Optical Second-Harmonic Generation with Surface Plasmons in Silver Films

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We report the first experimental and theoretical investigation of the coupling of second-harmonic generation of light to surface plasmons in thin silver films. A model of second-harmonic generation due to polarization sources at the silver-air interface correctly predicts the observed harmonic enhancement of one and a half orders of magnitude because of excitation of the surface plasmon.

This Letter reports the first experimental and theoretical investigation of the coupling of second-harmonic generation (SHG) of light to a collective normal mode of the electrons in the nonlinear medium, namely the surface-plasmon mode in a silver film. Reflected second-harmonic generation from media with inversion symmetry was first observed in silver films[1] and has been extensively investigated both experimentally and theoretically.[2] Earlier efforts to observe enhanced harmonic generation through interaction with the bulk-plasmon mode in silver were unsuccessful because of the equal importance of the contribution of the valence or d-band electrons and the conduction electrons to the optical nonlinear susceptibility.[3] Although nonradiative surface plasma waves have been known as solutions of Maxwell's equations since Sommerfeld,[4] the excitation of this mode was first accomplished by the method of frustrated total reflection.[5] The effect of damping on surface-plasmon dispersion has been studied and the backbending in these dispersion curves has been explained by use of Fresnel's equations.[6]

In this experiment, a nonopaque silver film was evaporated at 5×10^{-4} Torr on the hypotenuse face of a right crown-glass prism. A Q-switched ruby laser ($\lambda = 6943$ Å), p-polarized, was incident in total internal reflection on the silver film in air. The incident laser intensity was strongly filtered since power levels in excess of 1 MW damaged the thin silver films because of the enhanced plasmon absorption. The reflected second-harmonic light from the film passed through a $CuSO_4$ solution and a narrow-band-pass interference filter at the second-harmonic wavelength and was detected by a photomultiplier whose pulse output was amplified and digitized by an analog-to-digital converter. On each laser shot this signal was compared with the second-harmonic signal generated in a quartz crystal. The observed signal was tested to have the harmonic wavelength and $\cos^4\varphi$ dependence on laser polarization angle, φ; in addition, the harmonic light was observed to be noncollinear by 1.5° with respect to the reflected fundamental laser light as a result of the dispersion of the glass prism.

Collective oscillations in electron density at the surface of a metal may be described in terms of surface-plasmon waves.[7] These normal modes may also be described as surface polaritons, corresponding to those solutions of Maxwell's equations which are subject to the Ewald-Oseen extinction theorem with no incident field.[8] Such waves are evanescent since the momentum along the surface, $\hbar k_s$, of a nonradiative surface plasmon of wave vector k_s is greater than that of an electromagnetic wave in vacuum of the same angular frequency ω. The dispersion of surface plasmons on a semi-infinite dielectric bounded by vacuum is given by

$$k_s = (\omega/c)[\epsilon/(\epsilon+1)]^{1/2}, \tag{1}$$

where $\epsilon = \epsilon_1(\omega) + i\epsilon_2(\omega)$ is the complex dielectric function of the medium. The coupling of the electromagnetic wave to the surface plasmon is accomplished by the technique of attenuated total reflection (ATR).[9] The component of the photon wave vector parallel to the silver-vacuum interface, $k_{11} = (\omega/c)n\sin\theta$, is matched to the surface plasmon at the plasmon angle θ_p given by

$$n\sin\theta_p = [\epsilon/(\epsilon+1)]^{1/2}, \tag{2}$$

where n is the index of refraction of the glass prism and θ is the angle of incidence.

Since at present there is no first-principles calculation of the nonlinear optical susceptibility of a silver film due to the contribution of the valence-band electrons[10] we use a phenomenological model for the nonlinear polarization.[11] At the boundary between an isotropic medium and vacuum, the nonlinear polarization source for SHG may be written as due only to surface contributions in the following form:

$$p_z^{s}(2\omega) = \tfrac{1}{2}(\epsilon_s^{2} - 1)\alpha_{\text{eff}} E_z^{2}(\omega) + \frac{\gamma_{\text{eff}}}{2\epsilon_t} E^2(\omega),$$
$$p_{x,y}^{s}(2\omega) = (\epsilon_s - 1)\beta_{\text{eff}} E_z(\omega) E_{x,y}(\omega). \tag{3}$$

Here z is the surface normal direction, x is parallel to the surface in the plane of incidence, ϵ is the complex dielectric constant of the silver with the subscripts s and t referring to the fundamental and harmonic frequencies, respectively, and α_{eff}, β_{eff}, and γ_{eff} are nonlinear coefficients which are determined experimentally. $E_{x,y,z}(\omega)$ are the components of the fundamental electric field inside the metal film at the surface. Symmetry considerations show that the nonlinear surface polarization is spatially reversed between the glass-silver interface and the silver-air interface.

