Enhanced second-harmonic generation by surface polaritons on thin metal films

Michael G. Weber*
Department of Physics, University of California, Irvine, California 92717
(Received 12 November 1985)

For a critical film thickness we find a large resonant enhancement of second-harmonic generation by surface polaritons. The effect is due to perfect phase matching between surface polaritons on different branches of the surface-polariton dispersion curve. For the case of a free-standing copper film in the infrared, our calculation predicts a surface second-harmonic intensity 3000 times larger than that found at the surface of the semi-infinite metal.

I. INTRODUCTION

In recent years there has been considerable interest in the study of surface-polariton propagation on a variety of materials, but relatively little attention has been devoted to nonlinear interactions between these waves.[1]

Nonlinear electromagnetic effects in metals are normally small unless the condition of phase matching is achieved. An example of near phase matching has been proposed by Maddox and Mills[2] in a study of nonlinear interactions between surface-phonon polaritons on the surface of doped (n-type) zinc-blende semiconductors. When the plasma frequency is below that of the LO phonon, one can mix two waves on the lower branch of the two-branch dispersion curve to produce an output wave near a point on the upper branch. Another example of near phase matching is the case of surface-plasmon polaritons in the infrared, investigated by Mills.[3] In this case, the dispersion relation of the surface polaritons is approximately linear, and the phase-matching condition $2\omega(k)=\omega(2k)$ is nearly satisfied.

In this report we discuss a similar second-order nonlinear process which may proceed under conditions of *perfect* phase matching: second-harmonic generation by surface-plasmon polaritons propagating on a thin metal film. The process combines some of the features of both of the processes mentioned above. It takes place between two different dispersion-curve branches, but both of the interacting waves are surface-plasmon polaritons. If one chooses the film thickness such that modes exist at $\omega,k_{||}$ on the lower branch and $2\omega,2k_{||}$ on the upper branch of the dispersion curve, one finds surface second-harmonic fields many times larger than that at the surface of the semi-infinite metal. For example, our calculations show that for a 350-Å-thick free-standing (vacuum-metal-vacuum) copper film with a 0.1-eV incident surface polariton, the surface second-harmonic field is more than 50 time larger than that on semi-infinite copper. This then produces an enhancement of 3000 in the intensity of the second-harmonic output.

II. THEORY

The theoretical derivation of the second-harmonic field amplitude follows that of Mills,[3] mentioned above, except that the Green's function appropriate to a thin metal film is employed here. Since our method is not fundamentally different from the method presented by Mills, we shall present only a brief outline here.

The geometry we consider consists of a dielectric substrate for $z<0$ with a metal overlayer between $z=0$ and $z=d$ (see Fig. 1). The incident surface polariton, with frequency ω and wave vector $k_{||}$, propagates parallel to the x axis with fields given by

$$\mathbf{E}=\begin{cases} E_0\left[\hat{\mathbf{x}}+\dfrac{ik_{||}}{\alpha}\hat{\mathbf{z}}\right]e^{ik_{||}x}e^{-\alpha(z-d)}e^{-i\omega t}, & z>d \\ E_0\left[\hat{x}\left[\cosh[\beta(z-d)]-\dfrac{\beta}{\epsilon_1(\omega)\alpha}\sinh[\beta(z-d)]\right]\right. & \\ \quad\left.+\hat{z}\left[\dfrac{\beta}{\epsilon_1(\omega)\alpha}\cosh[\beta(z-d)]-\sinh[\beta(z-d)]\right]\dfrac{ik_{||}}{\beta}\right]e^{ik_{||}x}e^{-i\omega t}, & 0<z<d \\ E_0\left[\hat{\mathbf{x}}-\dfrac{ik_{||}}{\gamma}\hat{\mathbf{z}}\right]\left[\cosh(\beta d)+\dfrac{\beta}{\epsilon_1\omega\alpha}\sinh(\beta d)\right]e^{ik_{||}x}e^{+\gamma z}e^{-i\omega t}, & z<0 \end{cases}$$

