Second-harmonic generation from silver and aluminum films in total internal reflection

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We have measured optical second-harmonic generation (SHG) in the total-internal-reflection regime from opaque silver and aluminum films. A recent hydrodynamic theory of SHG from metal surfaces by Sipe shows that at large angles of incidence the SHG in total internal reflection will be sensitive to the normal component of the harmonic surface current. We find that the phenomenological parameter a which estimates the size of this normal component has a value of 0.9 for silver and 1.5 for aluminum. By calibrating the reflected SHG from the opaque metal films to the transmitted SHG from quartz we determine that the theoretical and experimental conversion factors for reflected SHG agree to within 20% for silver and 40% for aluminum. For thin metal films we observe new interference structure in the wings of the surface-plasmon resonance, which also is in good agreement with the theory. We conclude that for incident 1.06-μm radiation the SHG from silver and aluminum films is well described by Sipe's hydrodynamic model.

I. INTRODUCTION

It has been almost twenty years since Jha[1] predicted the second-harmonic generation (SHG) of light from a free-electron gas and Brown *et al.*[2] first observed reflected SHG from a silver film irradiated with ruby laser light. Today there continues to be renewed interest in SHG from metal surfaces due to a number of recent experiments. These include the observation of enhanced scattered SHG from roughened silver surfaces by Chen *et al.*,[3] the study of SHG from surfaces prepared using microlithography by Wokaun *et al.*,[4] and the detection of molecular monolayers absorbed on a silver surface by SHG by Chen *et al.*[5] The utility of SHG from centrosymmetric media as a new probe of surface-physics phenomena has been recently demonstrated by several workers.[6]

An excellent review of the literature discussing SHG from metal surfaces was recently published by Sipe and Stegeman.[7] Briefly, the sources for the SHG at a metal surface consist of a "volume" current density which extends about a skin depth into the metal and a "surface" current density with components normal and tangential to the surface which extends only a few Fermi wavelengths into the metal. The free-electron model is inadequate for describing electron dynamics within a few Fermi wavelengths of the surface. Rudnick and Stern[8] first pointed out the limitations of the free-electron model in describing the SHG surface current terms and presented phenomenological arguments to estimate the size of these terms. Their theory introduces phenomenological constants a and b which are estimated to be of order unity.

Sipe[9] has recalculated the SHG from a metal surface using a free-electron hydrodynamic model. He finds that $b=-1$ and estimates the value of a to be between $+2$ and -2 by comparison to an experiment of Simon *et al.*[10] on SHG in quartz which utilized surface-plasmon enhancement. This latter result is based on fitting the theory to that section of the experimental SHG angular dependence where there is interference between the surface-plasmon-enhanced SHG from the noncentrosymmetric quartz crystal and that from the silver film. Near the surface-plasmon angle the SHG is dominated by the nonlinearity of the quartz and thus it is difficult to accurately measure parameters associated with the metallic surface currents in such an experiment. Furthermore, the small angular interval between the fundamental and harmonic surface-plasmon angles in the experiment does not permit a sensitive measurement of the a parameter. As pointed out by Sipe, SHG in a total-internal-reflection (TIR) regime from a prism-metal interface at large angles of incidence is particularly sensitive to the value of the a parameter.

In order to quantitatively test this theory we have carried out a series of experiments in which we observe SHG in TIR over a broad range of angle of incidence from opaque silver and aluminum films deposited on several prisms. The three prisms were chosen with a large range of refractive indices in order to check the internal consistency of this theory, i.e., that the experimentally determined value of a is independent of the index of the prism. We have also carefully measured the ratio of reflected SHG from silver and aluminum films to that transmitted through a quartz crystal in order to compare the SHG conversion factor with that predicted by the theory. In addition, we have reexamined SHG in TIR from thin silver and aluminum films and observed interference structure in the vicinity of the surface-plasmon angle not previously detected.[11]

In the following sections we briefly summarize the results of Sipe's theory, describe the experimental procedures, display the results of the experiments, and discuss the comparison with the theory. We conclude with suggestions for future experiments.

