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Generation of second-harmonic surface plasmons in Al-quartz interface

F. De Martini, P. Ristori, E. Santamato,* and A. C. A. Zammit
Quantum Optics Laboratory, Istituto di Fisica "G. Marconi," Università di Roma, 00185 Roma, Italy
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We report the results of an experiment in which the linear excitation of a surface plasmon (SP) at frequency ω in an Al-quartz interface is followed by the generation of a second-harmonic surface plasmon at 2ω on the same interface. The Kretschmann geometry has been used to excite the fundamental SP while the second-harmonic SP is detected by nonlinear reflection and scattering at the interface. The theory of the second-harmonic generation by surface plasmons is briefly reviewed while a roughness scattering theory including nonlinear polarization-source terms is given. The experimental results are found to be in good agreement with the theory. A best-fit analysis leads to an accurate appraisal of the linear and nonlinear optical parameters of the media involved in the interaction.

I. INTRODUCTION

Resonant excitation of surface plasmons (SP) has drawn considerable attention in recent years.[1] It has been used to measure the optical properties of metal films[2] in the study of adsorbed molecules and overlayers on surfaces,[3,4] and to probe phase transitions.[5,6] In most cases linear optical techniques were employed both in the excitation and in the detection of the SP wave. The excitation of surface polaritons and plasmons by nonlinear mixing of bulk and surface waves was first proposed and verified by De Martini and Shen.[7] They investigated the dispersion and the damping characteristics of phonon polaritons in GaP and exciton polaritions in ZnO.[8,9]

Recently a coherent anti-Stokes Raman spectroscopy (CARS) experiment involving nonlinear mixing of surface plasmons was reported.[10] Enhancement of second-harmonic (SH) radiation near surface-plasmon resonance at the fundamental frequency ω was observed by Simon *et al.*[11] In a later experiment the excitation of an SH surface plasmon at 2ω by nonlinear mixing of surface waves has been investigated (Simon *et al.*[12]). Unfortunately these authors failed to obtain the direct experimental evidence of this process. In our opinion this was mainly due to the unwanted effect of a strong second-harmonic generation (SHG) process taking place in the coupling rutile prism which was used in the experiment

In this paper we report the results of an experiment in which the second-order nonlinear (NL) interaction induced on an Al-quartz interface involves surface waves only and, in particular, surface plasmons. The surface wave at the fundamental frequency ω is generated by an ATR (attenuated total reflection) method in the Kretschmann geometry, while the excitation of the surface resonant states of the field at ω and 2ω is probed by detection of the radiation which is linearly or nonlinearly reflected by the film or scattered by surface roughness.[13,14] A best-fit analysis of the experimental data leads to an accurate appraisal of the linear and nonlinear optical parameters of the media adjacent to the interface. We also determine the angular distribution of the light scattered at the second-harmonic and derive the roughness spectrum of the film surface.

In a limited region of K_x space this spectrum can be described by a Gaussian correlation function. Using this approximation it is possible to calculate the correlation length and the rms of the roughness.[13-15]

The paper is divided in the following way: In Sec. II a review of the theory of SH nonlinear surface-plasmon interaction in the parametric approximation is given along with the pertinent equations. In Sec. III a roughness scattering theory including nonlinear polarization-source terms is given. Section IV describes the experimental setup with details for film preparation and second-harmonic measurements. Section V reports a discussion of the results obtained in the experiment.[16]

II. SECOND-HARMONIC GENERATION BY INTERACTING SURFACE PLASMONS

The geometry of our experiment is shown in Fig. 1. A metal film of thickness d is evaporated on a nonlinear crystal (quartz) plate and is placed in optical contact with a glass prism. The values of the refraction index n_p of the prism at frequencies ω and 2ω are larger than the corresponding values of the same quantity for both ordinary and extraordinary waves in quartz. As is well known, this sandwich geometry can support, under appropriate conditions, TM-polarized surface-plasmon modes. The corresponding dispersion relation is expressed by the following resonance condition in k space[1]:

$$\overline{D}(k_x,\omega)=\epsilon_m k_{mz}(\epsilon_\perp k_{pz}+\epsilon_p k_{sz}) - i(\epsilon_p\epsilon_\perp k_{mz}^2+\epsilon_m^2 k_{sz}k_{pz})\tan(k_{mz}d)=0\ , \quad (1)$$

