Available online at www.sciencedirect.com

SCIENCE DIRECT®

Physics Letters A 357 (2006) 475–478

PHYSICS LETTERS A

www.elsevier.com/locate/pla

# Theory of nonlinear ac responses of inhomogeneous two-component composite films

B. Xu [a], J.P. Huang [a,*], K.W. Yu [b]

[a] *Surface Physics Laboratory (National Key Laboratory) and Department of Physics, Fudan University, Shanghai 200433, China*
[b] *Department of Physics and Institute of Theoretical Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

Received 26 November 2005; accepted 27 April 2006

Available online 4 May 2006

Communicated by R. Wu

**Abstract**

Chemical deposition techniques as well as diffusing techniques can be used to produce inhomogeneous composite films. We put forth a theory to investigate the nonlinear ac responses of a model graded film. We find that the responses are strongly dependent on the gradation profile and the thickness of the film, due to the local field effect. Thus, it seems possible to real-time-monitor the gradation profile and the thickness of the film by measuring the nonlinear ac response of inhomogeneous composite films.


*PACS:* 77.55.+f; 42.79.Ry; 77.22.Ej; 77.84.Lf

*Keywords:* Nonlinear ac responses; Composite graded films

Chemical deposition techniques (Fig. 1(a)) as well as diffusing techniques (Fig. 1(b)) can be used to produce inhomogeneous composite films or interfaces. Inhomogeneous (e.g., graded) materials [1–9] often have different physical properties from the homogeneous materials. In particular, graded thin films were found to show better dielectric properties than single-layer films [3]. So far, the authors [4] have investigated corrugated interfaces in composite materials by modifying the standard Bergman spectral representation [10]. Far from the interface region in Fig. 1(b), one can distinguish medium 1 and medium 2 unambiguously. However, it is not true inside the interface region, because in the quasistatic limit, the roughness cannot be resolved in that region. Thus, we can regard the interface region as a graded region in which one component varies gradually and continuously to the other component. In this way, an effective medium is just suitable to describe the physics inside the interface region. The (surface) spectral density function from the graded effective medium approximation just describes the simulation data very well [11]. In fact, traditional theories [12] cannot be used to deal with the composites of graded materials directly. For this purpose, we have put forth a first-principles approach [5,6] and a differential effective dipole approximation [7].

When a composite consisting of dielectric particles having nonlinear characteristics is subjected to a sinusoidal ac electric field with angular frequency $\omega$, the electric response will generally consist of ac fields at frequencies of the higher-order harmonics [13–22]. In this work, we shall put forth a theory to investigate the nonlinear ac responses of model graded films.

Let us start by considering the effective linear dielectric constant $\epsilon_e$ of a two-component composites with constituent dielectric constants $\epsilon_1$ and $\epsilon_2$ of volume fraction $p_1$ and $p_2$, respectively,

$$\epsilon_e \equiv F(\epsilon_1, \epsilon_2, p). \tag{1}$$

We shall use the perturbation theory to extract the nonlinear dielectric constants, assuming the nonlinear coefficients $\chi_1 E_0^2$, and $\chi_2 E_0^2$ are small compared with the linear response. The mean-square averaged (linear) local fields in each component

* Corresponding author.
*E-mail address:* jphuang@fudan.edu.cn (J.P. Huang).

0375-9601/$ – see front matter 
doi:10.1016/j.physleta.2006.04.092

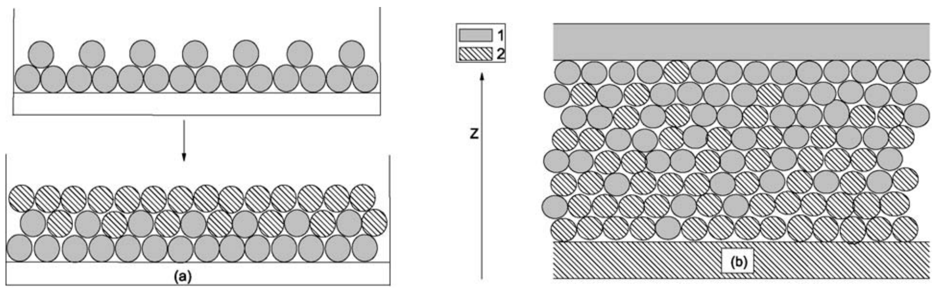


Fig. 1. Schematic graph showing (a) the chemical deposition technique to form a graded composite film, and (b) the diffusing technique to form a graded interface (composite film) between two bulk composites.