II. THEORY

Sipe[9] has provided a detailed theoretical analysis of SHG of light at metal surfaces using a hydrodynamic theory of the electron gas. We display here only those formulas necessary to interpret our experimental results. Consider a wave incident in a dielectric prism onto a metal film of thickness d as shown in Fig. 1. The conversion factor R for the ratio of the reflected SHG irradiance to the square of the incident fundamental irradiance, both external to the prism in vacuum, is written in the form $R=|A|^2T$. Here A is the ratio of the second harmonic electric field to the square of the fundamental electric field inside the prism and is written $A=A_m+A_0+A_d$, where the subscripts indicate the contribution to the SHG from the bulk metal, the front prism-metal selvedge, and the back metal-air selvedge, respectively. The factor T contains all the appropriate Fresnel and geometrical factors which describe the entering of the fundamental beam from vacuum into the prism and the exiting of the harmonic beam from the prism back into vacuum. The contribution to the SHG from the bulk metal is given by

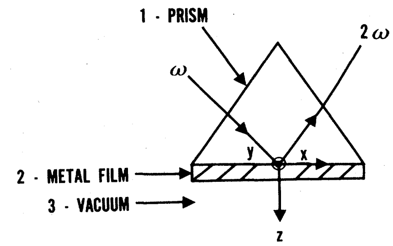

FIG. 1. Prism geometry for SHG in TIR from metal films.

$$A_m=MT_{21}(t_{12}m)^2\frac{2k(e/m)[\epsilon_2(2\omega)-1]}{ic^2\tilde{\omega}_2^2W_2\tilde{\Omega}_2}\{(1+R_{23})e^{i(2w_2+W_2)d}[k^2(1+r_{23})^2+w_2^2(1-r_{23})^2]$$
$$-(1+R_{23}e^{i2W_2d})[k^2(1+r_{23}e^{2iw_2d})^2+w_2^2(1-r_{23}e^{2iw_2d})^2]\} . \quad (1)$$

The contribution from the prism-metal selvedge is given by

$$A_0=2\pi iMT_{21}\left[\frac{K\tilde{\Omega}_2}{W_2}(1+R_{23}e^{i2W_2d})Q_0^z+\frac{\tilde{\Omega}^2}{\tilde{\Omega}_2}(1-R_{23}e^{i2W_2d})Q_0^k\right] . \quad (2)$$

Finally, the contribution from the metal-air selvedge is given by

$$A_d=2\pi iT_{21}T_{32}Me^{iW_2d}\left[\frac{k\tilde{\Omega}_3}{W_3}Q_d^z+\frac{\tilde{\Omega}^2}{\tilde{\Omega}_3}Q_d^k\right] . \quad (3)$$

Here

$$m=(1+r_{12}r_{23}e^{2iw_2d})^{-1}$$

and (4)

$$M=(1+R_{12}R_{23}e^{2iW_2d})^{-1}$$

are the modification factors which account for multiple reflections in the film at ω and 2ω. We have set the free-space wave vector $\tilde{\omega}=w/c$, the wave vector in the ith medium, $\tilde{\omega}_i=\tilde{\omega}[\epsilon_i(\omega)]^{1/2}$, and the normal component of the wave vector in the ith medium, $w_i=(\tilde{\omega}_i^2-k^2)^{1/2}$. The Fresnel coefficients for reflection and transmission, r_{ij} and t_{ij}, are given by

$$r_{ij}=\frac{w_i\epsilon_j-w_j\epsilon_i}{w_i\epsilon_j+w_j\epsilon_i}$$

and (5)