where $\epsilon_p \equiv n_p^2$, $\epsilon_m = \epsilon_m' + i\epsilon_m''$, and $(\epsilon_\perp, \epsilon_\parallel)$ are, respectively, the dielectric constants of the prism, of the metal film, and the quartz substrate. $\epsilon_\perp$ and $\epsilon_\parallel$ correspond to electric-field polarizations, respectively, orthogonal and parallel to the optic axis z of the quartz plate. Furthermore, the z components of the wave vector defined, respectively, in the prism, in the metal film, and in the nonlinear substrate are

$$k_{pz} \equiv (k_0^2\epsilon_p - k_x^2)^{1/2}; \quad k_0 \equiv \omega/c$$
$$k_{mz} \equiv (k_0^2\epsilon_m - k_x)^{1/2} \tag{2}$$
$$k_{sz} \equiv [k_0^2\epsilon_\perp - (\epsilon_\perp/\epsilon_\parallel)k_x^2]^{1/2}.$$

In deriving Eq. (1) we have further supposed that the quartz crystal is oriented in a way such that the crystallographic $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes coincide with the geometrical axis x, y, and z, respectively, that the z axis is perpendicular to the metal film oriented from the prism to the quartz plate, and the x-z plane coincides with the incidence plane having all SP phase velocities parallel to the x axis (see Fig. 1).

In Eq. (2), k_x is the common x component of the wave vectors of the surface waves. The phases of all complex k_z are chosen so that these quantities have positive real parts.

Equation (1) should be viewed as an implicit transcendental equation for k_x giving the complex SP wave vector $K_x = K_x' + iK_x''$ as a function of the real frequency.[17] An explicit solution of Eq. (1) can be easily found in the limit of large film thickness and $\epsilon_m'' \sim 0$. With this assumption, for $d \to \infty$, $\tan(k_{mz}d) \to 1$ and Eq. (1) reduces to the pair of equations

$$k_x = \frac{\omega}{c}\left(\frac{\epsilon_m\epsilon_p}{\epsilon_m + \epsilon_p}\right)^{1/2}, \tag{3a}$$

$$k_x = \frac{\omega}{c}\left(\frac{\epsilon_m\epsilon_\parallel(\epsilon_\perp - \epsilon_m)}{\epsilon_\perp\epsilon_\parallel - \epsilon_m^2}\right)^{1/2}, \tag{3b}$$

which are the usual SP dispersion relations at metal-glass (prism) and metal-quartz interfaces, respectively. For $\epsilon_m'' \simeq 0$, $-\epsilon_m > \epsilon_p$, and $(\epsilon_\perp, \epsilon_\parallel) > 0$, both values of k_x turn out to be real. Equations (3) give a two-branch solution corresponding to surface-plasmon waves propagating on both sides of the metal film. These solutions give complex values for K_x'' when $\epsilon_m'' \neq 0$. In our Kretschmann geometry an incident light beam propagating in the prism can only excite the branch corresponding to propagation in the metal-quartz interface provided that the condition

$$O < \mathrm{Re}\{[\epsilon_m\epsilon_\parallel(\epsilon_\perp - \epsilon_\parallel)]/(\epsilon_\perp\epsilon_\parallel - \epsilon_m^2)\,\epsilon_p\} < 1$$

is satisfied. This is due to the requirement that the resonant values of k_x be matched by the x component of the exciting bulk wave in the prism: $k_x = (\omega/c)n_p \sin\theta$. ($\vartheta$ is the incidence angle of the wave propagating in the prism at the metal-film interface). We can easily see that phase matching cannot be achieved by our geometry for resonant propagation at the glass-metal interface. For finite film thickness K_x is a complex quantity even if all ϵ_s are real. In general we achieve a maximum energy transfer from the incident beam to the surface wave when D is minimum, i.e., when $k_x \equiv k_0 n_p \sin\vartheta = K_x'$. We shall refer to this condition as the "resonance condition." Note that the dispersion relation (1) includes the effects of absorption and radiation damping of the SP due, respectively, to the intrinsic dissipation of energy in the metal and to the effect of the film thickness.[1,17] By solving Maxwell equations with the appropriate boundary condition for an incident infinite plane wave, we obtain the expression of the magnetic field at the fundamental frequency, corresponding to the TM-polarized surface wave at the metal-quartz interface:

$$H_t(\omega) = [D(\omega, k_x)]^{-1} \cdot [2\epsilon_m\epsilon_\perp k_{mz}k_{sz}\sec(k_{mz}d)] \times \exp[i(k_x x - \omega t)]. \tag{4}$$

Near the resonance condition, $D(k_x, \omega)$ reaches its minimum value and H_t is enhanced. In our experiment the frequency ω was kept constant and the resonant condition $k_x = K_x'$ in k_x space was obtained by turning the incidence angle in the prism.