are [23]

$$p_1\langle E_1^2\rangle = \frac{\partial\epsilon_e}{\partial\epsilon_1}E_0^2 = F_1(\epsilon_1,\epsilon_2,p)E_0^2, \tag{2}$$

$$p_2\langle E_2^2\rangle = \frac{\partial\epsilon_e}{\partial\epsilon_2}E_0^2 = F_2(\epsilon_1,\epsilon_2,p)E_0^2, \tag{3}$$

where $F_1$ and $F_2$ are defined as the partial derivatives

$$F_1(\epsilon_1,\epsilon_2,p) = \frac{\partial F}{\partial\epsilon_1}, \tag{4}$$

$$F_2(\epsilon_1,\epsilon_2,p) = \frac{\partial F}{\partial\epsilon_2}. \tag{5}$$

In the perturbation theory, the effective nonlinear dielectric constant $\epsilon_e^{\mathrm{NL}}$ can be expressed as the (linear) local field averages

$$\begin{aligned}\epsilon_e^{\mathrm{NL}} &= F\big(\epsilon_1+\chi_1\langle E_1^2\rangle, \epsilon_2+\chi_2\langle E_2^2\rangle, p\big)\\ &= F(\epsilon_1,\epsilon_2,p) + F_1(\epsilon_1,\epsilon_2,p)\chi_1\langle E_1^2\rangle\\ &\quad + F_2(\epsilon_1,\epsilon_2,p)\chi_2\langle E_2^2\rangle + \cdots.\end{aligned} \tag{6}$$

In view of Eqs. (2) and (3), the local field averages can be rewritten as [23]

$$\langle E_1^2\rangle = \frac{1}{p_1}F_1E_0^2, \qquad \langle E_2^2\rangle = \frac{1}{p_2}F_2E_0^2. \tag{7}$$

Thus, the effective nonlinear dielectric constant $\epsilon_e^{\mathrm{NL}}$ (Eq. (6)) can be written as

$$\epsilon_e^{\mathrm{NL}} = F + \frac{1}{p_1}F_1^2\chi_1E_0^2 + \frac{1}{p_2}F_2^2\chi_2E_0^2 + \cdots. \tag{8}$$

Next we express the nonlinear ac electric displacement field $\tilde{D}^{\mathrm{NL}}$ as

$$\tilde{D}^{\mathrm{NL}} = F\tilde{E}_0 + \left(\frac{1}{p_1}F_1^2\chi_1 + \frac{1}{p_2}F_2^2\chi_2\right)\tilde{E}_0^3 + \cdots, \tag{9}$$

where

$$\tilde{E}_0 = E_0\sin\omega t \tag{10}$$

is an applied sinusoidal ac electric field with angular frequency $\omega$. Then, we define the fundamental and third harmonics, $D_\omega$ and $D_{3\omega}$, as

$$\tilde{D}^{\mathrm{NL}} = D_\omega\sin\omega t + D_{3\omega}\sin 3\omega t. \tag{11}$$

Higher-order (e.g., fifth and seventh) harmonics can also be investigated if one keeps more terms in Eq. (6). However, the strength of the higher-order harmonic responses are several orders of magnitude weaker than that of the third harmonic response, and hence they have been neglected in Eq. (11). By using the identity

$$\sin^3\omega t = \frac{3}{4}\sin\omega t - \frac{1}{4}\sin 3\omega t, \tag{12}$$

we obtain the harmonic terms

$$D_\omega = FE_0 + \frac{3}{4}\left(\frac{1}{p_1}F_1^2\chi_1 + \frac{1}{p_2}F_2^2\chi_2\right)E_0^3, \tag{13}$$

$$D_{3\omega} = -\frac{1}{4}\left(\frac{1}{p_1}F_1^2\chi_1 + \frac{1}{p_2}F_2^2\chi_2\right)E_0^3. \tag{14}$$

Now we can go straightforward to plot the ratio $D_{3\omega}/D_\omega$,

$$\frac{D_{3\omega}}{D_\omega} = \frac{-\frac{1}{4}\big(\frac{1}{p_1}F_1^2\chi_1 + \frac{1}{p_2}F_2^2\chi_2\big)E_0^2}{F + \frac{3}{4}\big(\frac{1}{p_1}F_1^2\chi_1 + \frac{1}{p_2}F_2^2\chi_2\big)E_0^2}, \tag{15}$$

as a function of the parameters describing gradation profiles (Figs. 2 and 3), the width $L$ of model graded films (Fig. 4), and so on.