$$t_{ij}=\frac{2(\epsilon_i\epsilon_j)^{1/2}w_i}{w_i\epsilon_j+w_j\epsilon_i}$$

for our case of p polarization. The corresponding capital letters indicate these quantities evaluated at $\Omega=2\omega$ and $K=2k$, where ω is the incident angular frequency and k is the tangential component of the incident wave vector with the subscripts 1, 2, and 3 denoting prism, metal, and vacuum, respectively, in the geometry of this experiment as shown in Fig. 1. Here **Q** is the dipole moment per unit area of the harmonic currents sheets. At the prism-metal selvedge its components tangential, Q_0^k, and normal, Q_0^z, to the surface are given by, respectively,

$$Q_0^k=bFkw_2(r_{23}^2e^{i4w_2d}-1)$$

and (6)

$$Q_0^z=aF\frac{k^2}{2}(r_{23}e^{i2w_2d}+1)^2 ,$$

while at the metal-vacuum selvedge its components are given by

$$Q_d^k=-bFkw_2(r_{23}^2-1)e^{i2w_2d} ,$$

and (7)

$$Q_d^z=-aF\frac{k^2}{2}(r_{23}+1)^2e^{i2w_2d} .$$

In the above expressions the common factor F is given by

$$F=\frac{e}{m}\frac{[\epsilon_2(\omega)-1](t_{12}m)^2}{8\pi\omega^2\tilde{\omega}_2^2} , \quad (8)$$

where e/m is the charge to mass ratio of the electron and $\epsilon_2(\omega)$ is the metal dielectric constant. Here a and b are the phenomenological constants originally introduced by Rudnick and Stern to account for the effects of the boundary on the normal and tangential harmonic surface current, respectively. Sipe has shown in the hydrodynamic theory that $b=-1$ for a smooth surface and that a is the parameter of interest which must be determined experimentally. In total internal reflection (TIR) at large angles of incidence the contribution to the nonlinear polarization from the harmonic normal surface current, which is proportional to the a parameter, increases. The nonlinear reflectance is thus more sensitive to the value of a in a TIR experiment than in a front surface reflection experiment. By fitting the observed and calculated curves of nonlinear reflectance versus angle of incidence in TIR, the value of a may be determined to within 20%.

III. EXPERIMENT

The source of fundamental radiation was a passively mode-locked Nd glass laser with an output of 30 mJ over a cross section of 0.03 cm^2 in a pulse train of approximately 200 nsec. The output of the laser passed through a glass beam splitter which reflected 4% of the laser intensity into a z-cut quartz wedge which produced SHG for the reference channel. The main beam, which passed through an attenuator and a polarizer, was then incident on the entrance face of the prism which was mounted on a rotation platform that could be rotated in increments of 0.025°. The SHG detector was independently positioned to track the nonlinearly reflected harmonic. The metal films were evaporated on the prism hypotenuse face. SHG data were recorded digitally by means of a standard dual-channel arrangement. Each data point was an average of 5–10 laser shots. The observed signals were verified for correct wavelength, polarization dependence, and particularly specular reflectivity at an angular offset from the reflected fundamental due to the dispersion of the prism.[11]

The metal films were evaporated on the hypotenuse faces of a 45° Schott glass BK-7 prism, a 60° Schott glass SF-59 prism, and a 45° rutile prism. The Schott glass prisms had 1 in.×1 in. entrance-exit faces which permitted the use of large angles of incidence up to 80°, while the single crystal rutile prism had only $\frac{1}{2}$ in.×$\frac{1}{2}$ in. entrance-exit faces and was oriented with the c axis normal to the plane of incidence in order that the fundamental and harmonic p-polarized waves had ordinary polarization in the rutile. Each prism was initially placed in an ultrasonic bath, then carefully cleaned with distilled water, and finally rinsed with methanol prior to being placed in the evaporator. The silver and aluminum metals (99.999%) were evaporated in a NRC model 3117 oil diffusion-pump evaporator at a base pressure of 10^{-6} torr. Evaporation rates were greater than 10 Å/sec and film thicknesses were measured with a Sloan 200 quartz-crystal digital monitor. All opaque films had thicknesses greater than 2000 Å. The SHG data were taken immediately after the prism was removed from the evaporator. It was found that if the prism was reinserted in the evaporator and removed several days later the data were highly reproducible. The entire experiment for each prism, including the cleaning and coating process, was repeated several times to ensure reproducibility of all the data reported here. Since the SHG source in the thick-film experiments was at the glass/metal interface, which was protected from the ambient atmosphere by the film, these measurements are not sensitive to the surface contaminants associated with front-surface SHG from metal films.[12]