At resonance, the field-strength increases and all nonlinear effects are enhanced. The resonant angle turns out to be always greater than the total internal reflection angle corresponding to the same experimental situation. As a consequence the fields are evanescent exponentially along the z direction in the nonlinear crystal, and the nonlinear effects arise from a strip of the nonlinear substrate with thickness of the order of the radiation wavelength.

The field (4) creates in the substrate a nonlinear polarization, which in turn drives a new surface-

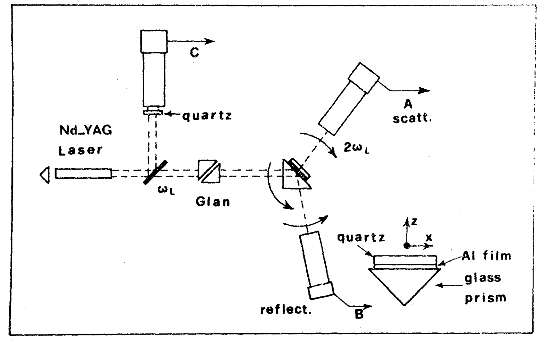

FIG. 1. Experimental setup for nonlinear generation and detection of the second-harmonic surface plasmons.

plasmon wave at the second-harmonic frequency. The nonlinear polarization source at 2ω can be written as

$$\vec{P}^{NL}(2\omega) = \vec{P}^{NL'} \exp[2i(k_{sz}x + k_x x - \omega t)], \qquad (5a)$$

where

$$\vec{P}^{NL'} = \underline{\chi}^{(2)}:\ \vec{e}(\omega)\vec{e}(\omega)[H_t^2(\omega)/\epsilon_\perp] \qquad (5b)$$

and $\vec{e}(\omega) = (c/\omega)\,[-k_{sz}, 0, (\epsilon_\perp/\epsilon_\parallel)k_x]$ is an adimensional vector parallel to the electric field at ω in the substrate; $\underline{\chi}^{(2)}$ (2) is the second-order susceptibility of quartz and H_t is given by Eq. (4).

Maxwell's equations, with the source term (5a) in the substrate, can be exactly solved with boundary conditions to give the field distribution produced by the nonlinear polarization in the three media.

If the dielectric constants satisfy the condition

$$\left(\frac{1}{\epsilon_\perp}\right) - \left(\frac{1}{\epsilon_p}\right) > -\left(\frac{1}{\epsilon'_m}\right) > 0 \qquad (6)$$

both at ω and at 2ω, the fields are evanescent in the metal and in the substrate but are oscillating waves in the prism.

In this case, an SP at 2ω can be generated by the $P^{NL}(2\omega)$. Due to the finite thickness of the metal film, the SH energy can leak from the SP into the prism by tunneling through the film, and a nonlinearly "reflected" second-harmonic wave is created. In addition to this reflected wave, there is a "transmitted" wave at 2ω, which is scattered out of the active interface into the substrate by surface roughness. Both reflected and transmitted waves have been detected in our experiment.

Solving Maxwell's equations for the TM configuration with the source term (5a) in the substrate, we found the magnetic field of the reflected wave at 2ω in the prism in the form

$$H_r(2\omega) = [D(2k_x, 2\omega)]^{-1} \cdot [2\bar{\epsilon}_m \bar{\epsilon}_p \bar{k}_{mz} \bar{k}_{pz} \sec(\bar{k}_{mz} d)] \times H_{NL} \cdot \exp[-i\bar{k}_{pz}(z+d) + 2i(k_x x - \omega t)]\ (z \leq -d). \qquad (7)$$

The x and z components of the surface wave vectors at 2ω, K_x, and $(\bar{k}_{pz}, \bar{k}_{mz}, \bar{k}_{sp})$ are obtained by replacing in Eqs. (2) and (3b), ω and k_x with 2ω and $2k_x$, and the dielectric constants of the media with the corresponding parameters $(\bar{\epsilon}_p, \bar{\epsilon}_\parallel, \bar{\epsilon}_\perp, \bar{\epsilon}_m)$ measured at frequency 2ω. Equation (7) shows that the reflected field has a resonance when $D(2k_x; 2\omega)$ reaches its minimum value. However, due to the dispersion of the media, this second-harmonic resonance is slightly shifted toward a larger value of k_x with respect to the resonance at the fundamental. In Eq. (7) the quantity H_{NL} is given by

$$H_{NL} = \left(\frac{2\pi(2\omega/c)}{\bar{k}_{sz}(\bar{k}_{sz} + 2k_{sz})} \cdot (\bar{k}_{sz} P_x^{NL'} + k_x P_z^{NL'})\right). \qquad (8)$$

We assume that the geometry of our experiment is such that $P_y^{NL'} = 0$. Only in this way are pure TM modes driven by the nonlinear polarization. This is the case of our experiment.