By using a two-step solution [24], we first derive the response of a slice inside the graded film. For simplicity, we assume $\chi_2 = 0$ (namely, linear host). (In fact, according to Eq. (15), we can also discuss the case that the host is nonlinear, i.e., $\chi_2 \neq 0$.) Let us take the well-known Maxwell Garnett expression [25,26] for the effective dielectric constant $\epsilon_e(z)$ for the slice at $z$:

$$\frac{\epsilon_e^{(1)}(z) - \epsilon_2}{\epsilon_e^{(1)}(z) + 2\epsilon_2} = p_1(z)\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}, \tag{16}$$

$$\frac{\epsilon_e^{(2)}(z) - \epsilon_1}{\epsilon_e^{(2)}(z) + 2\epsilon_1} = p_2(z)\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}. \tag{17}$$

For $p_1(z) \leqslant 0.5$ or $p_2(z) \equiv 1 - p_1(z) \geqslant 0.5$, $\epsilon_e(z) = \epsilon_e^{(1)}(z)$, which represents the case that medium 1 is embedded in medium 2 (Eq. (16)). Otherwise, for $p_1(z) > 0.5$ or $p_2(z) < 0.5$, $\epsilon_e(z) = \epsilon_e^{(2)}(z)$ instead, which corresponds to the inverse case that medium 2 is embedded in medium 1 (Eq. (17)). The microstructure can have a significant effect on the ac responses. The film is now graded and the volume fraction has to be small (or close to unity) away from the interface region. In this case, the dispersion microstructure (Eqs. (16) and (17)) is relevant.

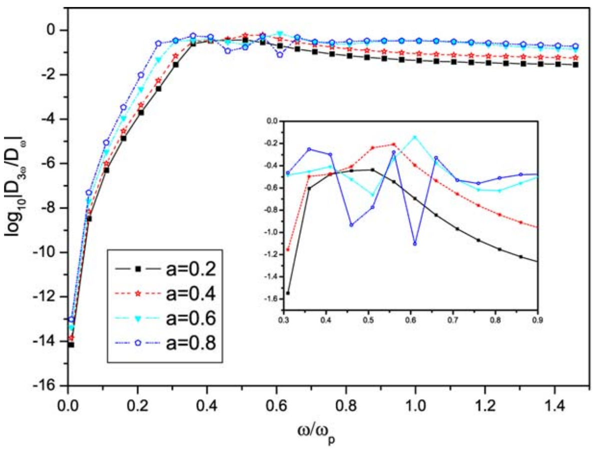


Fig. 2. (Color online) $\log_{10}|D_{3\omega}/D_\omega|$ as a function of the $\omega/\omega_p$ for different $a$. $|\cdots|$ denotes the absolute value or modulus of $\cdots$. Parameters: $\chi_1 E_0^2 = 0.8\epsilon_0$, $L = 1$, and $m = 1.0$.

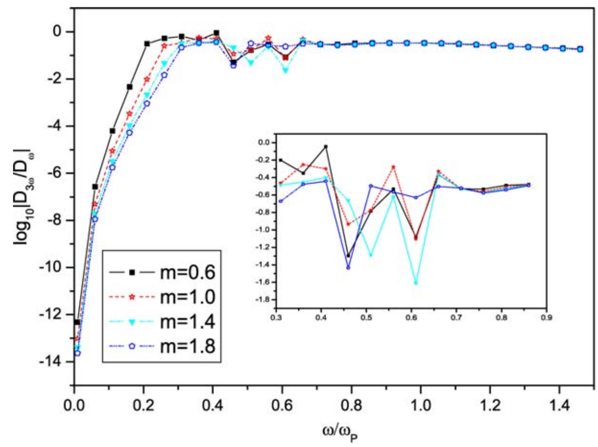


Fig. 3. (Color online) $\log_{10}|D_{3\omega}/D_\omega|$ as a function of the $\omega/\omega_p$ for different $m$. Parameters: $\chi_1 E_0^2 = 0.8\epsilon_0$, $L = 1$, and $a = 0.8$.

