Intensification of the surface-enhanced second-harmonic signal from island silver films in a geometry of frustrated total internal reflection

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(Submitted 20 January 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **43**, No. 5, 219–221 (10 March 1986)

Experiments have been carried out on surface-enhanced second-harmonic generation at island silver films. The second-harmonic signal is found to increase sharply if the pump beam is incident on the film at an angle exceeding the angle of total internal reflection for the substrate-air interface. An appropriate choice of substrate material can raise the efficiency of second-harmonic generation at such films.

Below a certain thickness, metal films on an insulating substrate are known to have an island structure instead of being solid films. This circumstance makes these films useful for studying anomalous optical absorption,[1] the surface-enhanced Raman effect,[2,3] and surface-enhanced second-harmonic generations.[4,5] These effects become

 0021-3640/86/050277-04$01.00

possible because there can be a local field intensification in and near the metal islands as a result of the excitation of localized surface plasmons. The efficiency of the process depends to large extent on the values of the local-field factor L at the frequency of the exciting wave and at the signal frequency. The value of L at the frequency ω depends on the dielectric constant of the metal, $\epsilon(\omega)$, the shape of the metal particles, and the coverage factor q (Ref. 3). In a previous study of the anomalous optical absorption, we showed experimentally that the effective value of the factor $L(\omega)$ also depends on the experimental geometry.[6] In the case of frustrated total internal reflection, for example, in which the light beam is incident on the island film from the substrate side at an angle exceeding the total-internal-reflection angle for the insulator-air interface, the effective value of the local-field factor may increase significantly. As the present study shows, the use of the frustrated-total-internal-reflection geometry makes it possible to significantly intensify the signal of surface-enhanced second-harmonic generation from island silver films.

The films are synthesized by vacuum deposition on the hypotenuse of preheated glass prisms. Several films differing in mass thickness $d = m/\rho$ (m is the mass deposited on a unit area, and ρ is the density of the metal) are synthesized in a single deposition cycle. The deposition rate is constant at 0.5–1 Å/s during each cycle. The mass thickness of the films is determined by weighing a control sample. The error in the determination of d does not exceed 10%. We observe a complete reproducibility in the properties of the films of identical mass thickness synthesized in different deposition cycles.

In the experiments we used the beam from a Nd:YAG laser with a wavelength of 1064 nm and a pulse length of 15 ns. The intensity of the pump beam does not exceed 0.5 MW/cm^2. The second-harmonic signal excited by part of the pump at the surface in InSb is used for a calibration. Most of the pump beam passes through the lateral face of the prism and is incident on the film from the side of the glass. The angle of incidence, θ, can be varied. The second-harmonic signal is measured with a photomultiplier. It was found that in the geometry of frustrated total internal reflection the signal of surface-enhanced second-harmonic generation from island silver films has a small divergence, not exceeding that of the pump beam. Because of the dispersion of the prism material, the propagation direction of the second-harmonic beam and that of reflected part of the pump beam should differ slightly,[7] and this difference is comfirmed experimentally. We observe a quadratic dependence of the intensity ($I_{2\omega}$) of the surface-enhanced second harmonic on the pump intensity I_ω. The polarization of the second harmonic is that of the pump beam.

In addition to the directed, polarization second-harmonic beam, we detected an undirected, depolarized, broad-band background of unknown nature. The dependence of the intensity of this background on I_ω is stronger than quadratic. The total power of this background emitted by the film over a broad spectral range into a solid angle of 2π sr is far greater than the power of the directed component of the second harmonic. However, measurements with a narrow-band interference filter showed that the directed component contains at least 90% of the total signal at 2ω, so that the scattered component of the second harmonic can be ignored.