We conclude this section by giving the expression for the field at 2ω created at the metal-quartz interface (plane $z=0$):

$$H_0(2\omega) = [D(2K_x; 2\omega)]^{-1}[\bar{\epsilon}_b \bar{k}_{mz} - i\bar{\epsilon}_m \bar{k}_{bz} \tan(k_{mz} d)] \times 2\bar{\epsilon}_m \bar{k}_{sz} \cdot H_{NL}\quad (z=0). \qquad (9)$$

We shall need the field (9) in the next section for evaluating the scattered radiation at 2ω due to surface roughness. To summarize, the k_x dependence of the nonlinearly reflected and scattered fields at the second harmonics should show two resonance peaks. One of them is due to the resonant enhancement of the fundamental fields entering in the expression of $P^{NL'}$. The second one corresponds to the excitation of a new surface plasmon at frequency 2ω driven by the nonlinear polarization field. In addition to other SP excitation schemes,[1,7-9] the present one should be considered as a new technique involving only nonlinear coupling between surface waves.[10]

In the absence of optical dispersion, the two resonant peaks overlap. In general, however, this does not occur even for large $\epsilon''_m(\omega)$ and for values of d of the order of one hundred angstroms. The peak at a larger value of k_x is expected to be substantially smaller and broader than the other one. This is due to the larger attenuation of the metal at frequency 2ω causing a faster damping of the second-harmonic SP.[18] As we shall see, all these predictions are verified in our experiment.

III. SURFACE ROUGHNESS SCATTERING

A surface-plasmon wave at the interface between two media may radiate energy with the help of surface roughness. A perturbation theory of this effect has been proposed by Juranek.[19] He starts from the exact boundary conditions at the rough surface and makes a perturbative calculation for the amplitude of the roughness. Kroger and Kretschmann[15] showed that Juranek's theory is equivalent to a model consisting of a smooth surface and surface current sources. This model has an obvious physical meaning and allows a simple calculation of the scattered fields. For this reason, we adopt this model for the scattered light at the second harmonic.

The Kretschmann theory holds for linear media; however, a generalization is needed if we want to include the effect of the nonlinear response of one of the media. The polarization source of the scattered radiation can be written as

$$\vec{P}_s(x, y, z) = \vec{P}^{(1)}(x, y) S(x, y) \delta(z) \exp(-2i\omega t)\,, \quad (10)$$

where $\delta(z)$ is the Dirac function and

$$z = S(x, y) \quad (11)$$

gives the exact profile of the boundary metal-substrate.

In Eq. (10), $\vec{P}^{(1)}(x, y)$ is given by

$$\vec{P}^{(1)}(x, y) = \left(\frac{\epsilon_m - 1}{4\pi}\right) \vec{E}_m^{(0)}(x, y) + \left(\frac{\epsilon_s - 1}{4\pi}\right) \vec{E}_s^{(0)}(x, y) + \vec{P}^{NL}(2\omega)\,, \quad (12)$$

where ϵ_s is the dielectric constant tensor of quartz, $P^{NL}(2\omega)$ is given by Eqs. (5a) and (5b), and $\vec{E}_m^{(0)}$ and $\vec{E}_s^{(0)}$ are the electric fields in the metal and in the substrate, respectively. These are evaluated at the boundary $z = 0$ in the approximation of smooth surface (i.e., for $S = 0$). The last term on the right-hand side of (12) is due to the nonlinear properties of quartz while the first two terms correspond to the linear surface scattering sources.

The δ function appearing in Eq. (10) localizes the source of the scattering at the plane $z = 0$; however, according to Kretschmann's model, this source must be placed in a thin vacuum layer, of infinitesimal thickness, between the metal and the quartz substrate. An explicit theoretical calculation of the fields radiated from a surface polarization source is shown in the Appendix of Ref. 15.