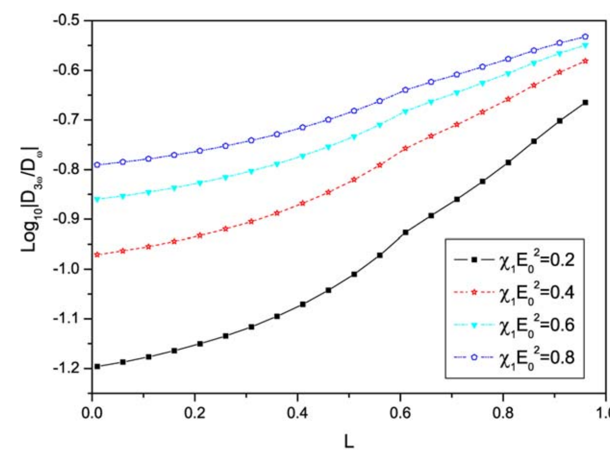


Fig. 4. (Color online) $\log_{10}|D_{3\omega}/D_\omega|$ as a function of the width $L$ of the graded film for different $\chi_1 E_0^2$. Parameters: $a = 0.8$, $\omega = 0.8\omega_p$, and $m = 1.0$.

To compute $D_{3\omega}/D_\omega$, we adopt the Drude dielectric function for $\epsilon_1$

$$\epsilon_1/\epsilon_0 = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \tag{18}$$

where $\omega$ is the frequency of the external electric field, $\omega_p$ the plasma frequency, $\gamma$ the relaxation rate, and $\epsilon_0$ the dielectric constant of free space. We shall take $\gamma = 0.01\omega_p$, which is a typical value for metals. Without loss of generality, we take a power-law gradation profile

$$p_1(z) = az^m \tag{19}$$

as an example, in order to determine the volume fraction of component 1 inside a slice at $z$ within the graded film. Here $0 \leqslant z \leqslant L$, and $a$ and $m$ are parameters which could be changed during fabrication. Then the total volume fractions of the components 1 and 2 within the whole graded film are given by

$$p_1 = \frac{1}{L}\int_0^L p_1(z)\,dz, \qquad p_2 = 1 - p_1. \tag{20}$$

Next, the overall responses of the graded film can be derived, by using the equivalent capacitance of a series combination, namely,

$$F = L\left(\int_0^L \frac{1}{\epsilon_e(z)}\,dz\right)^{-1}. \tag{21}$$

The substitution of Eq. (21) into Eq. (4) and Eq. (5) yields $F_1$ and $F_2$, respectively.

So far, we can take one step forward to calculate the ratio $D_{3\omega}/D_\omega$ (Eq. (15)), as a function of $\omega$, $L$, $a$, $m$, and $\chi_1 E_0^2$. We set $\epsilon_2 = (3/2)^2\epsilon_0$. In Fig. 2, $|D_{3\omega}/D_\omega|$ is plotted as a function of the reduced frequency $\omega/\omega_p$ for different gradation parameter $a$. For all $\omega$ except for $0.4\omega_p < \omega < 0.7\omega_p$, larger $a$ yields larger $|D_{3\omega}/D_\omega|$. Within the frequency range $0.4\omega_p < \omega < 0.7\omega_p$, for various $a$, irregular behavior may appear, due to the effect of local-field fluctuation. For small $\omega$ ($<0.4\omega_p$), $|D_{3\omega}/D_\omega|$ monotonically increases as $\omega$ increases. However, for large $\omega$ ($>0.7\omega_p$), the effect of frequency $\omega$ on $|D_{3\omega}/D_\omega|$ is not significant.

Fig. 3 displays $|D_{3\omega}/D_\omega|$ as a function of the $\omega/\omega_p$ for different gradation parameter $m$. For $\omega$ ($<0.3\omega_p$), smaller $m$ yields larger $|D_{3\omega}/D_\omega|$. Within $0.3\omega_p < \omega < 0.7\omega_p$, for different $m$, irregular behavior may also appear because of a local-field fluctuation. For small $\omega$ ($<0.3\omega_p$), $|D_{3\omega}/D_\omega|$ monotonically increases as $\omega$ increases. However, for large $\omega$ ($>0.7\omega_p$), the effect of either frequency $\omega$ or gradation parameter $m$ almost plays no role in $|D_{3\omega}/D_\omega|$.

In addition, we also investigate the effect of nonlinear characteristics $\chi_1 E_0^2$ on the harmonics $|D_{3\omega}|$ (rather than $D_{3\omega}/D_\omega$) as a function of the frequency $\omega/\omega_p$ (no figures shown here). As expected, stronger nonlinear characteristics yield stronger harmonic responses $D_{3\omega}$. In other words, the strength of harmonics can be used to indicate the strength of the nonlinear characteristic [13].

