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Nondegenerate four-wave mixing in graded metallic films

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The effective nondegenerate four-wave mixing (NDFM) susceptibility of graded metallic films with weak nonlinearity is exactly derived by invoking the local-field effects. It is found that the presence of gradation in metallic films can yield a broad resonant plasmon band in the optical region, which results in a large enhancement in the NDFM response and thus a large figure of merit. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1828610]

I. INTRODUCTION

Nonlinear optical materials with large nonlinear susceptibility or optimal figure of merit (FOM) are in great need. In this connection, much work has been done on how to gain a large nonlinearity enhancement or optimal FOM of bulk composites by the surface-plasmon resonance in metal-dielectric composites (for a review, see Ref. 1), as well as by taking into account the structural information.[1–4] In particular, a large nonlinearity enhancement was experimentally reported for a subwavelength multilayer (i.e., graded thin film) of titanium dioxide and conjugated polymer,[3] and theoretically found for graded metallic films.[5]

Owing to the additional control of gradation, graded thin films play a key role in many applications and hence are essential for material fabrication. When compared to bulk materials, the corresponding thin films often possess different optical properties.[6,7] It is also known that graded materials[8,9] have quite different physical properties from the homogeneous materials.[10] Further, one found that the graded thin films may have better dielectric properties than a single-layer film.[11] However, the traditional theories[12,13] cannot be used to the composites of graded particles directly. For this purpose, we put forth a first-principles approach[14,15] and a differential effective dipole approximation.[16]

Nondegenerate four-wave mixing[17] (NDFM) has received much attention due to the abundant application in phase conjugate mirrors, wave restoration, real time holography, etc. In the particular NDFM we consider, there are four waves: forward pump wave E_f and backward pump wave E_b at angular frequency ω_1 (propagating in opposite directions); probe wave E_p and signal wave E_s at ω_2. We shall impose the two pump fields (incident field) at ω_1 of high intensity to generate the desired nonlinearity, while the probe field at ω_2 of lower intensity is measured. This is experimentally observable. When $\omega_2=\omega_1$, one has degenerate four-wave mixing susceptibility, which is exactly the same as the usual effective third-order nonlinearity susceptibility $\overline{\chi}^{(3)}(\omega_2)$, namely,

$$\overline{\chi}^{(3)}(\omega_2) = \langle \chi(\omega_2) F(\omega_2)^2 |F(\omega_2)|^2 \rangle, \tag{1}$$

where F denotes the local-field enhancement factor, $\chi(\omega_2)$ the (intrinsic) third-order nonlinear susceptibility, and $\langle\cdots\rangle$ the volume average of $\cdots$. For the present effective NDFM susceptibility $\overline{\chi}(\omega_2)$, we obtain the general form such that[1,18]

$$\overline{\chi}(\omega_2) = \langle \chi(\omega_2) F(\omega_2)^2 |F(\omega_1)|^2 \rangle. \tag{2}$$

It is worth remarking that all the above-mentioned E fields can make an angle to the gradient which is directed along the z axis. However, only the components that are parallel to the z axis give rise to a significant enhancement while the other components that are perpendicular to the z axis lead to no enhancement.[3] Thus, the third-order nonlinear susceptibility plays a crucial role in the effective NDFM susceptibility, as given by Eq. (2).

This paper is organized as follows: In Sec. II, we derive the effective NDFM susceptibility of a graded metallic film by invoking the local-field effects exactly. In Sec. III, the numerical results are presented for different gradation profiles of plasmon frequency and relaxation rate, and different film thicknesses. This paper ends with a discussion and conclusion in Sec. IV.

