roughness on metals, since second-harmonic generation can occur in a surface-enhanced regime.[7] Figure 1 shows $I^{ps}_{2\omega}(N)$, the intensity of the giant second harmonic as a function of the number of silver monatomic layers N which have been etched away in the electrochemical cycle. As the unit on the ordinate scale we have adopted the intensity of the allowed *p,p* harmonic on a smooth surface of a polished electrode. The forbidden second harmonic is detected even at $N \lesssim 1$, signifying the appearance of a roughness with granules of superatomic size and the excitation of localized surface plasmons in them. The threshold value of N at which the *p,s* harmonic is detected is

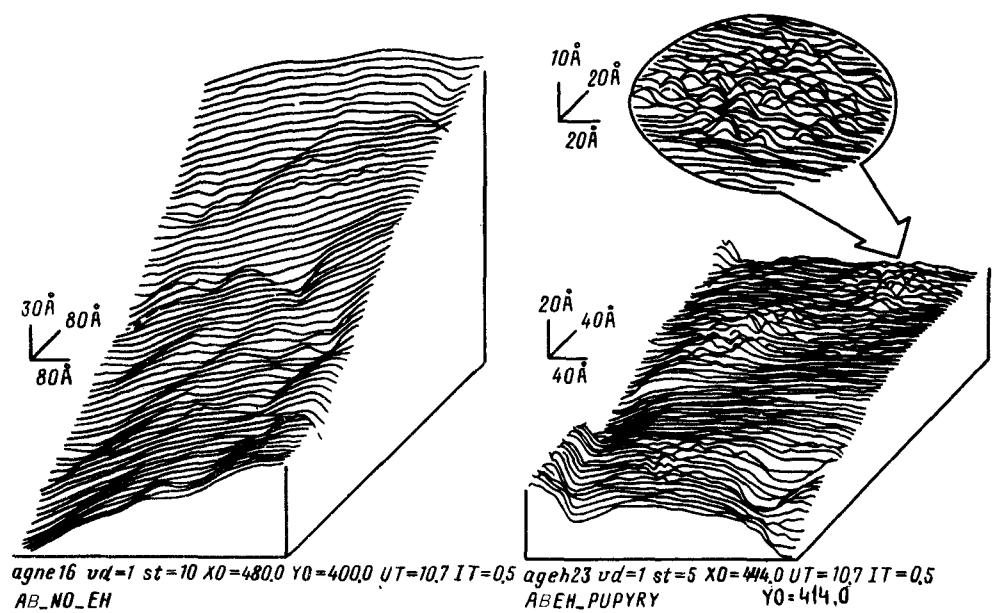

FIG. 2. Surface topography of a silver electrode (a) after mechanical polishing and (b) after one or two surface monolayers of silver have been removed by electrochemical etching.

determined by the sensitivity of the measurement apparatus; it could be reduced.

We studied the surface topography in air with a high-resolution scanning tunneling microscope.[8] Figure 2a shows the typical appearance of the surface of a silver electrode after mechanical polishing. The removal by electrochemical etching of one or two monolayers substantially changes the shape of the surface, as can be seen in Fig. 2b, which reveals irregularities with a vertical dimension $\Delta z \sim 7$–10 Å and a base size $\Delta l \sim 15$–20 Å. Since the surface of the electrode was studied in a scanning tunneling microscope with a fairly prolonged exposure to air, the irregularities which were found consisted of stable metal granules, not metastable cluster formations, which could exist only at a metal-electrolyte interface. The volume of the granules can be used to estimate the number of silver atoms in the largest granules: $n \sim 10^2$. This result means that surface electromagnetic modes could localize at these irregularities (dipole oscillations of the gas of free electrons could be excited in the metal particles). The resonant frequency of such localized surface plasmons would probably fall in the visible part of the spectrum, because of (first) the significant deviation of the particles from a spherical shape[9] and (second) the strong dipole-dipole interaction of the excitations in neighboring particles,[10] since the granules are combined in tight groups (see the inset in Fig. 2b).

In summary, direct topographic studies and observation of the giant second harmonic have made it possible to establish that the surface enhancement is of an electromagnetic nature in surface-enhanced Raman scattering of light in the case of an electrochemical etching of a silver surface at the monolayer scale.

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