IV. RESULTS AND DISCUSSION

In the first set of experiments reflected SHG in TIR from opaque silver films was observed over a broad range of angle of incidence. The range of the internal angle of incidence was varied from approximately 40° to 80° so that the SHG would reach a maximum value within this interval. The shape of the SHG versus angle of incidence curves and particularly the ratio of the maximum to the minimum value of the SHG within this interval was sensitive to the value of the parameter a. The use of prisms with different indices of refraction permitted two checks on the internal consistency of the theory: first, that the value of a was independent of the prism, and, second, that

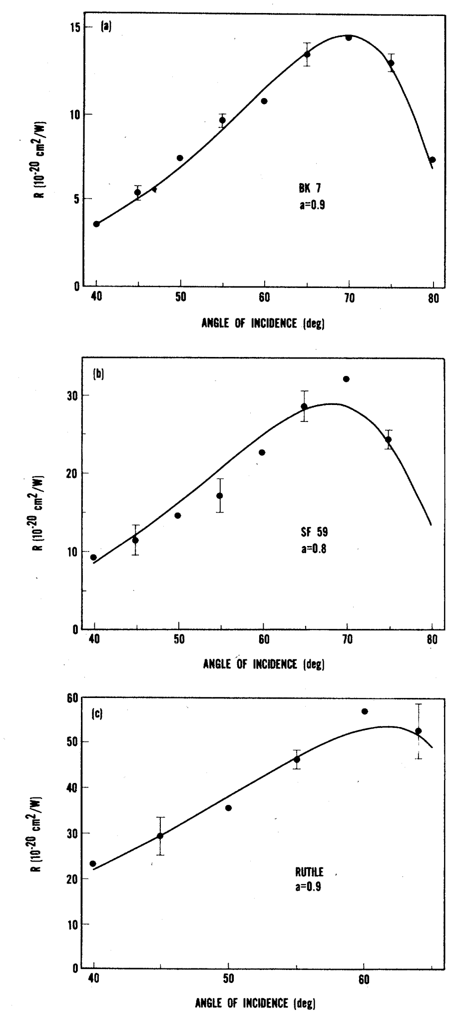

FIG. 2. Reflected SHG versus internal angle of incidence from opaque silver films evaporated on prisms made from (a) Schott BK-7 glass, (b) Schott SF-59 glass, and (c) rutile crystal. The value of the a parameter indicated provides the best fit of the theory to the experiment.

the SHG conversion factors which varied by as much as a factor of 5 for silver and 10 for aluminum among the prisms used agreed with the theory.