II. FORMALISM

Let us consider a graded metallic film of width L. Its gradation is directed along the z axis, i.e., perpendicular to the film. For each layer at position z inside the graded film, the local constitutive relation between the displacement $\mathbf{D}(z,\omega)$ and the electric field $\mathbf{E}(z,\omega)$ is given by

$$\mathbf{D}(z,\omega) = \epsilon(z,\omega)\mathbf{E}(z,\omega) + \chi(z,\omega)|\mathbf{E}(z,\omega)|^2\mathbf{E}(z,\omega), \tag{3}$$

where $\epsilon(z,\omega)$ and $\chi(z,\omega)$ stand for the linear dielectric constant and third-order nonlinear susceptibility, respectively. Here both $\epsilon(z,\omega)$ and $\chi(z,\omega)$ are gradation profiles as a function of position z, and ω denotes the angular frequency of the fields, which will be distinguished in the following, see Eq. (8). Next, we assume that the weak nonlinearity condition is satisfied. That is, the contribution of the second term [i.e., nonlinear part $\chi(z,\omega)|\mathbf{E}(z,\omega)|^2$] in the right-hand side of Eq. (3) is much less than that of the first term [namely, linear part

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$\epsilon(z,\omega)$].[19] We further focus on the quasistatic approximation, under which the whole graded film can be regarded as an effective homogeneous one with an effective (overall) linear dielectric constant $\overline{\epsilon}(\omega)$ and effective (overall) third-order nonlinear susceptibility $\overline{\chi}(\omega)$. They both satisfy the following definition:[19]

$$\langle \mathbf{D} \rangle = \overline{\epsilon}(\omega)\mathbf{E}_0 + \overline{\chi}(\omega)|\mathbf{E}_0|^2\mathbf{E}_0, \tag{4}$$

where $\mathbf{E}_0 = E_0\hat{e}_z$ is the applied field along the z axis.

Then, we adopt the graded Drude dielectric profile

$$\epsilon(z,\omega) = 1 - \frac{\omega_p^2(z)}{\omega[\omega + i\gamma(z)]}, \quad z \leqslant L, \tag{5}$$

where $\omega_p(z)$ and $\gamma(z)$ represent the plasma-frequency gradation profile and relaxation-rate gradation profile, respectively, and are both functions of z. Fortunately, a z-dependent profile for the plasma frequency and the relaxation rate is possible to achieve. In detail, one possible way is to impose a temperature profile, as it has been observed that surface-enhanced Raman scattering is sensitive to temperature.[20] Thus, the surface-plasmon frequency is expected to be tuned by imposing an appropriate temperature gradient.[21] Also, a temperature gradient may be used in materials with a small band gap or with a profile on dopant concentrations. In this case, one may 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 may replace the Drude form of the dielectric function 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 desired relaxation-rate gradation profile. It is worth noting that our results will not depend crucially on the particular form of the dielectric function. The only requirement is that one must have a sufficiently large gradient, either in $\omega_p(z)$ and/or in $\gamma(z)$, to yield a broad plasmon band. In view of the present graded film (layered geometry) of interest, we are allowed to use the equivalent capacitance of series combination to calculate the effective linear dielectric constant $\overline{\epsilon}(\omega)$ for the metallic film,

$$\frac{1}{\overline{\epsilon}(\omega)} = \frac{1}{L}\int_0^L \frac{dz}{\epsilon(z,\omega)}. \tag{6}$$

Next, we are in a position to derive the nonlinear optical response. First, we calculate the local electric field $E(z,\omega)$ by using the identity

$$\epsilon(z,\omega)E(z,\omega) = \overline{\epsilon}(\omega)E_0, \tag{7}$$

which arises from the continuity of the electric displacements. In view of the existence of nonlinearity inside the graded film, based on Eq. (2), the effective NDFM susceptibility $\overline{\chi}(\omega_2)$ can be rewritten as an integral over the whole graded film such that

$$\overline{\chi}(\omega_2) = \frac{1}{L}\int_0^L dz\chi(z,\omega_2)\left[\frac{\overline{\epsilon}(\omega_2)}{\epsilon(z,\omega_2)}\right]^2\left|\frac{\overline{\epsilon}(\omega_1)}{\epsilon(z,\omega_1)}\right|^2. \tag{8}$$

