Giant enhancement of optical nonlinearity in multilayer metallic films

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(Received 28 April 2005; accepted 17 January 2006; published online 2 March 2006)

The local electric field has been derived analytically inside multilayer metallic films with weak nonlinearity, and hence the effective linear dielectric constant and third-order nonlinear susceptibility of the layered structures are calculated. As the number of layers increases, the comparison with the previous results of graded metallic films shows a gradual transition from sharp peaks to a broad continuous band. These results give further evidence of the emerging absorption band reported recently [J. P. Huang and K. W. Yu, Appl. Phys. Lett. **85**, 94 (2004)]. Thus, multilayer metallic films can serve as optical materials with a giant enhancement of optical nonlinearity and a large figure of merit. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2175477]

I. INTRODUCTION

Nonlinear optical materials with a large value of the third-order nonlinear susceptibility[1–3] are in great need in industrial applications, such as nonlinear optical switching devices for use in photonics and real-time coherent optical signal processors, and so on. Thus, many authors (e.g., see Refs. 2–5) have devoted themselves in obtaining a large nonlinearity enhancement or optimal figure of merit (FOM) of bulk composites by taking into account various elements, such as the surface plasmon resonance in metal-dielectric composites, structural information, etc.

Unfortunately, the surface plasmon resonant nonlinearity enhancement is often accompanied by a strong absorption, and this behavior renders the FOM of the resonant enhancement peak to be too small to be useful. To circumvent this problem, recently we proposed to exploit materials, namely, graded metallic films, in order to achieve a large nonlinearity enhancement and an optimal FOM.[6] This consideration arose from three issues.

(1) Thin films often possess different optical properties,[7,8] compared to the corresponding bulk materials.
(2) Graded (inhomogeneous) materials often have quite different physical properties from the homogeneous materials.[9–13]
(3) Graded thin films can have better dielectric properties and tunability than a single-layer film.[14]

As a matter of fact, in practice it is more convenient to fabricate multilayer metallic films than graded films as multilayer metallic films can be readily prepared in a filtered arc deposition system.[15] Therefore, the present work is necessary in the sense that we shall discuss the multilayer effect as the number of layers inside the films increases. In this regard, this work should be expected to have practical relevance. As the number of layers N increases, we shall show a gradual transition from sharp peaks to an emerging broad continuous band and the graded film results recover in the limit $N\to\infty$.

The paper is organized as follows. In Sec. II, the formalism is presented by means of the equivalent capacitance for capacitors in series to evaluate the effective perpendicular linear response and thus the desired nonlinear response. In Sec. III, numerical results are shown for the various number of layers inside the metallic film. This paper ends with a discussion and conclusion in Sec. IV.

II. FORMALISM

To discuss the multilayer effect on the effective nonlinear optical response, let us first start from a general case, i.e., graded metallic film. In detail, we consider a graded metallic film with width L, and its gradation is in the direction perpendicular to the film. As a matter of fact, for graded films, the formalism has been derived in detail in Ref. 6. So, below we shall do a brief review, and further add some related backgrounds accordingly.

Inside the graded film, the local constitutive relation between the displacement $\mathbf{D}$ and the electric field $\mathbf{E}$ is given by

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

where $\epsilon(z,\omega)$ and $\chi(z,\omega)$ stand for the linear dielectric constant and third-order nonlinear susceptibility, respectively, and both are gradation profiles as a function of position z. Throughout this paper, the weak nonlinearity condition is assumed to be satisfied. That is, the contribution of the sec-

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ond term [i.e., 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 [namely, linear part $\epsilon(z,\omega)$].[16] In the quasistatic approximation, the whole graded film can be regarded as an effective homogeneous one with effective linear dielectric constant $\bar{\epsilon}(\omega)$ and effective third-order nonlinear susceptibility $\bar{\chi}(\omega)$. Both $\bar{\epsilon}(\omega)$ and $\bar{\chi}(\omega)$ are defined as[16]

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

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.