In Figs. 2(a)—2(c) the solid circles show the observed reflected SHG versus internal angle of incidence from opaque silver films evaporated on BK-7 glass, SF-59 glass, and rutile prisms, respectively. The ordinate axes are labeled by the theoretical SHG conversion factor R. The curves are calculated from the equations given previously with d set equal to 2000 Å and with the linear optical constants given in Table I. The value of the a parameter shown on each curve was determined from a least-squares routine[16] which simultaneously fitted the value of a and the normalization constant on the vertical scale. This latter constant did not vary by more than 10% among the three curves. Error bars for a few representative data points are indicated. From these results the value of $a=0.9\pm0.2$ for a silver film is determined. The error assigned to this value not only includes statistical errors displayed in the data but additional errors estimated by repeating the entire experiment several times. We note that this determination of the a parameter is a significant improvement over the earlier estimation of the value of a to be between $+2$ and -2.[9] The theory further predicts that the peak SHG at large angle of incidence increases with increasing refractive index of the prism. In Fig. 3(a) we plot the reflected SHG conversion factor for the silver films at an angle of incidence equal to 60° for each of the three prisms versus the index of refraction of the prism. The open circles are the results of the theoretical calculation with $a=0.9$ and the solid circles are the experimental results. The latter are calibrated to the theoretical scale by comparison to the transmitted SHG from a wedged Z-cut quartz crystal.[17] Thus the experimental points are plotted on an absolute scale with no adjustable constants. Note the excellent agreement between theory and experiment for the front surface (prism refractive index equal unity), BK-7, and SF-59 cases. The larger discrepancy for the rutile prism was consistently observed. From these results we conclude that Sipe's theory predicts to within 20% the magnitude of the observed SHG in reflection from silver films with 1.06-μm incident radiation. An earlier effort by Sonnenberg and Hefner[18] to compare the SHG from a front-surface silver film using incident ruby-laser radiation to the value calculated from the original free-electron theory of Jha was off by almost an order of magnitude due to the effect of the interband transitions.[19]

TABLE I. Optical constants.

	ω (1.06 μm)	2ω(0.53 μm)	
Metal	Dielectric constant		Ref.
Ag	$-67+i2.44$	$-11.9+i0.33$	13
Al	$-95+i33$	$-33+i10$	14
Prism	Index of refraction		
BK-7	1.507	1.520	15
SF-59	1.908	1.970	15
Rutile (ordinary)	2.481	2.673	14

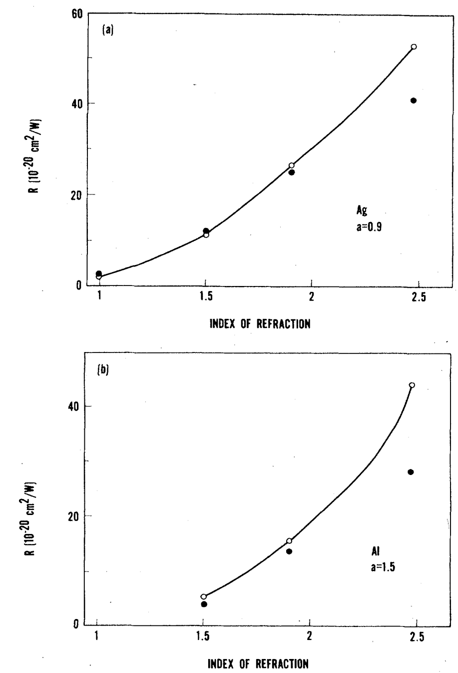

FIG. 3. Reflected SHG from opaque (a) silver and (b) aluminum films at an angle of incidence equal to 60° versus the index of refraction of the prism. The open circles are calculated from the theory with $a=0.9$ for silver and $a=1.5$ for aluminum. The solid line is drawn to aid the eye. The solid dots are the experimental points which are calibrated to the absolute scale by comparing with SHG from quartz.

In the second set of experiments opaque aluminum films were evaporated on the clean hypotenuse face of the same set of prisms. In Figs. 4(a)—4(c) the reflected SHG results for the aluminum-coated prisms are displayed. The angular dependence of the theoretical reflected SHG was fitted to the experimental results by the same least-squares procedure. From these results the value of the parameter $a=1.5\pm0.3$ for an aluminum film is determined. Again the error bars include both statistical error in the data and estimated error based on reproducibility of the experimental results.

In Fig. 3(b) we plot the reflected SHG conversion factor for the aluminum films at an angle of incidence of 60° versus the index of refraction of the prism. The point corresponding to reflected SHG from a front surface aluminum film was omitted because of the low signal level. The theoretical points are calculated for $a=1.5$ and the experimental points are normalized to the absolute scale by comparison with the transmitted SHG from quartz as before. Agreement between theory and experiment of 40% for the magnitude of the reflected SHG for aluminum films with incident 1.06 μm radiation is again quite good.