III. NUMERICAL RESULTS

To illustrate the NDFM response in graded films, we consider a model system in which the intrinsic NDFM susceptibility $\chi(z,\omega_2)$ is assumed to be a real and positive frequency-independent constant χ_1 and which does not have a gradation profile. By doing so, we could focus on the enhancement of the NDFM response. Without loss of generality, the film thickness L is set to be unity. For numerical calculations, we adopt the plasma-frequency gradation profile

$$\omega_p(z) = \omega_p(0)(1 - C_\omega \times z), \tag{9}$$

and the relaxation-rate gradation profile[22]

$$\gamma(z) = \gamma(\infty) + C_\gamma/z, \tag{10}$$

where C_ω is a constant tuning the profile. Here $\gamma(\infty)$ denotes the damping coefficient in the corresponding bulk material and C_γ is a constant which is related to the Fermi velocity.

Figure 1 displays (a) the linear optical absorption $\mathrm{Im}[\overline{\epsilon}(\omega_2)]$, (b) the enhancement of the NDFM susceptibility $|\overline{\chi}(\omega_2)|/\chi_1$, and (c) the FOM $\equiv |\overline{\chi}(\omega_2)|/\{\chi_1 \,\mathrm{Im}[\overline{\epsilon}(\omega_2)]\}$ versus the normalized incident angular frequency $\omega_2/\omega_p(0)$, for various C_ω. The dielectric function gradation profile is given in Eqs. (5), (9), and (10) with $C_\gamma=0$, i.e., only a graded plasmon frequency is included. To one's interest, when the plasmon-frequency gradation profile $\omega_p(z)$ is taken into account, a broad resonant plasmon band is observed always. In other words, the broadband is caused to appear by the effect of the gradation. In detail, as $C_\omega \to 0$, $\omega_p(z)/\omega_p(0) \to 1$. As C_ω increases, $\omega_p(z)$ has values within a broad range, thus yielding a broad plasmon band. Moreover, we find that increasing C_ω causes the resonant band not only to be enhanced, but also redshifted (namely, located at a lower-frequency region). The reason is that, in analogous to capacitors in series, the effective linear dielectric constant of the graded film (i.e., multilayer structure) is dominated by the layer with the smallest dielectric constant. From Fig. 1(b), we find that increasing C_ω causes the peak of the NDFM response to be both enhanced and redshifted. Also, it is apparent to observe a flat region shown in Fig. 1(b), which results from the ω_2-related (rather than ω_1-related) local-field enhancement factor $|\overline{\epsilon}(\omega_2)/\epsilon(z,\omega_2)|^2$ for the whole graded film. The reason is that the factor $|\overline{\epsilon}(\omega_2)/\epsilon(z,\omega_2)|^2$ is approximately constant as ω_2 is small. This is further due to the above-mentioned fact that the effective linear dielectric constant of the graded film of interest is dominated by the layer with the smallest dielectric constant at small ω_2. In other words, as ω_2 is small, the corresponding effective linear dielectric constant is approximately the same as the smallest layer dielectric constant at small ω_2. Thus, the ω_2-related enhancement factor is almost constant for small ω_2. In this connection, a flat region should be displayed. In a word, although the enhancement of the effective NDFM susceptibility is often accompanied with the appearance of the optical absorption, the FOM is still possible to be quite attractive due to the presence of the gradation of the metallic film; see Fig. 1(c).