Then, we adopt the following graded Drude dielectric profile:

$$\epsilon(z,\omega) = 1 - \frac{\omega_p^2(z)}{\omega(\omega + i\gamma)}, \tag{3}$$

where $0 \leqslant z \leqslant L$, and γ stands for the damping coefficient in the corresponding bulk material. The general form in Eq. (3) allows for the possibility of a gradation profile in the plasma frequency $\omega_p(z)$ [e.g., Eq. (6)]. In experiment, it is possible to achieve a z-dependent profile for the plasma frequency. For instance, one possible way may be to impose a temperature profile, as it has been observed that surface enhanced Raman scattering is sensitive to temperature.[17] Thus, one may tune the surface plasmon frequency by imposing an appropriate temperature gradient.[17,18] 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 above Drude form of dielectric constants by a Lorentz oscillator form.

In view of the z-dependent profile, let us use the equivalent capacitance for capacitors in series to evaluate the effective perpendicular linear response for a given frequency $\bar{\epsilon}(\omega)$,[6]

$$\frac{1}{\bar{\epsilon}(\omega)} = \frac{1}{L}\int_0^L \frac{dz}{\epsilon(z,\omega)}. \tag{4}$$

Next, we take one step forward to write the effective nonlinear response $\bar{\chi}(\omega)$ as an integral over the film,[6]

$$\bar{\chi}(\omega) = \frac{1}{L}\int_0^L dz\chi(z,\omega)\left|\frac{\bar{\epsilon}(\omega)}{\epsilon(z,\omega)}\right|^2\left[\frac{\bar{\epsilon}(\omega)}{\epsilon(z,\omega)}\right]^2, \tag{5}$$

where $\chi(z,\omega)$ denotes the local third-order nonlinear susceptibility for a given frequency. It is worth noting that the real $\bar{\chi}(\omega)$ should involve an integral over x, y, and z of the local $\chi(x,y,z,\omega)$ multiplied by terms involving $\epsilon(x,y,z,\omega)$. Thus, Eq. (5) offers an approximate $\bar{\chi}(\omega)$, as expected.

To investigate the multilayer effect, we shall use some finite difference approximation of the graded Drude profile [Eq. (3)] for a finite number of layers.

To mimic a multilayer system, we divide the interval $[0,L]$ into N equally spaced subintervals, $[0,z_1],(z_1,z_2],\ldots,(z_{N-1},L]$. Then we adopt the midpoint value of $\omega_p(z)$ for each subinterval as the plasma frequency of that sublayer. In this way, we calculate the effective dielectric constant and the effective third-order nonlinear susceptibility, as well as the figure of merit for each N. It is worth noting that for $N\to\infty$ (e.g., $N=1024$) the graded film results[6] recover in this limit.

