Second-harmonic generation in graded metallic films

J. P. Huang* and K. W. Yu

Department of Physics, The Chinese University of Hong Kong, Shatin, NT, Hong Kong

Received June 3, 2004

We study the effective second-harmonic generation (SHG) susceptibility in graded metallic films by invoking the local field effects exactly and further numerically demonstrate that graded metallic films can serve as a novel optical material for producing a broad structure in both the linear and the SHG response and an enhancement in the SHG signal.

OCIS codes: 160.4330, 310.6860, 160.4670, 160.4760.

Recently, there has been much interest in and a practical need for nonlinear optical materials that can process a large nonlinear susceptibility or an optimal figure of merit. A large enhancement in the nonlinear response was found for a subwavelength multilayer (i.e., a thin film) of titanium dioxide and conjugated polymer.[1] For nonlinear effects other than the Kerr effect, Hui and Stroud[2] derived general expressions for the effective susceptibility for second-harmonic generation (SHG) in a binary composite of random dielectrics. They also studied the thickness dependence of the effective SHG susceptibility in films of random dielectrics and in composites with coated small particles.[3,4] Graded materials with various functionalities appear in nature and in fabricated materials. Graded thin films have many applications because the gradation profile provides an additional control on the physical properties. Graded thin films often have optical properties[5] that are different from those of bulk materials. It is also known that graded materials have physical properties that are different from those of homogeneous materials.[6] In addition, it has been observed that compositionally graded barium strontium titanate thin films have better electric properties than single-layer barium strontium titanate films with the same composition.[7] Until now, achieving enhanced SHG has been a challenge.[8,9] In this Letter we investigate SHG in a graded metallic film with an intrinsic SHG response and a graded linear response in the metallic dielectric function.

Let us consider a graded metallic film with thickness L with the gradation profile in the direction perpendicular to the film. If we include only quadratic nonlinearities, the local constitutive relation between displacement field $\mathbf{D}(z)$ and electric field $\mathbf{E}(z)$ in the static case would be $D_i(z) = \sum_j \epsilon_{ij}(z)E_j(z) + \sum_{jk} \chi_{ijk}(z)E_j(z)E_k(z)$ (Refs. 3 and 4), with $i = x, y, z$, where $D_i(z)$ and $E_i(z)$ are the ith components of $\mathbf{D}(z)$ and $\mathbf{E}(z)$, respectively, and χ_{ijk} is the SHG susceptibility. Here $\epsilon_{ij}(z)$ denotes the linear dielectric function, which we assume for simplicity to be isotropic, $\epsilon_{ij}(z) = \epsilon(z)\delta_{ij}$. Both $\epsilon(z)$ and $\chi_{ijk}(z)$ are functions of z and describe the gradation profiles. In general, when a monochromatic external field is applied, the nonlinearity will generate local potentials and fields at all harmonic frequencies. For a finite-frequency external electric field of the form $E_0 = E_0(\omega)\exp(-i\omega t) + \text{c.c.}$, the effective SHG susceptibility $\overline{\chi}_{2\omega}$ can be extracted if we consider the volume average of the displacement field at frequency 2ω in the inhomogeneous medium.[2–4] Next we adopt a graded dielectric profile that follows the Drude form

$$\epsilon(z, \omega) = 1 - \frac{\omega_p^2(z)}{\omega[\omega + i\gamma(z)]}, \tag{1}$$

where $0 \le z \le L$. The general form in Eq. (1) allows for the possibility of a gradation profile in the plasma frequency [e.g., Eq. (4)] and the relaxation rate [e.g., Eq. (5)]. For a z-dependent profile we can make use of the equivalent capacitance for capacitors in series to evaluate the effective perpendicular linear response for a given frequency, $1/\overline{\epsilon}(\omega) = (1/L)\int_0^L \mathrm{d}z[1/\epsilon(z, \omega)]$. By use of the continuity of the electric displacement field, the local electric field $E(z, \omega)$ satisfies

$$\epsilon(z, \omega)E(z, \omega) = \overline{\epsilon}(\omega)E_0(\omega), \tag{2}$$

where $E_0(\omega)$ is the applied field along the z axis. A z-dependent profile for the plasma frequency and the relaxation time can be achieved experimentally. One possible way may be to impose a temperature profile, because it has been observed that surface-enhanced Raman scattering is sensitive to temperature.[10] Thus one can tune the surface plasmon frequency by imposing an appropriate temperature gradient.[11] A temperature gradient can also be used in materials with a small bandgap or with a profile on dopant concentrations. In this case one can impose a charge carrier concentration profile to a certain extent. This effect, when coupled with materials with a significant intrinsic nonlinear susceptibility, will give us a way to control the effective nonlinear response. For less-conducting materials one can replace the Drude form of the dielectric constants by a Lorentz oscillator form. It may also be possible to fabricate dirty metal films in which the degree of disorder varies in the z direction and hence leads to a relaxation-rate gradation profile.