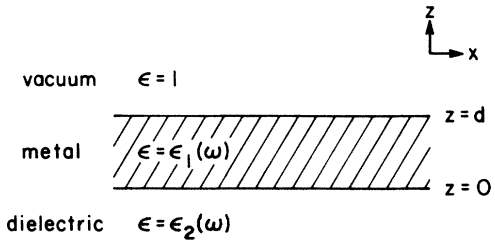

FIG. 1. Dielectric substrate with a metal overlayer of thickness d.

where

$$\alpha=\left[k_{\|}^2-\frac{\omega^2}{c^2}\right]^{1/2},\quad \beta=\left[k_{\|}^2-\epsilon_1(\omega)\frac{\omega^2}{c^2}\right]^{1/2},$$

$$\gamma=\left[k_{\|}^2-\epsilon_2(\omega)\frac{\omega^2}{c^2}\right]^{1/2},\quad \mathrm{Re}(\alpha,\beta,\gamma)>0\ .$$

The frequency-dependent dielectric constant of the metal is assumed complex and is taken from experimental data.[4,5]

Rudnick and Stern[6] have presented a phenomenological description of the second-harmonic currents generated at the surface of a simple metal, and within its skin depth, when the metal is irradiated with an electromagnetic wave of frequency ω. Their prescription forms the basis of this study. They describe three contributions to the second-harmonic current density $\mathbf{j}^{(2\omega)}(\mathbf{x})$. These are as follows.

(i) A surface current normal to the interfaces which can be written as

$$j_{sz}^{(2\omega)}(\mathbf{x})=\frac{ie\omega_p^2 a}{8\pi m\omega}\{\delta(z-d^+)[E_z^{(\omega)}(z=d^-)]^2-\delta(z-0^-)[E_z^{(\omega)}(z=0^+)]^2\}\ ,$$

where a is a dimensionless constant of order unity, m is the conduction electron mass, ω_p is the metal's plasma frequency, and $d^{\pm}$ is the film thickness d plus or minus a positive infinitesimal.

(ii) A surface current parallel to the interfaces given by

$$j_{sx}^{(2\omega)}(\mathbf{x})=\frac{ie\omega_p^2 b}{4\pi m\omega^3}[\delta(z-d^+)E_z^{(\omega)}(z=d^-)E_x^{(\omega)}(z=d_-)+\delta(z-0^-)E_z^{(\omega)}(z=0^+)E_x^{(\omega)}(z=0^+)]\ ,$$

where b is a dimensionless constant of order unity.

(iii) A volume current that is appreciable within a skin depth of the interfaces

$$\mathbf{j}_v(\mathbf{k})=\frac{ie\omega_p^2}{16\pi m\omega^3}\nabla[\mathbf{E}^{(\omega)}(\mathbf{x})\cdot\mathbf{E}^{(\omega)}(\mathbf{x})]\ .$$

To calculate the second-harmonic fields, we insert the total current density given by the above three equations into Maxwell's equations and we use the Green's-function method devised by Mills and Maradudin.[7] Since this method has been fully described in their paper, we shall omit a description of the details and present the final result.

In the vacuum just above the metal the ratio of the magnitudes of the second-to-first harmonic fields is given by

$$\mathscr{E}(d)=\frac{E^{(2\omega)}(z=d^+,x=0,t=0)}{E^{(\omega)}(z=d^+,z=0,t=0)}=\frac{1}{2}\frac{\omega_p^2}{\omega^2}\frac{k_{\|}x_0(E_0)}{D(2\omega,2k_{\|})}f(\omega,k_{\|},d)\ ,$$

where $\omega,k_{\|}$ describe a point on the lower branch of the surface-polariton dispersion curve of a metal film of thickness d on a dielectric substrate, as shown in Fig. 1, and where

$$D(2\omega,2k_{\|})=\left[\epsilon_2(2\omega)+\frac{\gamma(2\omega)}{\alpha(2\omega)}\right]\cosh[\beta(2\omega)d]+\left[\epsilon_1(2\omega)\frac{\gamma(2\omega)}{\beta(2\omega)}+\frac{\epsilon_2(2\omega)\beta(2\omega)}{\epsilon_1(2\omega)\alpha(2\omega)}\right]\times\sinh[\beta(2\omega)d]\ ,$$

