Lightning rod effect in surface-enhanced second harmonic generation

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The second harmonic intensity is increased by a factor of more than 10^5 when light is reflected from a system of sharp conical points. This intensity is two orders of magnitude greater than the previously observed amplification by a system of ellipsoids.

Surface-enhanced second harmonic generation is the substantial intensification of the second harmonic which arises when light is reflected from a rough silver surface.[1–3] The effect, which is related to surface-enhanced Raman scattering, is attribut-

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ed to an increase in the incident radiation field $E(\omega)$ near a rough metal surface: $E_l(\omega) = L(\omega)E(\omega)$, where $L(\omega)$ is the local-field factor.

The intensification of the local field $E_l(\omega)$ is usually attributed to the resonant excitation of localized surface plasmons in the system of roughness irregularities. If the dimension of the irregularities is much smaller than the pump wavelength λ, the electrostatic approximation can be used, and the local-field factor in an elliptical roughness of a metal is given by[4]

$$L_{\rm int}^{\rm SP}(\omega) = 1/[1 - (1 - \epsilon_M(\omega)/\epsilon_0(\omega))A], \qquad (1)$$

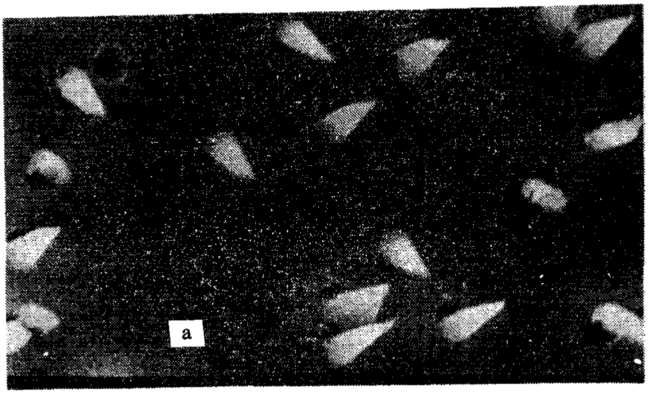
where $\epsilon_M(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and $\epsilon_0(\omega)$ are the dielectric constants of the metal and of the surrounding medium, $A = (1-e^2)\,(\tanh^{-1}e - e)/e$ is the depolarization factor, and $e = \sqrt{1 - b^2/a^2}$ is the eccentricity of the ellipsoid of revolution with semiaxes a and b. At resonance, with $\mathrm{Re}[1 - (1 - \epsilon_M(\omega){:}\epsilon_0(\omega))A] = 0$, the local-field factor is $L_{\rm int}^{\rm SP}(\omega) \sim 1/\epsilon_2(\omega)$. For silver in the visible region we have $L_{\rm int}^{\rm SP} \sim 10$, and the intensity of the surface-enhanced second harmonic generation, $I_{2\omega} \sim L^4(\omega)$, increases by three or four orders of magnitude. It is very important to note, however, that as the size of the irregularities increases, the resonant plasmon amplification at the surface falls off substantially, and at $a, b \sim \lambda$ we have[5] $L_{\rm int}^{\rm SP} \lesssim 1$.

Liao[6] has shown that an additional factor $L^{\rm LR} + (3/2)(a/b)^2(1 - A)$ appears in (1) in the exact solution of the boundary-value problem; this factor is related not to a resonance of the surface plasmons but to an increase in the local field on a surface of large curvature: a "lightning rod" effect.[7] Experimentally, the plasmon amplification can be suppressed by using large-scale irregularities $(a, b \sim \lambda)$; in this case the amplification due to the lightning rod effect may remain significant if a system of sharp points is used.

In this letter we report a study of the surface-enhanced second harmonic generation in a system of large conical sharp points fabricated by the method proposed by Flerov.[8] Silver replicas were fabricated from polyester films perforated by high-energy heavy ions and chemically etched. Figure 1 shows photographs of a replica obtained at two magnifications in a scanning electron microscope (the sample is tilted $\sim 30°$ with respect to the electron beam). The scale dimension of the base of the "cone" is ~ 0.5 μm, the height of the cone is 2–3 μm, the radius of curvature of the tip is < 100 Å, and the filling factor (the ratio of the lateral area of the sharp points to the apparent area of the replica) is $\eta \sim 0.1$–0.2.

We observed a surface-enhanced second harmonic generation upon the reflection of light with $\lambda = 1.06$ μm from a pulsed Nd:YAG laser with a power density $W \sim 10$ kW/cm^2. The system for detecting the second harmonic emission with $\lambda = 0.53$ μm is similar to that of Ref. 2. We studied the directional pattern of the surface-enhanced second harmonic emission and found it to be essentially uniform in a solid angle of 2π sr. Excitation by linearly polarized light resulted in substantially depolarized surface-enhanced second harmonic emission. The efficiency of the emission was essentially the same for s- and p-polarized pump beams. Over a broad range of W, the functional dependence $I_{2\omega}(W)$ is quadratic.

The intensity of the diffuse surface-enhanced second harmonic signal was compared with the intensity of the specular second harmonic from a monolithic silver



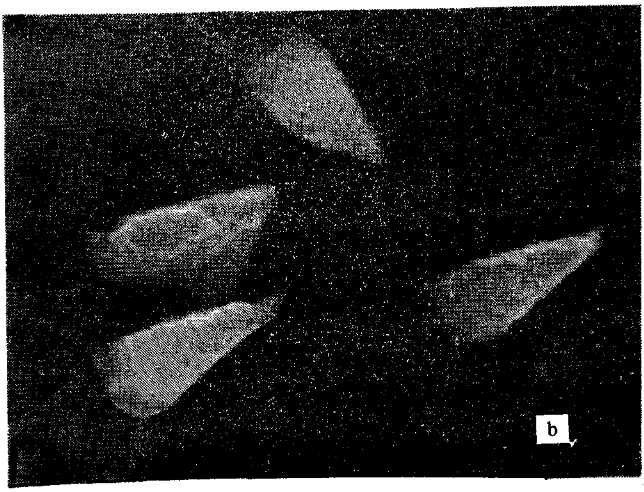


FIG. 1. Photographs of the surface of a silver replica of a sharp point obtained in a scanning electron microscope. The replica was photographed from a polyester film perforated by argon ions. a—Magnification of 10^4; b—3×10^4. The sample is tilted $\sim 30°$ from the direction of the electron beam. The scale marker corresponds to 1 μm.

sample or from a replica obtained from an unperforated part of the film. The absolute increase in the signal—by a factor of $(1–2)\times10^2$, when allowance is made for the coefficient for collection of the diffuse second harmonic emission by the lens system (~ 0.01) and for the filling factor η—can be used to estimate a lower limit on the surface enhancement: $(1–2)\times10^5$. The enhancement is apparently greater, however, since it is dominated not by the entire surface of the sharp point but by the region with the high curvature. Calculations[9] for prolate ellipsoids $(a/b=2)$ show that effectively only 0.2–0.3 of the entire area of the ellipsoids is operating. It can thus be assumed that the surface enhancement of the second harmonic by the structure of these experiments is approximately 10^6 and is due primarily to the lightning rod effect.

A plasmon surface enhancement has been observed previously only for the second harmonic in silver and gold. Surface-enhanced second harmonic generation has not been observed for metals other than noble metals, nor has the amplification of higher harmonics been observed.[10] With the sharp-point structures of the present experiments we were able to observe emission of a surface-enhanced third harmonic in silver and a surface enhancement of the second harmonic in aluminum.

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