Calculation of the effective nonlinear optical response then proceeds by applying the expressions derived in Refs. 2 and 3. Next, effective SHG susceptibility $\overline{\chi}_{2\omega}$ is given by $\overline{\chi}_{2\omega} = \langle \chi_{2\omega}(z)E_{\text{lin}}(z, 2\omega)E_{\text{lin}}(z, \omega)^2\rangle/[E_0(2\omega)E_0(\omega)^2]$, where

E_{lin} is the linear local electric field in the graded film with the same gradation profile but with a vanishing nonlinear response at the frequency concerned. By use of Eq. (2) for the linear local fields, the effective SHG susceptibility can be rewritten as an integral over the film as

$$\overline{\chi}_{2\omega} = \frac{1}{L}\int_0^L \mathrm{d}z\,\chi_{2\omega}(z)\left[\frac{\overline{\epsilon}(2\omega)}{\epsilon(z,2\omega)}\right]\left[\frac{\overline{\epsilon}(\omega)}{\epsilon(z,\omega)}\right]^2. \quad (3)$$

To illustrate the SHG in graded films, we consider a model system in which intrinsic SHG susceptibility $\chi_{2\omega}(z) = \chi_1$ is a real and positive frequency-independent constant and does not have a gradation profile. In so doing, we are allowed to focus on the enhancement of the SHG response compared with χ_1. To show the effects of gradation, here we take as a model plasma-frequency gradation profile

$$\omega_p(z) = \omega_p(0)\,(1 - C_\omega z) \quad (4)$$

and a model relaxation-rate gradation profile[12]

$$\gamma(z) = \gamma(\infty) + C_\gamma/z\,, \quad (5)$$

where C_ω and C_γ are constant parameters tuning the profile that is assumed to be linear in z. Here $\gamma(\infty)$ denotes the bulk damping coefficient, i.e., for $z \to \infty$. We set thickness $L = 1$ so that we can focus on the film with a fixed thickness. Regarding the thickness dependence, we refer the reader to Hui *et al.*[3]

Figure 1 shows the real and imaginary parts of the effective linear dielectric constant [Figs. 1(a) and 1(b), respectively] and the real and imaginary parts of the effective SHG susceptibility [Figs. 1(c) and 1(d), respectively] as a function of frequency $\omega/\omega_p(0)$. Also shown is the modulus of $\overline{\chi}_{2\omega}/\chi_1$ [see Fig. 1(e)]. The dielectric function gradation profile is given in Eqs. (1), (4), and (5) with $C_\gamma = 0$, i.e., only a graded plasmon frequency is included. Throughout the calculations, the real part of the (linear) dielectric constant is negative naturally. In this case a broad resonant plasmon band is observed. Note that for $C_\omega \to 0$, $\omega_p(z)/\omega_p(0) \to 1$. As C_ω increases, $\omega_p(z)$ takes on values within a broader range across the film and leads to a broad plasmon band. Increasing C_ω also causes the plasmon peak to shift to lower frequencies. The reason is that, in analogy with capacitors in series, the effective dielectric constant of the film is dominated by the layer with the smallest dielectric constant. For the SHG response the frequency dependence is complicated. As C_ω increases, it is noted that structures in the SHG response also shift to lower frequencies, and the range of values of the SHG susceptibility increases as well. Figure 2 displays the results of model calculations in which a gradation profile of the relaxation rate of the form in Eq. (5) is also included. The effects are similar to those in Fig. 1. The SHG response is found to be enhanced more strongly in the presence of both a relaxation-rate gradation and a plasma-frequency gradation (see Fig. 1) than for plasmon-frequency gradation alone, especially at low frequencies. As C_γ increases, the structures in the linear and SHG response both show a shift to lower frequencies. In Figs. 1 and 2 the quantities that can be both positive and negative are plotted in a logarithm of modulus. When the quantities pass through zero, the logarithm is very large, thus yielding spikes. In addition, we used the normalized numbers to describe a general origin of SHG in metal films rather than in a specified metal film.

The point of achieving the present results is that one needs a sufficiently large gradient rather than a crucially particular form of the dielectric function or gradation profiles. Thus it is expected that an enhancement in SHG responses will also be found in compositionally graded metal–dielectric composite films in which the fraction of metal component varies perpendicularly with the film. In the present work, because of the symmetry of the film, we have enhancement for only the polarization perpendicular to the film (i.e., parallel to the direction of the gradient). In this polarization the tangential component of electric field E vanishes identically. Thus the continuity of the normal component of D [see Eq. (2)] gives rise