The reflected SHG due to the coupling to the surface-plasmon mode is calculated by using the glass-silver-air geometry shown in the inset in Fig. 1. The incident fundamental field is p-polarized (polarized in the plane of incidence). First the linear boundary value problem is solved to calculate the electric field amplitudes in the metal at the two surfaces. Second the nonlinear boundary value problem is solved separately for each of the contributions to the nonlinear surface polarization in Eq. (3). Since it has been shown that the dominant contribution to the SHG in silver is due to the β_{eff} component of the nonlinear polarization, we give our results here for only this component. A more complete calculation has shown that the angular dependence of the SHG in the vicinity of the plasmon angle is identical for each nonlinear component. The results of the combined linear and nonlinear calculations may

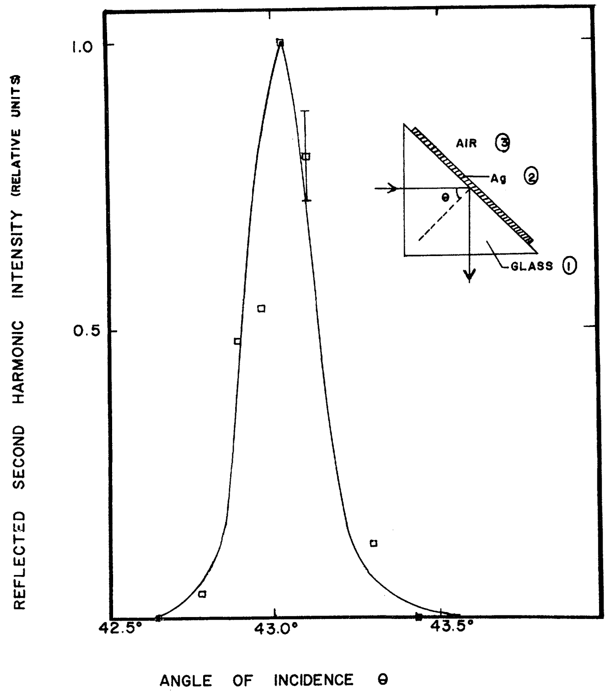

FIG. 1. Reflected second-harmonic intensity versus angle of incidence in vicinity of plasmon angle for 560 Å of Ag on a glass prism. Smooth curve calculated from theory in text and normalized to experimental peak.

be written as

$$I^R(2\omega) = (cn_2/8\pi)\,|E_\beta^{R} F^{\text{NLP}}|^2, \tag{4}$$

where $I^R(2\omega)$ is the total reflected harmonic intensity. E_β^{R} is the reflected harmonic electric field amplitude due to the contribution of $P_x^{s}(2\omega)$ evaluated for an infinitely thick silver film in the ATR geometry, and is similar to previous calculations for SHG from front air-silver interfaces. The contribution due to the surface plasmon is contained in the nonlinear plasmon Fresnel factor F_β^{NLP} which is given by

$$F^{\text{NLP}} = (1 + r_{12} r_{23} e^{-kd})^{-2} (1 + R_{12} R_{23} e^{-Kd})^{-1} \times \{[(1 - r_{23}^{2} e^{-2kd})(1 - R_{23} e^{-Kd})] - [(\epsilon_s - 1)(\epsilon_s - n_1^{2})^{-1}(1 - r_{23}^{2}) e^{-kd} e^{-Kd/2}(1 + R_{23})\epsilon_t^{1/2}]\}. \tag{5}$$

The r's refer to linear Fresnel reflection amplitude coefficients[12] evaluated at the fundamental frequency, while the R's refer to the same quantities evaluated at the harmonic frequency; subscripts 12 and 23 refer to the glass-silver and silver-air interfaces, respectively; k and K are the absorption coefficients at non-normal incidence of the silver at the fundamental and harmonic frequencies; d is the thickness of the film; n_1 and n_2 are the indices of refraction of the glass prism at the fundamental and harmonic frequencies, respectively.

In Fig. 1 we show both the experimental points and the theoretical curve for the reflected second-harmonic intensity as a function of the angle of incidence in the region beyond the critical angle for total internal reflection. At the plasmon angle defined by Eq. (2) where the fundamental reflected light is at a minimum because of plasmon-enhanced absorption, the reflected SHG is resonantly enhanced. The theoretical curve which is calculated from Eqs. (4) and (5) with use of published values for the linear[13] and nonlinear[11] optical constants of the silver film, and averaged over the angular divergence of the ruby laser beam, is normalized to the experimental peak value of SHG. The thickness of the film is determined to be 560 Å from a best fit to the linear reflectivity minimum and from transmission measurements on a microscope slide adjacent to the prism face in the evaporator. The observed sharp angular dependence of the SHG is well described by the theory.