The successive steps of this theory are (i) the polarization source is Fourier transformed in its plane-wave spectrum; (ii) the fields created by each plane-wave component are determined by solving Maxwell's equations in vacuum; (iii) the far-field radiation is calculated by the method of multiple reflections and by using the appropriate Fresnel coefficients in order to avoid field discontinuities at the boundaries $z = \pm a$ of the vacuum layer; (iv) the layer thickness $2a$ is set equal to zero, and finally (v) the Fourier-transformed fields in the far zone are recombined, using the saddle-point approximation.[19]

In this way we obtain the electromagnetic power $P_{2\omega}$ scattered in the solid angle $d\Omega$ at frequency 2ω as

$$\frac{dP_{2\omega}}{d\Omega} = \frac{2\pi}{c}\left(\frac{2\omega}{c}\right)^4 |W(\vartheta, \varphi)|^2 |s(\Delta K)|^2 \frac{P_\omega^2}{\sigma_0 \cos\vartheta_0}\,, \quad (13)$$

where P_ω, σ_0, and ϑ_0 are the total power, the cross-section, and the incidence angle of the beam at the fundamental frequency, respectively, and $|s(\Delta K)|^2$ is the power spectrum of the roughness, given by[14,15]

$$|s(\Delta\vec{k})|^2 = \lim_{F \to \infty} \frac{1}{(2\pi)^2} \frac{1}{F} \left| \int_F S(x, y) e^{-i\Delta\vec{k} \cdot \vec{r}_\parallel} dx\,dy \right|^2, \quad (14)$$

where $S(x, y)$ is given by (11) and $r_\parallel = (x, y, 0)$.

The explicit expression for the function $W(\vartheta, \varphi)$ appearing in Eq. (13), is

$$W(\vartheta, \varphi) = 4\pi |W_{TE} \cos\psi + W_{TM} \sin\psi|\,, \quad (15)$$

where W_{TE} and W_{TM} are the dipole functions corresponding to TE and TM polarization states and the angles ϑ, φ, and ψ are shown in Fig. 2. Angle ψ represents the polarization of the radiation scattered in direction (ϑ, φ). W_{TE} and W_{TM} are expressed as functions of the polarization source (12) by

$$W_{TE} = \left(\frac{(1 - r_{vs}^2)(1 - r_{vm})^2}{1 - r_{vs} r_{vm}}\right)_{TE} \cdot (P_y^{(1)} \cos\varphi - P_x^{(1)} \sin\varphi) \quad (16)$$

and

$$W_{TM} = \left(\frac{1 - r_{vs}^2}{1 - r_{vs} r_{vm}}\right)_{TM} \{(1 + r_{vm})_{TM} P_z^{(1)} \sin\vartheta - (1 - r_{vm})_{TM} [P_x^{(1)} \cos\varphi + P_y^{(1)} \sin\varphi] \cos\vartheta\}\,, \quad (17)$$

where r_{vs} and r_{vm} are the reflection Fresnel coefficients relative to the vacuum-substrate and vacuum-metal interfaces, respectively.

In the Kretschmann model, the presence of the r's is due to the multiple reflections at the boundaries of the infinitesimal vacuum layer placed between the metal and the substrate.

Equation (15) shows that the scattered power is proportional to the squares of the fields $E_m(0)$ and

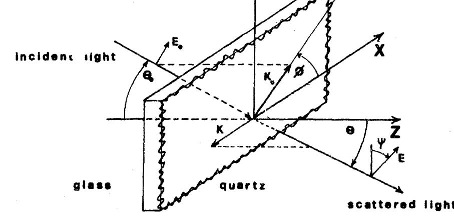

FIG. 2. Geometry of the scattering experiment. A small fraction of surface-plasmon energy at 2ω is scattered by surface roughness and detected in a small solid angle $d\Omega$ at an angle ϑ with the normal to the surface. The incidence plane is the (x', z) plane and the scattered light is observed in the (x, z) plane. In our experiment, this plane coincides with the incidence plane, i.e., $\varphi = 0$.

$E_s(0)$ calculated at $z=0$ for a smooth surface in metal and in the substrate, respectively. For TM modes, these fields are proportional to the magnetic-field strength H_0 given by Eq. (9). Thus, we conclude that the two resonances observed in the reflected second-harmonic radiation should be observable also in the scattered-field intensity. This is verified by our experiment (see Figs. 3 and 4).

Furthermore, we note that the scattered power is a function of the transfer momentum $\Delta\vec{K}$. We can therefore measure directly the power spectrum $|s(\Delta\vec{K})|^2$ of the rough surface by detecting the angular distribution of the scattered light.[14,15,20]

If we assume a Gaussian correlation function for the roughness, we have[14,20]

$$|s(\Delta\vec{K})|^2 = \frac{1}{4\pi}\sigma^2\overline{S}^2 \exp[-\tfrac{1}{4}(\Delta K)^2\sigma^2], \tag{18}$$

where σ is the autocorrelation length (supposed the same in x and y directions) and $(\overline{S}^2)^{1/2}$ is the rms roughness of the surface.