where

$$\alpha(2\omega)=2\alpha(\omega)=2\alpha\ ,$$

$$\beta(2\omega)=\left[4k_{\|}^2-4\epsilon_1(2\omega)\frac{\omega^2}{c^2}\right]^{1/2},$$

$$\gamma(2\omega)=\left[4k_{\|}^2-4\epsilon_2(2\omega)\frac{\omega^2}{c^2}\right]^{1/2},$$

and where after considerable calculation, we find

$$f(\omega,k_{\|},d)=\frac{\beta(2\omega)}{4k_{\|}}\left\{\left[e^{-\beta(2\omega)d}\left[C_-d+\frac{C_+}{2\beta(2\omega)}\right]-e^{-\beta(2\omega)d}\right]\left[\frac{-k_{\|}}{8}\left[1-\frac{k_{\|}^2}{\beta^2}\right]\left[1-\frac{\beta}{\epsilon_1\alpha}\right]^2\right]\right.$$

$$\left.+\left[e^{+\beta(2\omega)d}\left[\frac{C_-}{2\beta(2\omega)}-C_+d\right]-e^{-\beta(2\omega)d}\frac{C_-}{2\beta(2\omega)}\right]\left[-\frac{k_{\|}}{8}\left[1-\frac{k_{\|}^2}{\beta^2}\right]\left[1-\frac{\beta}{\epsilon_1\alpha}\right]^2\right]\right.$$

$$+\left[\frac{2\epsilon_2(2\omega)}{\beta(2\omega)\epsilon_1(2\omega)}-e^{+\beta(2\omega)d}\frac{C_+}{\beta(2\omega)}-e^{-\beta(2\omega)d}\right]\left[k_{||}e^{-2\beta d}\frac{[\beta-(\epsilon_1/\epsilon_2)\gamma]}{[\beta+(\epsilon_1/\epsilon_2)\gamma]}\right]$$

$$+(e^{+\beta(2\omega)d}C_+-e^{-\beta(2\omega)d}C_-)\frac{bk_{||}}{\epsilon_1\alpha}$$

$$+\left[\left[1+\frac{\beta}{\epsilon_1\alpha}\right]^2e^{2\beta d}-\left[1-\frac{\beta}{\epsilon_1\alpha}\right]^2e^{-2\beta d}\right]\left[-\frac{\gamma(2\omega)k_{||}b}{\beta(2\omega)}\right]\Bigg\}$$

$$+\frac{1}{2}\Bigg\{\left[e^{-\beta(2\omega)d}\left[C_-d-\frac{C_-}{2\beta(2\omega)}\right]+e^{+\beta(2\omega)d}\frac{C_+}{2\beta(2\omega)}\right]\left[\frac{\beta}{8}\left[1-\frac{k_{||}^2}{\beta^2}\right]\left[\frac{\beta}{\epsilon_1\alpha}-1\right]^2\right]$$

$$+\left[e^{+\beta(2\omega)d}\left[\frac{C_-}{2\beta(2\omega)}+C_+d\right]-e^{-\beta(2\omega)d}\frac{C_-}{2\beta(2\omega)}\right]\left[-\frac{\beta}{8}\left[1-\frac{k_{||}^2}{\beta^2}\right]\left[\frac{\beta}{\epsilon_1^a}+1\right]^2\right]$$

$$+(e^{+\beta(2\omega)d}C_++e^{-\beta(2\omega)d}C_-)\left[-\frac{a}{2}\frac{k_{||}^2}{\epsilon_1^2\alpha^2}\right]$$

$$+\left[\left[\frac{\beta}{\epsilon_1\alpha}+1\right]e^{\beta d}+\left[\frac{\beta}{\epsilon_1\alpha}-1\right]e^{-\beta d}\right]^2\left[\frac{a}{4}\frac{\epsilon_2(2\omega)}{\epsilon_1(2\omega)}\frac{k_{||}^2}{\beta^2(2\omega)}\right]\Bigg\},$$

where

$$C_+=\frac{\epsilon_2(2\omega)}{\epsilon_1(2\omega)}+\frac{\gamma(2\omega)}{\beta(2\omega)},$$

$$C_-=\frac{\epsilon_2(2\omega)}{\epsilon_1(2\omega)}-\frac{\gamma(2\omega)}{\beta(2\omega)}.$$

