

Optical nonlinearity enhancement of graded metallic films

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The effective linear and third-order nonlinear susceptibility of graded metallic films with weak nonlinearity have been investigated. Due to the simple geometry, we were able to derive exactly the local field inside the graded structures having a Drude dielectric gradation profile. We calculated the effective linear dielectric constant and third-order nonlinear susceptibility. We investigated the surface plasmon resonant effect on the optical absorption, the optical nonlinearity enhancement, and the figure of merit of graded metallic films. It is found that the presence of gradation in metallic films yields a broad resonant plasmon band in the optical region, resulting in a large enhancement of the optical nonlinearity, and hence a large figure of merit. We suggest experiments be done to check our theoretical predictions, because graded metallic films can be fabricated more easily than graded particles. © 2004 American Institute of Physics. [DOI: 10.1063/1.1769086]

Thin films can possess different optical properties (see, e.g., Ref. 1) when compared to their bulk counterparts. Also, graded materials have quite different physical properties from the homogeneous materials, hence making the composite media consisting of graded inclusions more useful and interesting. Recently, some authors found experimentally that the graded thin films may have better dielectric properties than a single-layer film.² In fact, graded materials³ are the materials whose material properties can vary continuously in space. These materials have attracted much interest in various engineering applications.⁴ However, the traditional theories^{5,6} fail to deal with the composites of graded inclusions. Recently, for treating these composites, we presented a first-principles approach^{7,8} and a differential effective dipole approximation.^{9,10}

The problem becomes more complicated by the presence of nonlinearity in realistic composites. Besides gradation (inhomogeneity), nonlinearity plays also an important role in the effective material properties of composite media.^{11–21} There is a great need for nonlinear optical materials with large nonlinear susceptibility or optimal figure of merit (FOM). For these purposes, many studies have been devoted to achieving a large nonlinearity enhancement or optimal FOM of bulk composites by the surface-plasmon resonance in metal-dielectric composites,^{18,20} as well as by taking into account the structural information, like random distribution of particles²² and particle shape distribution.²³ More recently, a large nonlinearity enhancement was found when the authors studied a subwavelength multilayer of titanium dioxide and conjugated polymer.²⁴

Regarding the surface-plasmon resonant nonlinearity enhancement, there is always a concomitantly strong absorption, that renders the FOM of the resonant enhancement peak to be too small to be useful. In this work, we will consider graded metallic films to circumvent the problem. We have found that the presence of gradation in metallic films yields a broad resonant plasmon band in the optical region. We have

succeeded in gaining a large nonlinearity enhancement, as well as an optimal FOM by considering the effect of inhomogeneity due to gradation.

Let us consider a graded metallic film with width L , and the gradation under consideration is in the direction perpendicular to the film. The local constitutive relation between the displacement (\mathbf{D}) and the electric field (\mathbf{E}) inside the graded layered geometry is given by

$$\mathbf{D}(z, \omega) = \epsilon(z, \omega)\mathbf{E}(z, \omega) + \chi(z, \omega)|\mathbf{E}(z, \omega)|^2\mathbf{E}(z, \omega), \quad (1)$$

where $\epsilon(z, \omega)$ and $\chi(z, \omega)$ are, respectively, the linear dielectric constant and the third-order nonlinear susceptibility. Note that both $\epsilon(z, \omega)$ and $\chi(z, \omega)$ are gradation profiles as a function of position z . Here we assume that the weak nonlinearity condition is satisfied; that is, the contribution of the second term [nonlinear part $\chi(z, \omega)|\mathbf{E}(z, \omega)|^2$] in the right-hand side of Eq. (1) is much less than that of the first term [linear part $\epsilon(z, \omega)$].¹¹ We further restrict our discussion to the quasistatic approximation, under which the whole layered geometry can be regarded as an effective homogeneous one with effective (overall) linear dielectric constant $\bar{\epsilon}(\omega)$ and effective (overall) third-order nonlinear susceptibility $\bar{\chi}(\omega)$. To show the definitions of $\bar{\epsilon}(\omega)$ and $\bar{\chi}(\omega)$, we have¹¹

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

where $\langle \cdots \rangle$ denotes the spatial average, and $\mathbf{E}_0 = E_0 \hat{e}_z$ is the applied field along the z axis.