In our experiment the scattered radiation was measured in the plane of incidence (see Fig. 2) and thus we must put $\varphi=0$ in Eqs. (16) and (17). Since the light is detected in vacuum, the transfer momentum $\Delta\vec{K}$ is, in our case,

$$\Delta K = (\sin\vartheta - \sqrt{\epsilon_p(\omega)}\sin\vartheta_0, 0, \cos\vartheta)\cdot 2k_0, \tag{19}$$

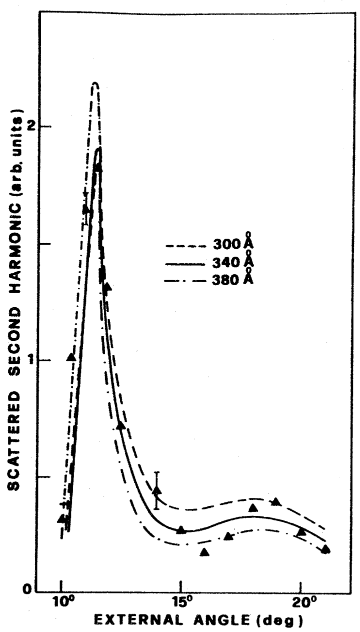

FIG. 3. Intensity of the SH scattered radiation as function of the external angle of incidence on the prism of the fundamental beam at $\lambda=1.06$ μm, for TM and TE polarization. The three theoretical curves correspond to the same values of the best-fit parameters except for a 10% variation of the metal dielectric constant at 2ω (see text).

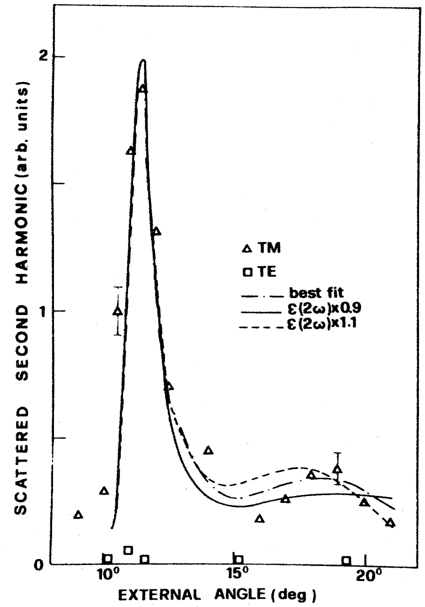

FIG. 4. Intensity of the SH scattered radiation as in Fig. 3. The theoretical curves correspond to different values of the film thickness.

where ϑ_0 is the incidence angle on the metal film at the fundamental frequency.

IV. THE EXPERIMENTAL APPARATUS

Our SHG experiment was carried out using an evaporated aluminum film of thickness $d \simeq 340$ Å. The film was first deposited by fast evaporation on a z-cut quartz plate (the Al metal was 99.998% pure; evaporation was done at 10^{-6} torr). An equilateral flint glass prism (Shott SF 10) was then kept in optical contact with the Al film, using bromonaphthalene as index-matching fluid. The experimental setup is shown in Fig. 1. A 100-kW Q-switched Nd:YAG (yttrium aluminum garnet) laser beam with 20-nsec pulse width and 0.1-cm^2 cross section was used for the excitation of the surface plasmons.

The polarization of the laser radiation hitting the film was selected by proper orientation of a Glan-Thomson polarizer inserted in the exciting beam. The prism assembly was mounted at the center of an adjustable goniometer with an angular resolution of 0.015°. Furthermore, a special mounting of the prism was devised in order to minimize the translation of the laser spot across the Al film upon rotation of the table of the goniometer.[2] Thus a major source of fluctuations in our measurements has been almost entirely removed. The scattered radiation at the second-harmonic was detected by a photomultiplier with the cathode 4 cm away from the metal film. The corresponding acceptance angle was 1.2 rad. The nonlinearly reflected second-harmonic signal was detected simultaneously by another photomultiplier mounted on an adjustable arm of the goniometer together with a collimating telescope. The orientation of this detector was optimized for each selection of the incidence angle on the film. With our geometry, the SH reflected signal was about five times larger than the corresponding scattered one.

Measurements of reflected and scattered second-harmonic light were performed with both TM and TE polarizations for the incident laser beam. In separate experiments, the surface plasmons at the fundamental ($\lambda = 1.06\ \mu$m) and second-harmonic ($\lambda = 0.53\ \mu$m) wavelengths were excited *linearly* in our sample, making use, in the second case, of a KDP (potassium dihydrogen phosphate) crystal as frequency doubler. The results of these linear measurements were compared with the corresponding results on the second-harmonic SP excitation.