The quantity $X_0(E_0)$ is the amplitude of oscillation experienced by an electron in an external electric field of magnitude E_0, given by

$$X_0(E_0)=\frac{eE_0}{m\omega^2}.$$

The second-to-first harmonic-field ratio is directly proportional to this length divided by the wavelength of the incident polariton. For copper at 0.1 eV, and for a surface polariton with an electric field of magnitude 30 statvolts/cm, $k_{||}X_0$ is about 10^{-6}. Such a surface polariton could be excited if one could couple in 10% of the incident light from a 4-kW CO_2 laser with a spot diameter of 100 μm. Away from the resonant condition where $D(2\omega,2k_{||})=0$, the remaining combination of factors in the expression for d is of order unity. Thus, $k_{||}X_0(E_0)$ is the small parameter which determines the second-to-first harmonic-field ratio. However, as we shall see, if one chooses the film thickness d so that $D(2\omega,2K_{||})$ is minimized, there results a very large resonant enhancement of the surface second-harmonic field intensity.

III. RESULTS

It is interesting to make comparisons with Mills' earlier work on the second-harmonic fields at the surface of a semi-infinite metal. It can be shown, after a bit of algebra and through use of the dispersion relation, that in the

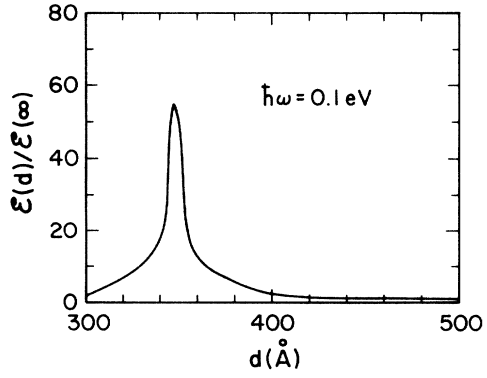

FIG. 2. Second-harmonic field-enhancement factor as a function of metal film thickness for a free-standing thin copper film in the infrared.

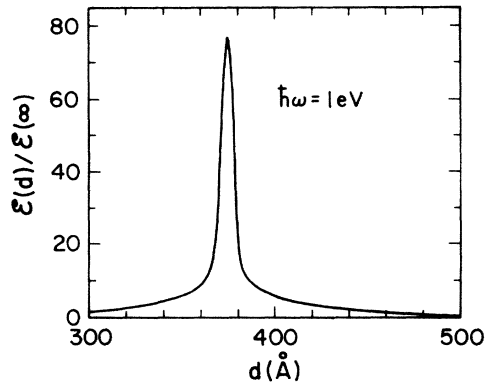

FIG. 3. Second-harmonic field-enhancement factor for a free-standing thin silver film in the visible.

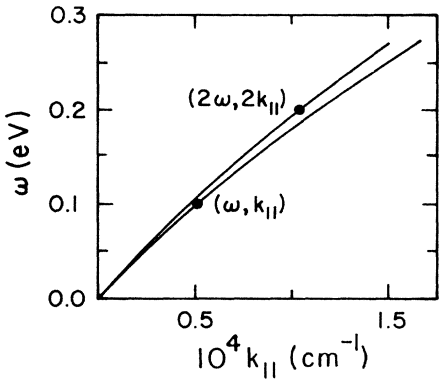

FIG. 5. Close-up view of the infrared portion of the dispersion curve shown in Fig. 4.

$d = \infty$ limit, Mills' result is recovered. In Fig. 2, we have plotted the second-to-first harmonic-field ratio $\mathscr{E}(d)$, divided by $\mathscr{E}(d = \infty)$, versus the film thickness d. The calculation was done for a free-standing copper film, with an incident surface polariton of energy 0.1 eV. It should be noted that the enhancement factor $\mathscr{E}(d)/\mathscr{E}(\infty)$ is independent of the field strength of the incident surface polariton. The plot in Fig. 2 thus shows the second-harmonic field enhancement obtained by using a thin film rather than a thick piece of metal. As the film thickness is increased from zero, the field-enhancement factor dramatically increases from around 1, at a film thickness of 300 Å, to a factor of 55 (corresponding to an intensity enhancement of about 3000) at a film thickness of 348 Å. Then, with increasing thickness, the enhancement falls back to the level of unity when the film reaches a thickness of 450 Å or so. Figure 3 shows the enhancement factor versus film thickness for a free-standing silver film, with a 1-eV incident surface polariton. We see that the enhancement factor is of the same order of magnitude in the optical region as that found for the infrared.