The next set of experiments involved the reexamination of SHG with surface plasmons from thin silver and aluminum films. In the original experiment of Simon *et al.*,[11] in which a ruby laser was used, the resonantly

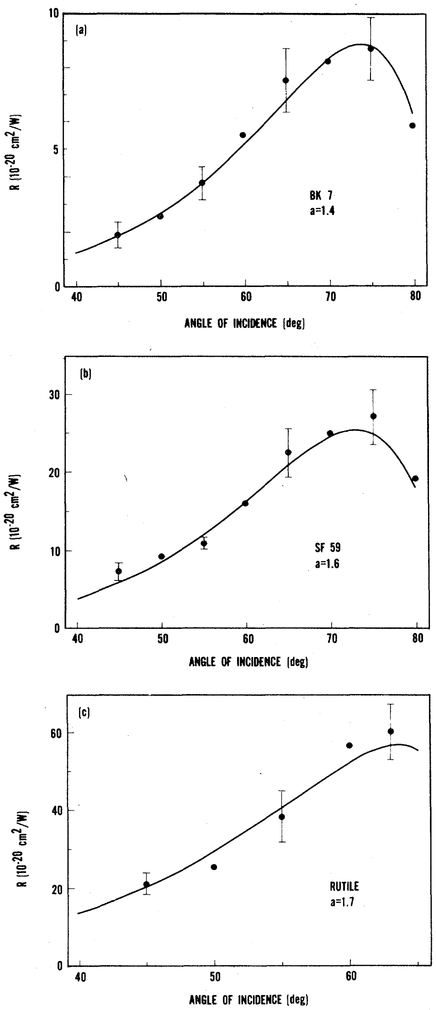

FIG. 4. Reflected SHG versus internal angle of incidence from opaque aluminum films evaporated on prisms made from (a) Schott BK-7 glass, (b) Schott SF-59 glass, and (c) rutile crystal. The value of the a parameter indicated provides the best fit of the theory to the experiment.

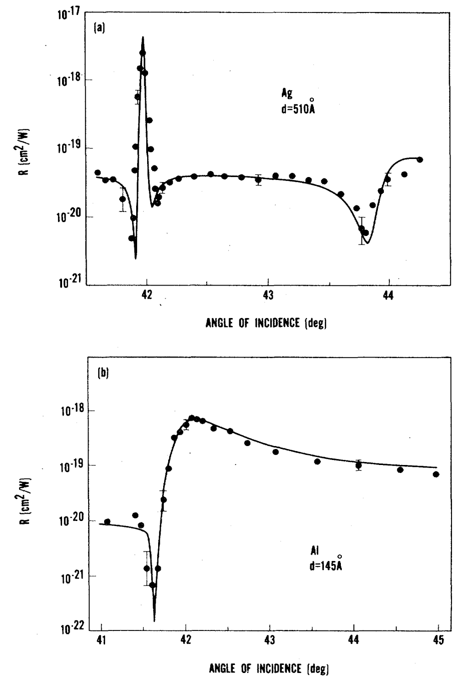

FIG. 5. Reflected SHG versus internal angle of incidence from a thin (a) silver film ($d=500$ Å) and (b) aluminum film ($d=145$ Å) on a BK-7 prism. Solid curves calculated from theory with $a=0.9$ for silver and $a=1.5$ for aluminum.