The angular distribution of the scattered radiation was also investigated in our apparatus. The results of this experiment will be reported in a forthcoming paper.

V. THE EXPERIMENTAL RESULTS

The experimental results are shown in Figs. 3–6. Figure 3 shows the scattered light intensity at the second harmonic as a function of the incidence angle of the input TM-polarized beam at the fundamental. The presence of two resonance peaks is clearly observable. We have checked experimentally that the angles corresponding to these resonances nearly coincide with the ones at which surface plasmons are linearly excited by independent sources at $\lambda = 1.06\ \mu$m and $\lambda = 0.53\ \mu$m, as indicated in Sec. IV. In this additional experiment we observed that the peak at $\lambda = 0.53\ \mu$m is about four times broader then the one at $\lambda = 1.06\ \mu$m, owing to the larger surface polariton damping at higher frequencies. This effect is also verified by the corresponding results of the nonlinear experiment, as shown in Figs. 3–5. The theoretical best-fit curve drawn in Fig. 3 was obtained with the following values of the parameters: Al-film thickness $d = 340$ Å; bromonaphthalene-film thickness; 600 Å; dielectric constants of Al: $\epsilon_m(\omega) = (-101.200 + i20.140)$; $\epsilon_m(2\omega) = (-37.744 + i10.700)$.

Furthermore, we have used in our calculations the following values of the dielectric constants[21]: for the prism glass, $\epsilon_p(\omega) = 2.897$, $\epsilon_p(2\omega) = 3.201$; for quartz, $\epsilon_{\parallel}(\omega) = 2.381$; $\epsilon_{\perp}(\omega) = 2.354$; $\epsilon_{\parallel}(2\omega) = 2.422$; $\epsilon_{\perp}(2\omega) = 2.393$; for bromonaphthalene, $\epsilon(\omega) = 2.550$, $\epsilon(2\omega) = 2.795$. All calculations of the theoretical curves corresponding to the experimental results of this paper were carried out by solving the exact boundary condition problem of a four-media stratified system (glass, matching fluid, metal film, quartz). Two theoretical curves corresponding to a 10% variation of $\epsilon_m(2\omega)$ with respect to the best-fit value, keeping $\epsilon_m(\omega)$ constant, are also shown in Fig. 3. These curves provide good evidence of the sensitivity of the shape of the second-harmonic SP spectrum to the value of $\epsilon_m(2\omega)$. We note that the resonant peak at a smaller angle, which corresponds to $D(k_x;\omega) \simeq 0$, is rather insensitive to the value of $\epsilon_m(2\omega)$, as expected from the theory. On the other hand, the position and shape of this peak has been found to be strongly affected (and the other peak nearly unaffected) by an equal variation of $\epsilon_m(\omega)$, $\epsilon_m(2\omega)$ being constant. The SH scattering spectrum corresponding to TE surface-plasmon excitation does not show clear resonant effects. However, a small resonant peak at about 19° should be present. As will be explained later in the paper, this resonance is due to the excitation of a surface plasmon driven by a nonresonant component of $P^{\rm NL}$ (see Fig. 6). However, it was not clearly detected in our scattering experiment because of the large statistical fluctuations associated with the very small signals emitted. The dependence of

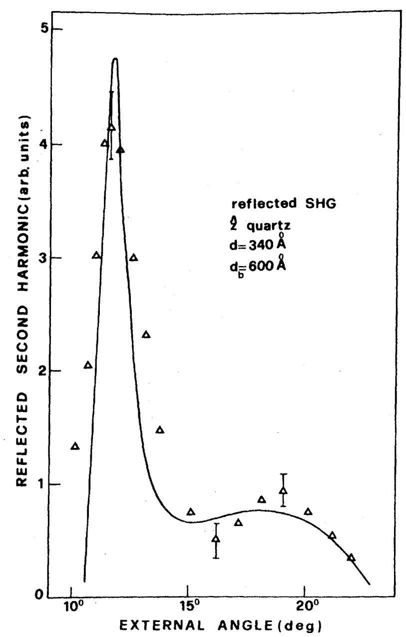

FIG. 5. Intensity of the SH reflected radiation for TM excitation. The theoretical curve corresponds to the best-fit curve shown in Fig. 3.