We adopt the graded Drude dielectric profile

$$\epsilon(z, \omega) = 1 - \frac{\omega_p^2(z)}{\omega[\omega + i\gamma(z)]}, \quad 0 \leq z \leq L. \quad (3)$$

In Eq. (3), we adopted the various plasma-frequency gradation profile

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

and the relaxation-rate gradation profile²⁵

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$$\gamma(z) = \gamma(\infty) + \frac{C_\gamma}{z}, \quad (5)$$

where C_ω is a dimensionless constant (gradient). Here $\gamma(\infty)$ denotes the damping coefficient in the corresponding bulk material. C_γ is a constant (gradient) that is related to the Fermi velocity. Due to the simple layered geometry, we can use the equivalent capacitance of series combination to calculate the linear response, i.e., the optical absorption for the metallic film

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

The calculation of nonlinear optical response can proceed as follows. We first calculate local electric field $E(z, \omega)$ by the identity

$$\epsilon(z, \omega)E(z, \omega) = \bar{\epsilon}(\omega)E_0,$$

by virtue of the continuity of electric displacement, where E_0 is the applied field.

In view of the existence of nonlinearity inside the graded film, the effective nonlinear response $\bar{\chi}(\omega)$ can be written as¹¹

$$\bar{\chi}(\omega)\mathbf{E}_0^4 = \langle \chi(z, \omega) |\mathbf{E}_{\text{lin}}(z)|^2 \mathbf{E}_{\text{lin}}(z)^2 \rangle, \quad (7)$$

where E_{lin} is the linear local electric field. Next, the effective nonlinear response can be written as an integral over the layer such as

$$\bar{\chi}(\omega) = \frac{1}{L} \int_0^L dz \chi(z, \omega) \left| \frac{\bar{\epsilon}(\omega)}{\epsilon(z, \omega)} \right|^2 \left(\frac{\bar{\epsilon}(\omega)}{\epsilon(z, \omega)} \right)^2. \quad (8)$$

For numerical calculations, we set $\chi(z, \omega)$ to be constant (χ_1), in an attempt to emphasize the enhancement of the optical nonlinearity. Without loss of generality, the layer width L is taken to be 1.

Figure 1 displays the optical absorption $\sim \text{Im}[\bar{\epsilon}(\omega)]$, the modulus of the effective third-order optical nonlinearity enhancement $|\bar{\chi}(\omega)|/\chi_1$, as well as the FOM $|\bar{\chi}(\omega)|/\{\chi_1 \text{Im}[\bar{\epsilon}(\omega)]\}$ as a function of the incident angular frequency ω . Here $\text{Im}[\dots]$ means the imaginary part of \dots . To one's interest, when the positional dependence of $\omega_p(z)$ is taken into account (namely, $C_\omega \neq 0$), a broad resonant plasmon band is observed. As expected, the broad band is caused to appear by the effect of the positional dependence of the plasma frequency of the graded metallic film. In particular, this band can be observed within almost the whole range of frequency, as the gradient C_ω is large enough. In other words, as long as the film under consideration is strongly inhomogeneous, a resonant plasmon band is expected to appear over the whole range of frequency. In addition, it is also shown that increasing C_ω causes the resonant bands to be red shifted (namely, located at a lower frequency region). In a word, although the enhancement of the effective third-order optical nonlinearity 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.

Similarly, in Fig. 2, we investigate the effect of the inhomogeneity of the relaxation rates $[\gamma(z)]$, which comes from the graded metallic film. It is evident to show that, in the low-frequency region, the positional dependence of re-