enhanced SHG was observed in only a narrow angular interval around the angle for fundamental surface-plasmon excitation. Since Sipe's theory predicts additional structure over a broader angular interval, the experiment was repeated now using the Nd laser with a 510-Å silver film evaporated on the BK-7 glass prism. The results are shown in Fig. 5(a), where the experimental points are fitted to the theoretical ordinate to within 20%. In addition to the large peak at the fundamental surface-plasmon angle, interference structure is observed in the wings of this resonance. At the resonant angle the SHG is dominated by the surface-plasmon mode at the back metal-air selvedge, while off resonance this contribution is severely damped relative to the contribution from the front prism-metal selvedge. In the wings of the resonance the interference of these two source terms is observed. The dip in the SHG at the harmonic plasmon angle was previously observed and discussed by Simon *et al.*[10] in the experiment which used surface-plasmon excitation with a quartz nonlinear crystal. When SHG is produced in the front prism-metal selvedge at the angle for harmonic surface-plasmon excitation, this harmonic light suffers attenuated total reflection in the metal film and thus a decrease in the SHG is observed. In Fig. 5(b) we display the SHG results from a similar experiment with a thin 145-Å aluminum film evaporated on a BK-7 prism. The theoretical curve is calculated from the same formulas as before with $a=1.5$ and with the optical constants of aluminum. The resonance in the SHG due to the excitation of the fundamental surface-plasmon mode is observed but considerably broadened relative to that in silver due to the absorption of the aluminum. The shape of the experimental curve which is normalized to the theoretical ordinate scale to within 40% is in good agreement with the theory.

V. SUMMARY AND CONCLUSIONS

There has been a resurgence of interest in using SHG from metals as a probe for studying surface phenomena. Although the original free-electron theory of SHG from metals is nearly twenty years old, this theory has only recently been modified by Sipe who used a hydrodynamical model for the free-electron gas. In order to experimentally test the predictions of this more rigorous and quantitative theory we have carried out a series of measurements of SHG in total internal reflection (TIR) from opaque silver and aluminum films. By examining the angular dependence of the SHG at large angles of incidence we find that the a parameter, originally introduced by Rudnick and Stern as a measure of the normal component of the SHG source current, is equal to 0.9 ± 0.2 for a silver film and 1.5 ± 0.3 for an aluminum film with 1.06-μm incident fundamental radiation. This determination of a is a significant improvement over an earlier estimate of only the absolute value of a to be of order unity. By measuring the SHG in TIR from prisms with a range of index of refractions values from 1.52 to 2.48, we observe that the SHG conversion factor for the metals changes by almost an order of magnitude as predicted by the theory. For thin silver and aluminum films SHG with surface-plasmon excitation is reexamined and interference between SHG from the surface-plasmon mode at the back metal-air selvedge and SHG from the front prism-metal selvedge is observed for the first time. The angular dependence of this interference structure is also well fit by the values of a given above.

In addition we have measured the SHG conversion factor in TIR for silver and aluminum films on an absolute scale by comparing to the SHG in transmission from a quartz crystal. Here the agreement between theory and experiment is 20% for a silver film and 40% for an aluminum film. Although this agreement is excellent, the presence of adsorbed molecular layers at the prism-metal selvedge could modify the SHG conversion ratio since these evaporated films were not prepared in ultrahigh vacuum. Also, the effect of surface roughness is not included in the present theory.[20] This measurement is a significant improvement over the results of earlier front-surface reflection experiments in which the discrepancy with the original theory was an order of magnitude. We conclude that for incident 1.06-μm radiation on silver and aluminum metal films the angular dependence and the conversion efficiency of SHG is well described by Jha's original free-electron theory as modified by Sipe's hydrodynamic model.

Future experiments should be performed utilizing metal films evaporated on prisms in ultrahigh vacuum in order to eliminate uncertainties associated with adsorbed molecular layers. An advantage of the TIR geometry with opaque metal films is that the SHG measurements may be done in air since the thick film protects the critical prism-metal selvedge. Since these experiments were done only at a single wavelength it would be interesting to measure the dispersion of the parameter a. Sipe has suggested that this parameter might show resonant behavior. It is well known that for a silver film excited by ruby-laser radiation the contribution from the bound electrons interferes with that from the free electrons;[19] thus, a value of a different from unity would be expected. On the other hand, the SHG from aluminum should obey the free-electron model for incident fundamental radiation throughout the visible spectrum. In addition, it would be interesting to extend these TIR measurements both to the free-electron alkali metals such as Na and K, and the noble metals such as Cu and Au.

ACKNOWLEDGMENTS

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