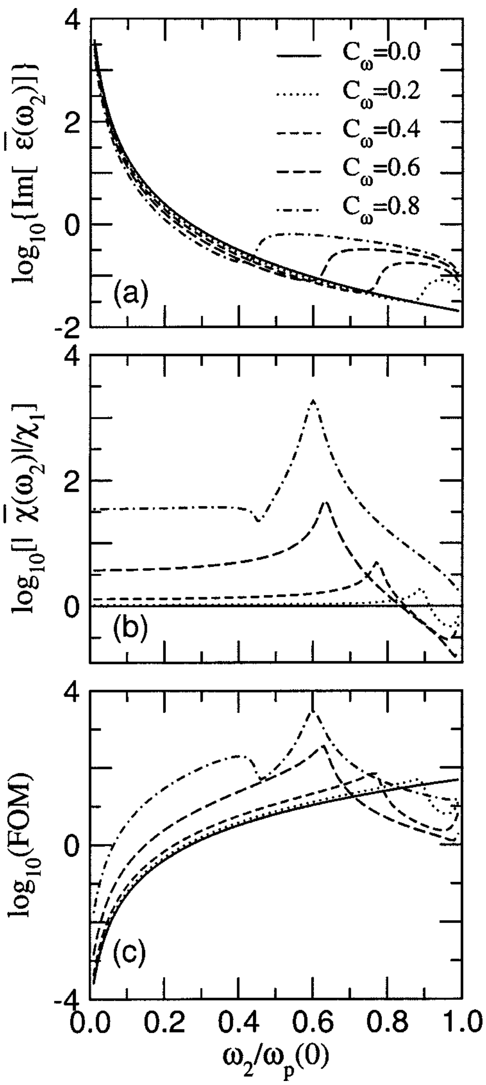

FIG. 1. (a) The linear optical absorption $\mathrm{Im}[\overline{\epsilon}(\omega_2)]$, (b) the enhancement of the NDFM susceptibility $|\overline{\chi}(\omega_2)|/\chi_1$, and (c) the figure of merit (FOM) $\equiv|\overline{\chi}(\omega_2)|/\{\chi_1\,\mathrm{Im}[\overline{\epsilon}(\omega_2)]\}$ vs the normalized incident angular frequency $\omega_2/\omega_p(0)$ for dielectric function gradation profile $\epsilon(z,\omega)=1-\omega_p^2(z)/(\omega[\omega+i\gamma(z)])$ with various plasma-frequency gradation profile $\omega_p(z)=\omega_p(0)(1-C_\omega\times z)$ [Eq. (9)] and relaxation-rate gradation profile $\gamma(z)=\gamma(\infty)+C_\gamma/z$ [Eq. (10)], for various C_ω, at $\gamma(\infty)=0.02\omega_p(0)$ and $\omega_1=0.6\omega_p(0)$. Parameter: $C_\gamma=0.0$.

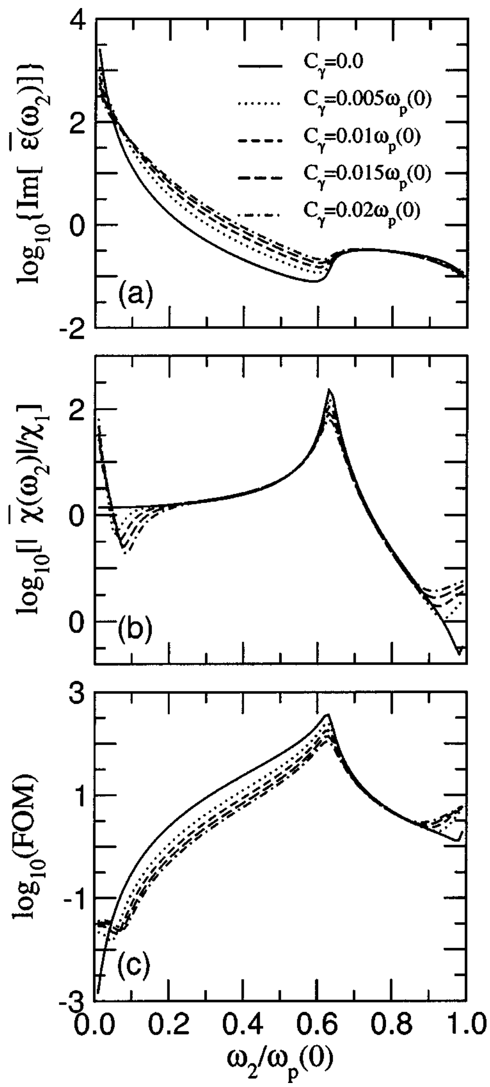

FIG. 2. Same as Fig. 1, but for various C_γ. Parameter: $C_\omega=0.6$.