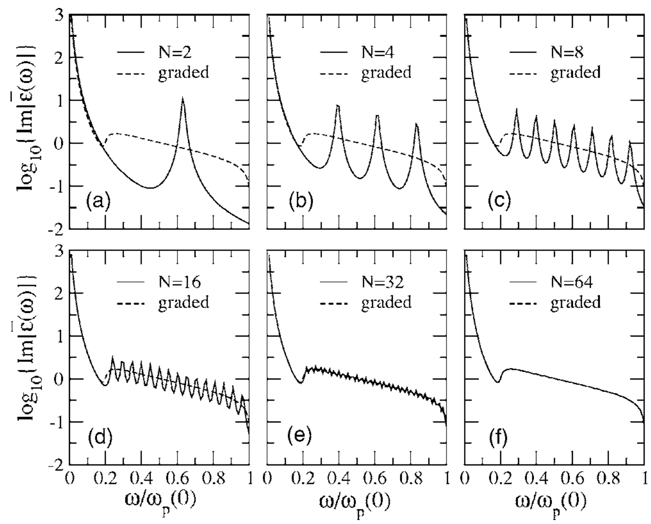

FIG. 1. The linear optical absorption $\mathrm{Im}[\bar{\epsilon}(\omega)]$ vs the normalized incident angular frequency $\omega/\omega_p(0)$ for dielectric function gradation profile $\epsilon(z,\omega)=1-\omega_p^2(z)/[\omega(\omega+i\gamma)]$ with various plasma-frequency gradation profiles $\omega_p(z)=\omega_p(0)(1-C_\omega\cdot z)$. Parameters: $\gamma=0.02\omega_p(0)$, $C_\omega=0.8$, $L=1$, and $\chi_1=1$.

III. NUMERICAL RESULTS

In what follows, we shall do some numerical calculations. We assume that the metal layers within the film have the same real and positive frequency-independent third-order nonlinear susceptibility $\chi(z,\omega)=\chi_1$, and do not have a gradation profile. In doing so, we could focus on the enhancement of the optical nonlinearity. Without loss of generality, the film width L is taken to be unity.

For numerical calculations, we take as a model plasma-frequency gradation profile,

$$\omega_p(z) = \omega_p(0)(1 - C_\omega \cdot z), \tag{6}$$

where C_ω is a constant (gradient) tuning the profile.

Figures 1–3, respectively, display the optical absorption $\sim\mathrm{Im}[\bar{\epsilon}(\omega)]$, and the modulus of the effective third-order optical nonlinearity enhancement $|\bar{\chi}(\omega)|/\chi_1$, as well as the FOM $|\bar{\chi}(\omega)|/\{\chi_1\,\mathrm{Im}[\bar{\epsilon}(\omega)]\}$ as a function of frequency $\omega/\omega_p(0)$. Here $\mathrm{Im}[\cdots]$ means the imaginary part of $\cdots$. In each panel of Figs. 1–3 the corresponding graded film results are shown as well.

It is evident from Figs. 1–3 that for a few layers, say $N=2,4,8$ [(a)–(c)], the optical absorption spectrum and the enhancement of optical nonlinearity consist mainly of sharp peaks. However, the strong optical absorption and the large fluctuation of the nonlinear optical enhancement near these sharp peaks render the FOM too small to be useful. When the number of layers becomes large [(d)–(f)], the sharp peaks accumulate to a broadband while the fluctuation has been reduced significantly. In this limit, the broad continuous absorption band emerges, and a large FOM persists.

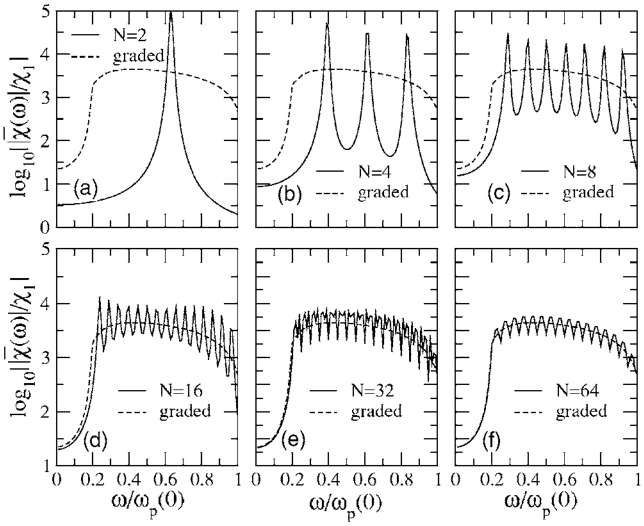

FIG. 2. Same as Fig. 1, but for the enhancement of the third-order optical nonlinearity $|\bar{\chi}(\omega)|/\chi_1$.