The second-harmonic field enhancement seen in Figs. 2 and 3 is caused by collinear phase matching between the incident surface polariton and the resulting second-harmonic field. Figure 4 shows the surface polariton dispersion curves for a free-standing thin copper film whose thickness is chosen to optimize the second-harmonic enhancement ($d = 348$ Å). Perfect phase matching occurs at 0.1 eV/0.2 eV, which is within the portion of the $\omega, k_{||}$ plane enclosed by the dotted lines. In Fig. 5 we enlarge this portion of the dispersion curve; we see that the $\omega, k_{||}$ point lies on the lower branch and the $2\omega, 2k_{||}$ lies on the upper one (the deviation of the dispersion curve from the light line is exaggerated here for clarity).

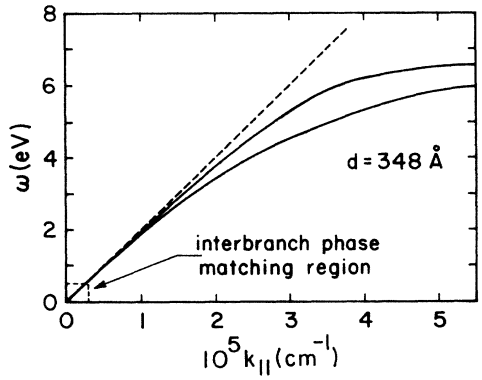

FIG. 4. Surface-polariton dispersion relation for a free-standing copper film with a thickness of 348 Å, corresponding to the peak in Fig. 2.

The limit to the enhancement caused by Joule losses in the metal, is described by the imaginary part of the complex dielectric function $\epsilon(\omega)$. Although the coherence length is infinite, the effective interaction length of the two waves is given by the second-harmonic surface polariton's mean free path, which is about 50 cm at 0.2 eV. In contrast, Mills finds a coherence length of 0.5 cm in his calculation of the second-harmonic fields at the surface of semi-infinite copper at the same frequencies. This factor of 100 difference between the interaction length of the first- and second-harmonic waves, when combined with the remaining factors of order unity accounts for the factor of 55 enhancement in the second-harmonic field ratio.

To our knowledge, this thickness-dependent resonant enhancement effect has not been tested experimentally.[1] Such an effect might be put to good use in nonlinear spectroscopy experiments where high-powered lasers are needed to produce second-harmonic fields of a useful strength. By choosing an optimal film thickness, one should be able to increase the surface second-harmonic intensity due to surface polaritons by more than three orders of magnitude.

ACKNOWLEDGMENTS

I am grateful to D. L. Mills for a helpful discussion of this problem. This work has been supported by NASA, through Contract No. NAG3-250.

*Present address: IFF-KFA, D-5170 Jülich, Federal Republic of Germany.

[1]For an excelletnt recent review, see Y. R. Shen and F. de Martini, in *Surface Polaritons,* edited by V. M. Agranovich and D. L. Mills (North-Holland, Amsterdam, 1982), Chap. 14.

[2]R. Maddox and D. L. Mills (unpublished). A summary of this work may be found in R. Maddox, Ph.D. thesis, University of California, Irvine, 1975.

[3]D. L. Mills, Solid State Commun. **24**, 669 (1977).

[4]For copper, we use the optical constants measured by A. P. Lenham and D. M. Treherne, J. Opt. Soc. Am. **56**, 683 (1966).

[5]For silver, we use optical constants reported by P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[6]J. Rudnick and E. A. Stern, Phys. Rev. B **4**, 4274 (1971).

[7]D. L. Mills and A. A. Maradudin, Phys. Rev. B **12**, 2943 (1975).