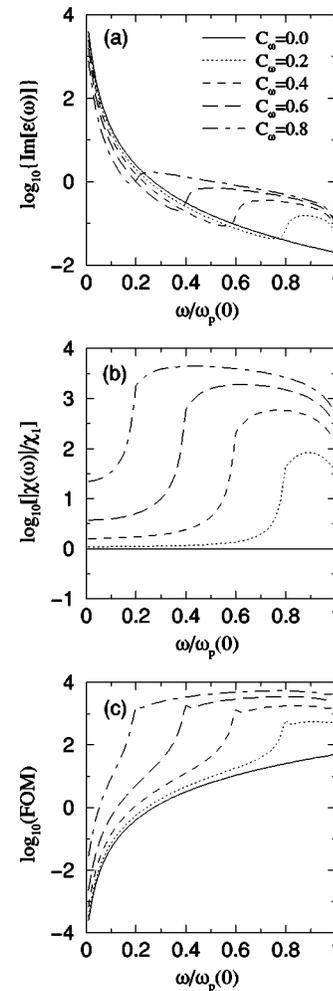


FIG. 1. (a) The linear optical absorption $\text{Im}[\bar{\epsilon}(\omega)]$, (b) the enhancement of the third-order optical nonlinearity $|\bar{\chi}(\omega)|/\chi_1$, and (c) the FOM $\equiv |\bar{\chi}(\omega)|/\{\chi_1 \text{Im}[\bar{\epsilon}(\omega)]\}$ versus the normalized incident angular frequency $\omega/\omega_p(0)$ for the dielectric function gradation profile $\epsilon(z, \omega) = 1 - \omega_p^2(z)/[\omega(\omega + i\gamma(z))]$ with various plasma-frequency gradation profile $\omega_p(z) = \omega_p(0)(1 - C_\omega z/L)$ and relaxation-rate gradation profile $\gamma(z) = \gamma(\infty) + [C_\gamma/(z/L)]$. Parameters: $\gamma(\infty) = 0.02\omega_p(0)$ and $C_\gamma = 0.0$.

laxation rate $\gamma(z)$ enhances not only the third-order optical nonlinearity, but also the FOM of such kind of graded metallic films.

Consequently, graded metallic films can be a suitable candidate material for obtaining the *optimal* FOM. Thus, corresponding experiments are expected to be done to check our theoretical predictions, since graded films can be fabricated easily.

Here, some comments are in order. We have discussed a graded metallic film (layered geometry), in an attempt to investigate the effect of gradation on the nonlinear enhancement and FOM of such materials. It should be remarked that the optical response of the layered geometry depends on polarization of the incident light, because the incident optical field can always be resolved into two polarizations. However, a large nonlinearity enhancement occurs only when the electric field is parallel to the direction of the gradient,²⁴ and the other polarization does not give nonlinearity enhancement at all.²⁴

In the conventional theory of surface-plasmon resonant nonlinearity enhancement, there is often a dielectric component in the system of interest. In this regard, it turns out that

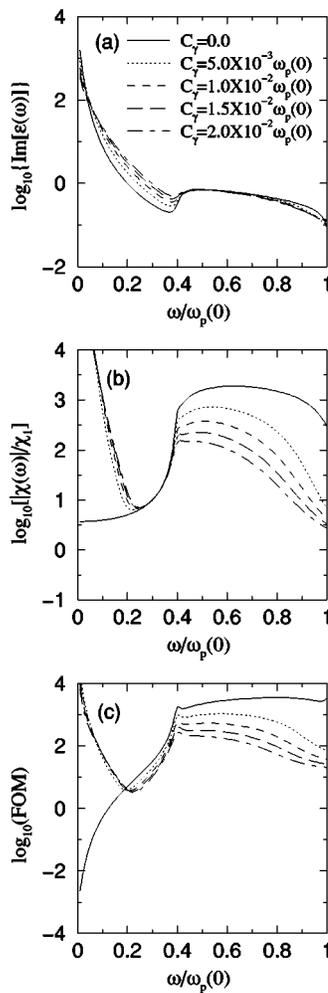


FIG. 2. Same as Fig. 1. Parameters: $\gamma(\infty)=0.02\omega_p(0)$ and $C_\omega=0.6$.

it is not difficult to add a homogeneous dielectric layer on the metallic film. The same theory still works, but a prominent surface-plasmon resonant peak appears at somewhat lower frequencies in addition to the surface-plasmon band. Due to the concomitantly strong absorption, the figure of merit of the resonant enhancement peak is too small to be useful. In the limit of the vanishing volume fraction of the dielectric component, however, the present results recover.

Since the surface-plasmon frequency is proportional to the bulk plasmon frequency, one showed that the bulk plasmon frequency can be tuned by appropriate temperatures.^{26,27} That is, a position-dependent plasma frequency can be achieved by imposing a temperature gradient in the direction perpendicular to the film. Nevertheless, the present results do not depend crucially on the particular form of the dielectric function. The only requirement is that we must have a sufficiently large gradient, either in $\omega_p(z)$ or in $\gamma(z)$ to yield a broad plasmon band. We have shown that the dielectric function of a metal-dielectric composite with a variation in the volume fraction of metal along the z axis can also give rise to a broad plasmon band.

It is instructive to extend our consideration to composites in which graded spherical particles are embedded in a

host medium²⁸ to account for mutual interactions among graded particles.²³ In addition, it is also interesting to study the strong nonlinearity case.²⁹

To sum up, we have investigated the effective linear and third-order nonlinear susceptibility of graded metallic films with weak nonlinearity. We calculated the effective linear dielectric constant and third-order nonlinear susceptibility. It has been found that the presence of gradation in metallic films yields a broad resonant plasmon band in the optical region, resulting in a large nonlinearity enhancement, and hence an optimal FOM.

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