In short Figs. 1–3 show a gradual transition from sharp peaks to a broad continuous band as the number of layers increases. This also gives an explanation of the intriguing findings reported in our recent work.[6]

It should be remarked that the key point for 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. In this regard, it is also expected that an enhancement in the nonlinear optical responses can be found in compositionally graded metal-dielectric films in which the fraction of metal component varies perpendicular to the film.[19]

In addition, since the incident optical field can always be resolved into the parallel and perpendicular polarizations, the optical response of the layered structure must depend on the polarization of the incident light. However, a large nonlinearity enhancement occurs only when the electric field is parallel to the direction of the gradient[5] (i.e., for the parallel polarization), and the other polarization does not produce nonlinearity enhancement at all[5] (i.e., for the perpendicular polarization). Fortunately, the nonlinear susceptibilities of both the parallel and perpendicular polarizations are related to the nonlinear phase shift, which can be measured by using the z-scan method.[5]

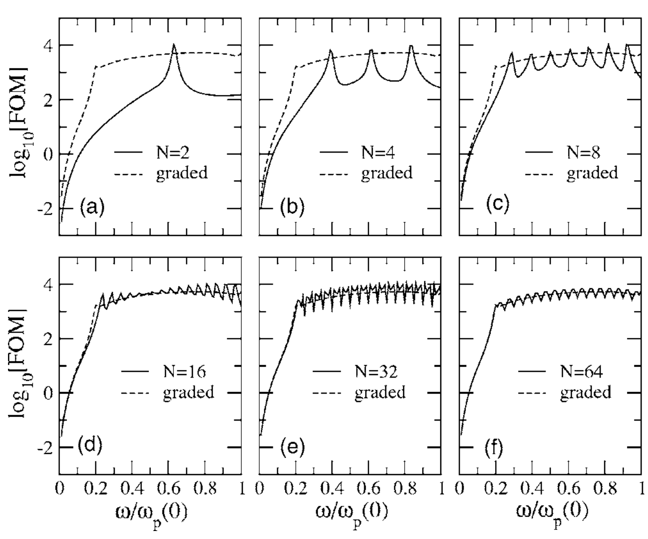

FIG. 3. Same as Fig. 1, but for the FOM $\equiv |\bar{\chi}(\omega)|/\{\chi_1 \operatorname{Im}[\bar{\epsilon}(\omega)]\}$.

IV. DISCUSSION AND CONCLUSION

In this work, we have investigated the effective nonlinear optical response of metallic films as the number of layers inside the film increases until the graded film results recover. This is of practical value since in practice it is more convenient to fabricate multilayer metallic films than graded films.

It is also instructive to study the spectral representation of graded composites. Our preliminary results show that the final representation and the definition of the spectral density function remain the same as the Bergman-Milton representation.[20] Moreover, the separation of the material parameter from the microstructure information still holds. However, the intermediate derivations as well as some of the salient properties, namely, the sum rule, the definition of the inner product, and the definition of the integral-differential operator, as well as the range of the spectral parameters, do change due to the presence of gradation.[21] To this end, it is instructive to apply the spectral representation to multilayer films and calculate the spectral density function versus the number of layers to reveal the broad continuous spectrum.

Also, it is of interest to extend the present consideration to composites in which graded spherical particles are embedded in a host medium to account for mutual interactions among graded particles. Similar considerations can be extended to other nonlinear optical properties such as the second-harmonic generation.[22]

To sum up, we have investigated the multilayer effect on the effective nonlinear optical response of metallic films. As the number of layers inside the metallic films increases, a gradual transition has been shown from sharp peaks to a broad continuous band until the graded film results recover.

ACKNOWLEDGMENTS

This work was supported by the Research Grants Council of the Hong Kong SAR Government under Project No. CUHK 403004, and in part by the Alexander von Humboldt Foundation in Germany which supports one of the authors (J.P.H.). J.P.H. also acknowledges the financial support by the Shanghai Education Committee and the Shanghai Education Development Foundation (Shu Guang project). Another author (K.W.Y.) acknowledges fruitful discussions with Professor S. P. Wong and Dr. J. J. Xiao.

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