We now compare the enhancement of the SHG with plasmon coupling to the standard SHG from a front-surface reflection of a thick silver film. Examination of F_β^{NLP} at the plasmon angle shows that the SHG at the silver-air interface, described by the second term in Eq. (5), is much greater than the SHG at the glass-silver interface described by the first term, because of the excitation of the plasmon mode. The enchancement of the reflected SHG near the plasmon angle may then be approximately rewritten from Eqs. (4) and (5) as

$$\frac{I^R(2\omega)}{I_\infty^R(2\omega)} = 3.6\times10^{-5}\left|\frac{1-r_{23}^2}{(1+r_{12}r_{23}e^{-kd})^2}\right|^2, \tag{6}$$

where $I_\infty^R(2\omega)$ is the reflected second-harmonic intensity from the front-surface reflection of an infinitely thick silver film at 45° angle of incidence and the numerical factor includes all the factors which remain constant throughout this angular range. This ratio is experimentally observed to be approximately 30 while the theoretical value is a factor of 5 larger. Since at the plasmon angle it can be shown that $r_{23} \simeq 2i\epsilon_1(\omega)/\epsilon_2(\omega)$ and since the peak SHG is proportional to this factor raised to the fourth power, the observed peak is very sensitive to the ratio of the real to imaginary parts of the optical constants of the silver film; e.g., an alternative choice of published linear optical constants reduces the theoretical SHG enhancement by a factor of 2. Since we are presently unable to perform this experiment in vacuum, growth of a silver sulfide layer on the silver film in air is unavoidable. The effect of the silver sulfide dielectric layer[14] will be to diminish the amplitude of the surface-plasmon mode and hence the SHG. The SHG enhancement ratio should be remeasured in high vacuum. The significant feature here is not just the agreement between the theory and the results of this particular experiment, but the sensitivity of the SHG enhancement to both the bulk and surface optical properties of the silver film.

The significance of SHG as a probe for evanescent fields in total reflection has been demonstrated previously.[15] When the fundamental plasmon mode is created at the silver-to-air interface, the internal evanescent fundamental electric field is resonantly enhanced and thus produces a large nonlinear polarization at this surface which in turn radiates the second-harmonic wave. For an ideal surface-plasmon mode without any damping, the Fresnel reflection amplitude factor, r_{23}, diverges[16] at the plasmon angle and the SHG increases exponentially with the thickness of the film. The behavior of the SHG is distinctly different from that of the linear reflectivity which under these ideal plasmon conditions remains unity at the plasmon angle since no linear resonance phenomenon is observed without damping. If the nonlinearity of the silver film is calculated from a recently corrected version of the free-electron model,[10] it can be shown that the surface terms in the second-harmonic polarization are directly proportional to the number density of the propagating electrons at the silver-vacuum interface[17]; i.e., the surface plasmon. Independent of the details of the nonlinear model it is clear that the surface contribution of the harmonic polarization should be closely related to the surface-plasmon collective electron oscillation. Observation of the SHG created by the internal optical fields in the metal film allows direct study of the surface-plasmon wave in contrast to all previous observations of surface-plasmon excitation which are derived from enhanced absorption of the mode.

In conclusion we have demonstrated the first experimental observation and theoretical calculation of the coupling of surface-plasmon waves in a silver film to the SHG of light. The resonantly enhanced SHG is directly related to the surface-plasmon excitation and is also very sensitive to the linear absorption of the thin film. It is anticipated that this technique may be useful both for studying surface-plasmon phenomena, and for measuring the linear and nonlinear optical response functions of metal films.

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Effect of Localized Electric Fields on the Evolution of the Velocity Distribution Function*

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The interaction between charged particles and sharply localized fields is investigated. The random particle scattering is described by a Fokker-Planck equation whose time-dependent solution exhibits the formation of a highly populated superthermal tail.

Recent theoretical,[1,2] experimental,[3] and computer simulation[4] studies have demonstrated that sharply localized electric fields of high intensity can be nonlinearly generated in a plasma by an external pump field whose frequency is close to the electron plasma frequency, ω_p. The underlying physical process which gives rise to these localized fields can be traced to the formation of density cavities by the ponderomotive force exerted by the total rf field in the plasma. Inside these cavities the field amplitude can build up to large levels as a result of both cavity-resonance and wave-trapping effects. These localized fields can be formed in nonuniform[2-4] as well as in uniform[1] plasmas, and can attain energy densities comparable with the mean particle kinetic energy density over a localized region of the order of a few Debye wavelengths (e.g., $\sim 10\lambda_D$). Such narrow and intense fields can accelerate certain electrons to very high velocities; hence they provide an efficient method of transforming external energy into plasma kinetic energy.

In this Letter we investigate the interaction between electrons and intense localized fields. In particular, we calculate the time evolution of the distribution function of a model plasma which is envisioned to be in a turbulent state consisting of random localized fields whose nature has been described above. Such turbulence is assumed to be driven and maintained by external agents (e.g., rf sources, lasers, relativistic beams). The formation and evolution of the turbulence itself is not investigated in the present work. This simplification permits the isolation of the fundamental particle-acceleration effects which should be contained in a more complete future theory of spiky turbulence.

The equation of motion for an electron subjected to a localized field of frequency ω, phase θ, and amplitude E_0 is

$$d^2x(t)/dt^2 = (e/m)E_0 g(x(t))\cos(\omega t + \theta), \tag{1}$$

in which e and m are the charge and mass of the electron, and x is its position at time t. Equation (1) is difficult to solve analytically because the shape function g must be evaluated at the particle trajectory, which is not known *a priori*. However, there are two limiting cases in which Eq. (1) becomes manageable. For small velocities one can extract the ponderomotive-force ef-