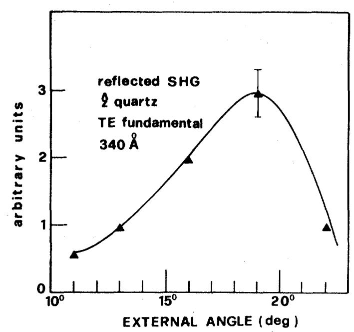

FIG. 6. Intensity of the SH reflected radiation for TE excitation (arbitrary units). The broad resonance peak at ~19° corresponds to the SP excitation at 2ω driven by a nonresonant component of the nonlinear (NL) polarization in quartz: P_x^{NL}.

the second-harmonic spectrum on the film thickness is shown by the theoretical curves of Fig. 4. These curves have been drawn using the remaining linear data corresponding to the best-fit one of Fig. 3.

Figures 5 and 6 give the reflected second-harmonic intensity, respectively, for TM and TE input beam at the fundamental. The profile of the curve of Fig. 5 reproduces essentially that shown in Fig. 3, as expected. More interesting is the case of TE input beam. As is well known, a TE-polarized beam cannot excite a surface-plasmon mode.[1] For this reason, no peak is observed in Fig. 5 at the lower angle, corresponding to the resonance at fundamental frequency. However, the quartz orientation in our experiment (crystallographic axes coincident with the x, y, z axes of the experiment) allow the resonant excitation of the surface plasmon at 2ω [i.e., $D(2K_x; 2\omega) \simeq 0$ resonance.] This one is driven by the x component of the nonlinear polarization $P_x^{NL} = \chi_{xyz}^{(2)} E_y(\omega) E_y(\omega)$, which is proportional to the square of the electric field of the TE input beam at the fundamental. Only in this case, the second peak should be observed with TE excitation. This effect is shown by our experimental results of Fig. 6. The maximum height of the peak of Fig. 6 is much smaller than the height of the corresponding peak of Fig. 5. The ratio 1:150 between the maximum values of the two peaks is in very good agreement with the theoretical predictions. The theoretical curves in Figs. 5 and 6 correspond to the best fit of Fig. 3 with the same values of the best-fit parameters. The number of photons scattered nonlinearly at second harmonic, in correspondence with the maximum of the lower peak in Fig. 3 and for a laser intensity of ~1 MW/cm^2, was $\simeq 200$. This is in order-of-magnitude agreement with the theory. Analogous agreement is found for the corresponding intensity of the nonlinearly reflected field.

The results of our experiment were reproducible with the same film maintained in an ambient laboratory environment over a period of several weeks. We observed only a change in the profile of the resonance curve for the scattered light from linearly excited surface waves. The shape of the resonance becomes more and more asymmetric and tends to assume a dispersive-like profile. This effect was already observed, for linearly driven SP, by Weber and McCarthy[2] in films grown at 77 K. They attribute the effect to the interference between the surface scattering of the SP wave and the bulk scattering inside the metal film. Bulk scattering provides a background signal always in phase with the incoming beam while the surface scattered signal undergoes a π-phase change when the incidence angle is tuned through the SP resonance. Thus, constructive interference occurs on one side of the resonance (at larger incidence angles) and destructive interference occurs on the other side. When the background bulk-scattering signal is comparable to the surface-scattering signal, a completely dispersive line shape is obtained. We conclude that the oxidation that occured in the laboratory over a considerable length of time, increases the film inhomogeneity and also the bulk-scattered light. No such effect was observed in the nonlinearly scattered second harmonic. Although a slight shift and broadening of the peaks was observed, there was no substantial shape change. This was to be expected, since the second-harmonic signal is generated in the quartz substrate and surface- and bulk-scattered fields are always in phase.

Finally, in Fig. 7 we plot the logarithm of the roughness power spectrum $|s(\Delta\vec{K})|^2$ as a function of the square of the momentum transfer $\Delta\vec{K}$, at the second harmonic. In the linear zone, we can reasonably assume a Gaussian correlation function for the roughness [cf. Eq. (18)]. By applying this approximation to our experimental results we have found an rms value of the roughness $(\overline{S^2})^{1/2} = 25.4$ Å and an autocorrelation length $\sigma = 1390$ Å. These

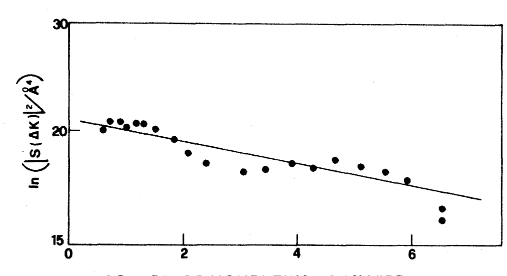

FIG. 7. Logarithm of the power spectrum of the film roughness versus the square of the relative transfer momentum ΔK Å at the second harmonic.

values are common values for Al films evaporated with our technique.[22]

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*Present address: Istituto di Fisica Sperimentale Via Tari, 3-Napoli, Italy.

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