Figure 2 shows the results of model calculations in which a gradation profile of the relaxation rate of the form in Eq. (10) is also included. It is found that the relaxation-rate gradation plays an important role in the NDFM response as $\omega_2\to\omega_p(0)$ or $\omega_2\sim\omega_1[=0.6\omega_p(0)]$. As a matter of fact, the enhancement in the NDFM response arises from the enhancement in the local field. In addition, by taking into account the relaxation-rate gradation, the FOM is also caused to increase at $\omega_2\to\omega_p(0)$.

It should be noted that the present results do not depend crucially on the particular form of the dielectric function and the gradation profile. The point is that one needs a sufficiently large gradient. Thus, it is expected that an enhancement in NDFM responses will also be found in compositionally graded metal-dielectric composite films in which the fraction of metal component varies perpendicular to the film.

Finally, let us compare the nondegenerate cases considered in this work with the degenerate cases which were extensively investigated in Ref. 5 (for details, see Figs. 1 and 2 of Ref. 5). Regarding the comparison between the NDFM susceptibility and the degenerate four-wave mixing (DFM) susceptibility, we found that the resonant plasmon band in the linear optical absorption appears to be narrower for the NDFM susceptibility than for the DFM. Similarly, the plasmon band in the enhancement of the nonlinearity becomes much narrower for the NDFM susceptibility than for the DFM. In this connection, for the NDFM susceptibility, the plasmon band shown in the FOM is caused to be narrower, too. Such phenomena are caused to occur by the local-field effect. In addition, for both the NDFM and DFM susceptibilities, increasing C_γ causes the nonlinearity enhancement and FOM to be increased at the low probe frequencies which are generally smaller than ω_c (for the NDFM susceptibility $\omega_c\approx 0.05\omega_p(0)$; for the DFM susceptibility $\omega_c\approx 0.2\omega_p(0)[>0.05\omega_p(0)]$). Also, owing to the local-field effect, the strength of the increment becomes lower for the NDFM susceptibility than for the DFM.

IV. DISCUSSION AND CONCLUSION

Here some comments are in order. In this paper, we have derived the effective linear dielectric constant and NDFM susceptibility of graded metallic films with weak nonlinearity exactly by invoking the local-field effects.

In the degenerate four-wave mixing setup, there are two pump fields, E_f and E_b, and two probe fields, E_p and E_s. Generally, the two pump fields are propagating in the opposite direction, i.e., the wave vectors satisfy $k_f+k_b=0$, while the two probe fields are also opposite, i.e., $k_p+k_s=0$. Thus, the four-wave vectors form a parallelogram. In this case, $\omega_p=\omega_s$, too, and we have calculated the NDFM susceptibility. However, we can also consider a more general case. Namely, the four-wave vectors form a trapezoid. In this configuration, k_f and k_b, being along the two nonparallel sides, are not exactly opposite to each other, although $\omega_f=\omega_b$. In this case, k_p and k_s are parallel (opposite) to each other, but ω_p is not equal to ω_s. In addition, it is also worth calculating the NDFM susceptibility for this trapezoid case.

To sum up, we have investigated the surface-plasmon resonant effect on the linear optical absorption, the enhancement in the NDFM response, and the FOM of the graded metallic films. It is found that the presence of gradation in metallic films can yield a broad resonant plasmon band in the optical region, resulting in a large enhancement of the NDFM response and hence a large FOM.

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