Fig. 4 shows $|D_{3\omega}/D_\omega|$ versus the width of the graded film $L$ for different nonlinear characteristics $\chi_1 E_0^2$, in an attempt to discuss the dependence of the film width $L$ on the harmonic responses. Apparently, the $L$ effect is significant. The harmonics monotonically increase as $L$ increases. It is also shown that stronger nonlinear characteristics yield stronger harmonic responses $|D_{3\omega}/D_{\omega}|$.

In a word, the harmonics are significantly dependent on the gradation profiles (Figs. 2 and 3) as well as the width of the composite film (Fig. 4). Thus, it becomes possible to real-time-monitor the gradation profile as well as the width of the composite graded film, by measuring the nonlinear ac responses of the film subjected to an ac electric field.

## Acknowledgements

B.X. and J.P.H. acknowledge the financial support by the Shanghai Education Committee and the Shanghai Education Development Foundation ("Shu Guang" project) under Grant No. KBH1512203, by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, China, and by Jiangsu Key Laboratory of Thin Films, Suzhou University, China. K.W.Y. acknowledges financial support from the RGC Earmarked Grant of the Hong Kong SAR Government.

## References

[1] G.W. Milton, The Theory of Composites, Cambridge Univ. Press, Cambridge, 2002, Chapter 7.
[2] T.B. Jones, Electromechanics of Particles, Cambridge Univ. Press, Cambridge, 1995.
[3] S.G. Lu, X.H. Zhu, C.L. Mak, K.H. Wong, H.L.W. Chan, C.L. Choy, Appl. Phys. Lett. 82 (2003) 2877.
[4] A.R. McGurn, A.R. Day, D.J. Bergman, L.C. Davis, M.F. Thorpe, Phys. Rev. B 70 (2004) 144205.
[5] L. Dong, G.Q. Gu, K.W. Yu, Phys. Rev. B 67 (2003) 224205.
[6] G.Q. Gu, K.W. Yu, J. Appl. Phys. 94 (2003) 3376.
[7] J.P. Huang, K.W. Yu, G.Q. Gu, M. Karttunen, Phys. Rev. E 67 (2003) 051405.
[8] L. Gao, Phys. Rev. E 71 (2005) 067601.
[9] Z.F. Sang, Z.Y. Li, Phys. Lett. A 334 (2005) 422.
[10] D.J. Bergman, Phys. Rep. 43 (1978) 379.
[11] C.T. Yam, M.Ph. Thesis, Chinese University of Hong Kong, 2005.
[12] J.D. Jackson, Classical Electrodynamics, Wiley, New York, 1975.
[13] D.J. Klingenberg, MRS Bull. 23 (1998) 30.
[14] G.Q. Gu, P.M. Hui, K.W. Yu, Physica B 279 (2000) 62.
[15] O. Levy, D.J. Bergman, D. Stroud, Phys. Rev. E 52 (1995) 3184.
[16] P.M. Hui, D. Stroud, J. Appl. Phys. 82 (1997) 4740.
[17] P.M. Hui, P.C. Cheung, D. Stroud, J. Appl. Phys. 84 (1998) 3451.
[18] J.P. Huang, J.T.K. Wan, C.K. Lo, K.W. Yu, Phys. Rev. E 64 (2001) 061505(R).
[19] J.P. Huang, J. Phys. Chem. B 109 (2005) 4824.
[20] P.M. Hui, C. Xu, D. Stroud, Phys. Rev. B 69 (2004) 014203.
[21] E.B. Wei, J.B. Song, G.Q. Gu, J. Appl. Phys. 95 (2004) 1377.
[22] J.P. Huang, P.M. Hui, K.W. Yu, Phys. Lett. A 342 (2005) 484.
[23] K.W. Yu, P.M. Hui, D. Stroud, Phys. Rev. B 47 (1993) 14150.
[24] J.P. Huang, K.W. Yu, J. Opt. Soc. Am. B 22 (2005) 1640.
[25] J.C. Maxwell Garnett, Philos. Trans. T. Soc. London Ser. A 203 (1904) 385.
[26] J.C. Maxwell Garnett, Philos. Trans. R. Soc. London Ser. A 205 (1906) 237.