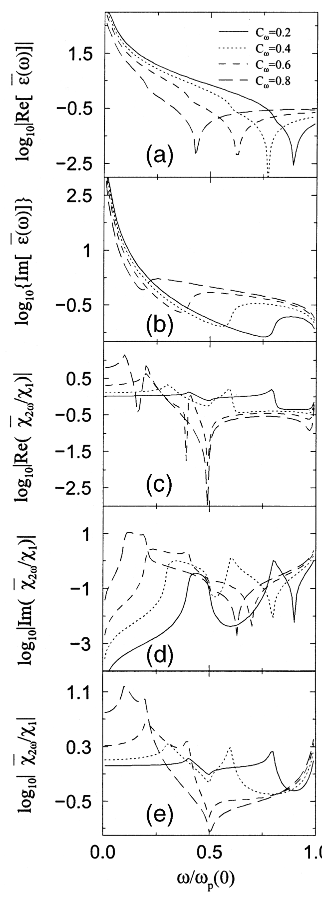

Fig. 1. (a) $\mathrm{Re}[\overline{\epsilon}(\omega)]$, (b) $\mathrm{Im}[\overline{\epsilon}(\omega)]$ (linear optical absorption), (c) $\mathrm{Re}(\overline{\chi}_{2\omega}/\chi_1)$, (d) $\mathrm{Im}(\overline{\chi}_{2\omega}/\chi_1)$, and (e) modulus of $\overline{\chi}_{2\omega}/\chi_1$ versus the normalized incident angular frequency $\omega/\omega_p(0)$ for the dielectric function gradation profile [Eq. (1)] with various plasma-frequency gradation profiles [Eq. (4)] and relaxation-rate gradation profiles [Eq. (5)]. Here | | denotes the absolute value or modulus. Parameters: $\gamma(\infty) = 0.02\omega_p(0)$, $C_\gamma = 0.0$.

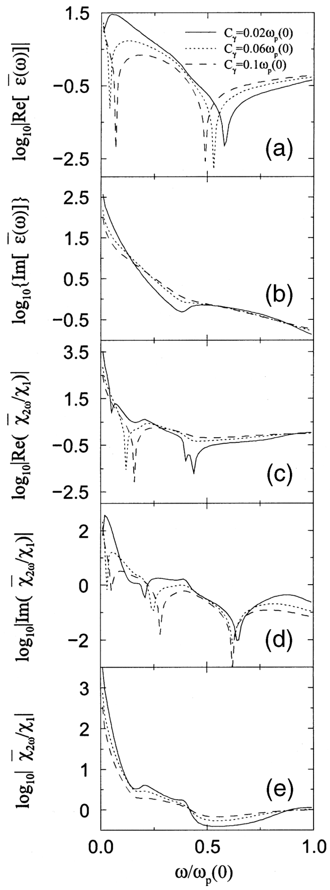

Fig. 2. Same as Fig. 1. Parameters: $\gamma(\infty) = 0.02\omega_p(0)$, $C_\omega = 0.6$.

to the enhanced SHG. However, for polarization parallel to the film the tangential component does not vanish. In this polarization it is the continuity of the tangential component of E that leads to no enhancement at all.[1]

We thank Pak-Ming Hui for fruitful discussions and suggestions as well as a critical reading of the manuscript. This work was supported by the Research Grants Council of the Hong Kong SAR Government. J. P. Huang's e-mail address is jphuang@mpip-mainz.mpg.de.

*Present address, Max Planck Institute for Polymer Research, Mainz, Germany.

References

1. G. L. Fischer, R. W. Boyd, R. J. Gehr, S. A. Jenekhe, J. A. Osaheni, J. E. Sipe, and L. A. Weller-Brophy, Phys. Rev. Lett. **74,** 1871 (1995).
2. P. M. Hui and D. Stroud, J. Appl. Phys. **82,** 4740 (1997).
3. P. M. Hui, C. Xu, and D. Stroud, Phys. Rev. B **69,** 014202 (2004).
4. P. M. Hui, C. Xu, and D. Stroud, Phys. Rev. B **69,** 014203 (2004).
5. H. Grüll, A. Schreyer, N. F. Berk, C. F. Majkrzak, and C. C. Han, Europhys. Lett. **50,** 107 (2000).
6. G. W. Milton, *The Theory of Composites* (Cambridge U. Press, Cambridge, England, 2002).
7. S. G. Lu, X. H. Zhu, C. L. Mak, K. H. Wong, H. L. W. Chan, and C. L. Choy, Appl. Phys. Lett. **82,** 2877 (2003).
8. D. Pezzetta, C. Sibilia, M. Bertolotti, R. Ramponi, R. Osellame, M. Marangoni, J. W. Haus, M. Scalora, M. J. Bloemer, and C. M. Bowden, J. Opt. Soc. Am. B **19,** 2102 (2002).
9. G. Purvinis, P. S. Priambodo, M. Pomerantz, M. Zhou, T. A. Maldonado, and R. Magnusson, Opt. Lett. **29,** 1108 (2004).
10. B. Pettinger, X. Bao, I. C. Wilcock, M. Muhler, and G. Ertl, Phys. Rev. Lett. **72,** 1561 (1994).
11. H.-P. Chiang, P. T. Leung, and W. S. Tse, J. Phys. Chem. B **104,** 2348 (2000).
12. A. E. Neeves and M. H. Birnboim, J. Opt. Soc. Am. B **6,** 787 (1989).