Figure 1 shows, in logarithmic scale, the experimental values of the efficiency

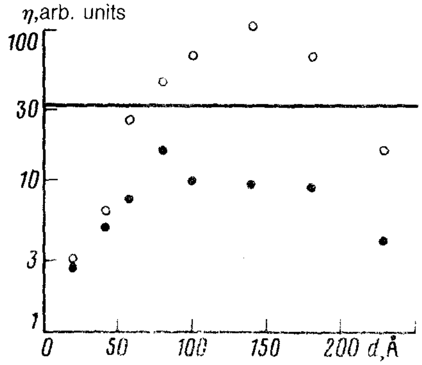

FIG. 1.

$\eta = I_{2\omega}/I_{\omega}^2$ of the second-harmonic generation versus the mass thickness of the film, d, for the angle of incidence $\theta = 45°$ for a p-polarized pump beam (filled circles) and for an s-polarized pump beam (open circles). On this scale, unity corresponds to the sensitivity of our measurement apparatus. We see that the maximum signal is achieved at $d = 80$ Å in the case of the p-polarized pump or at $d = 140$ Å in the case of the s-polarized pump. Figure 2 shows experimental values of the efficiency of the second-harmonic generation versus the angle of incidence θ for a fixed film thickness $d = 80$ Å. We see that the second-harmonic signal increases sharply at angles of incidence θ exceeding the angle of total internal reflection (shown by the arrow along the abscissa) for the glass-air interface. To calculate absolute values of the efficiency of the second-harmonic generation, we used the volume second-harmonic signal from a thin plate of crystalline quartz. In these figures, the horizontal bar corresponds to 10^{-3} of the maximum efficiency of the second-harmonic generation from a quartz plate. Comparing the efficiencies of the second-harmonic generation from the quartz plate (6.3×10^{-15} cm^2/W) and from the smooth silver surface (2.4×10^{-21} cm^2/W; Ref. 4) with the data of the present experiments, we conclude that the maximum efficiency of the generation of the surface-enhanced second-harmonic achieved here in the geometry of frustrated total internal reflection is $\eta = 2.05 \times 10^{-17}$ cm^2/W, or 8.5×10^3 times that from a smooth silver surface.

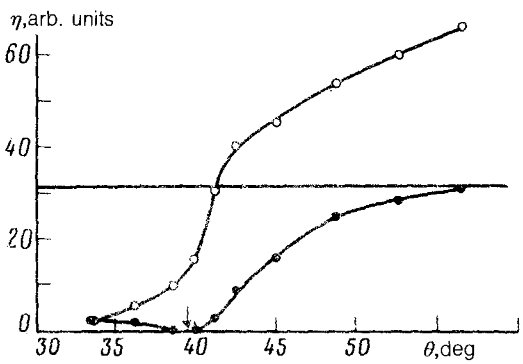

FIG. 2.

It is important to note that the excitation of localized plasmons has the consequence that the electromagnetic field increases not only in the metal but also in a surface layer of the substrate; this increase can also lead to an increase in the second-harmonic signal. Wokaun *et al.*,[4] for example, attribute their measured efficiency of second-harmonic generation, $\eta = 2.5 \times 10^{-18}$ cm^2/W, to an island silver film on a sapphire substrate. We have obtained a similar value of η using sapphire as a substrate. However, when we used a glass substrate, we were not able to detect a signal in the geometry in which the pump beam is incident on the island film from the side of the air. A surface layer of the substrate, rather than the volume of the silver, is probably the source of the second-harmonic signal in the case of the sapphire substrate. The maximum second-harmonic signal is achieved at film thickness corresponding to the highest local-field factor (at $d = 36$ Å in Ref. 4). In our case, the height of the signal also depends on the volume of metal involved in the second-harmonic generation. Relatively thick films are best here.

The geometry of frustrated total internal reflection has made it possible to increase the efficiency of the generation of the surface-enhanced second harmonic from island silver films by at least two orders of magnitude. Since the anomalous optical absorption also increases in the case of frustrated total internal reflection, as we mentioned earlier, it may be that the effective value of the local-field factor increases significantly in this geometry. Since this method for efficiently exciting localized plasmons does not complicate the experiments in any way, there is the hope that this method will find widespread use for studying the surface-enhanced Raman effect also.

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Translated by Dave Parsons