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Tetrahedron model for the dielectric function of amorphous silicon-carbon alloys

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A Si- and C-centered tetrahedron model is developed for the determination of the optical dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ of amorphous silicon-carbon (a-$\mathrm{Si}_{1-x}\mathrm{C}_x$) alloys. The Phillips—Van Vechten—Levine dielectric model, along with the scaling procedure of Aspnes and Theeten, is used to obtain predictions for ϵ_1 and ϵ_2 for the individual Si-$\mathrm{Si}_{4-\nu}\mathrm{C}_\nu$ and C-$\mathrm{Si}_{4-\nu}\mathrm{C}_\nu$ ($\nu=0$–4) tetrahedra. The tetrahedron model then uses these tetrahedra as the components in the Bruggemann effective-medium approximation to obtain predictions for ϵ_1 and ϵ_2 for the a-$\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys. These predictions for ϵ_1 and ϵ_2, and for the optical energy-gap parameter E_{opt}, are obtained for three different types of chemical ordering in the films: (1) no chemical ordering, (2) complete chemical ordering with homogeneous dispersion, and (3) complete chemical ordering with phase separation. The predictions of this model are presented in detail in this paper and are compared with experimental results for ϵ_1, ϵ_2, and E_{opt} for a series of a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H alloys in the following paper.

I. INTRODUCTION

Amorphous silicon-carbon alloy films have important applications as p-type layers in p-i-n a-Si:H photovoltaic devices[1] and also as potentially useful optical and solar selective coatings.[2] As a result of these applications and also due to continuing interest in the properties of tetrahedrally coordinated amorphous semiconductors, it has become important to determine the optical response of these films and its dependence on the microstructure and local bonding present in the films. We have recently undertaken an experimental determination of the optical constants of a series of hydrogenated amorphous silicon-carbon alloy films (a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H), and our experimental results for ϵ_1 and ϵ_2, the real and imaginary parts of the dielectric function, are presented in the following paper.[3] In this paper we present and develop a tetrahedron-based model from which predictions for ϵ_1 and ϵ_2 for these alloy films can be made as functions of the [Si/C] ratio and also for different types of chemical ordering present in the films. A comparison between the predictions of this model and our experimental results for ϵ_1 and ϵ_2, included in the following paper, has allowed us to determine the nature of the chemical ordering present in these films.

The model which we will present for calculating ϵ_1 and ϵ_2 for these amorphous silicon-carbon alloys considers Si- and C-centered tetrahedra to be the fundamental structural units which determine the optical response of the films. This type of approach was first discussed by Philipp[4] who proposed that the optical response of films based on silicon, oxygen, and nitrogen was determined by the response of Si-centered tetrahedra such as Si-$\mathrm{Si}_{4-\nu}\mathrm{O}_\nu$ and Si-$\mathrm{Si}_{4-\nu}\mathrm{N}_\nu$ ($\nu=0$–4). Aspnes and Theeten[5] further developed this approach and combined it with the Bruggemann[6] effective-medium approximation (EMA) and scaling of the dielectric function to determine ϵ_1 and ϵ_2 for $\mathrm{Si}_{1-x}(\mathrm{SiO}_2)_x$ and $\mathrm{Si}_{1-x}(\mathrm{SiN}_{4/3})_x$ mixtures. We note that Si-centered tetrahedra have also been proposed to be the fundamental units which determine both the frequencies of the Si—H stretching modes observed in the infrared absorption spectra of hydrogenated amorphous Si-based alloys[7] and the Si $2p$ core-level binding energies in a-$\mathrm{Si}_x\mathrm{N}_{1-x}$:H alloys.[8]

An important factor for the determination of the dielectric function of amorphous semiconducting alloys of Si and C involves the question of whether or not chemical ordering occurs in the bonding between the Si and C atoms. If there exists no preferential chemical bonding between Si and C atoms, then the alloys are said to be chemically disordered. Complete chemical ordering, on the other hand, refers to the situation where C atoms have only Si nearest neighbors in Si-rich alloys and where Si atoms have only C nearest neighbors in C-rich alloys. Thus, completely chemically ordered films contain the maximum possible number of Si—C bonds. If the Si—C bonds are randomly dispersed throughout the film, then the chemical ordering is said to be homogeneous. If, however, the Si—C bonds are clustered, then in addition to chemical ordering there is also phase separation (for example, separate regions corresponding to pure Si and stoichiometric SiC in Si-rich films).

The issue of chemically ordering can be dealt with in a straightforward way within the framework of the Si- and C-centered tetrahedron model presented here since the different types of chemical ordering can be readily specified by giving the appropriate probabilities for the various Si- and C-centered tetrahedra (i.e., Si-$\mathrm{Si}_{4-\nu}\mathrm{C}_\nu$ and C-$\mathrm{Si}_{4-\nu}\mathrm{C}_\nu$, $\nu=0$–4) present in the films.

With tetrahedra identified as the fundamental units determining the optical response of the alloy films, the dielectric function for the film may be defined via the Bruggemann EMA,[6] given by the following equations:

$$\sum_i v_i \frac{\epsilon_i-\epsilon}{\epsilon_i+2\epsilon}=0 \, , \qquad \sum_i v_i = 1 \, , \tag{1}$$

where v_i and ϵ_i are the volume fraction and dielectric function, respectively, of the ith component. In our model we use ten components corresponding to the ten distinct Si- and C-centered tetrahedra present in the films. Using values for the v_i and ϵ_i as determined for the tetrahedra from our model, the ϵ appropriate for the silicon-carbon alloy in question will be calculated using the EMA expressed in Eq. (1). Our results shown below indicate that it is indeed the Si- and C-centered tetrahedra, as opposed to simply Si—Si, Si—C, and C—C bonds, which are more appropriately considered to be the fundamental structural units present in the films which determine the optical response.

We note that although hydrogen atoms have not been explicitly included at this stage in the Si- and C-centered tetrahedron model, their presence in the a-$Si_{1-x}C_x$:H alloy films has been at least indirectly taken into account in the model as the ϵ_i spectra for the individual tetrahedra have been scaled from the ϵ spectrum for a-Si:H which clearly does reflect the contribution of the incorporated H atoms.

We will now develop the tetrahedron-based model in Sec. II, with the predictions of the model presented in Sec. III.

II. TETRAHEDRON MODEL—DEVELOPMENT

The objective of the tetrahedron model to be developed in this section is to provide a framework for calculating the dielectric constants ϵ_1 and ϵ_2 for amorphous silicon-carbon alloys, using the EMA expressed in Eq. (1). For this purpose we will need to obtain from the model results for the volume fractions v_i and complex dielectric functions ϵ_i for the individual Si- and C-centered tetrahedra which are to be used as the components in the EMA. We will first consider the volume fractions v_i which are functions of the individual tetrahedron volumes V_i and tetrahedron probabilities P_i. We will then turn to the ϵ_i which will be obtained from the measured ϵ for a-Si:H using a scaling procedure whose parameters will be determined using the plasma sum rule and the dielectric model of Phillips, Van Vechten, and Levine.[9–11]

A. Si- and C-centered tetrahedra: Probabilities and volume fractions

The probabilities P_i for the individual Si-$Si_{4-\nu}C_\nu$ and C-$Si_{4-\nu}C_\nu$ ($\nu=0$–4) tetrahedra are functions both of the composition parameter x in these a-$Si_{1-x}C_x$ alloys and of the type of chemical ordering present in the films. For the case of no chemical ordering, i.e., no preferential bonding between Si and C atoms, the probability for a particular bond in a given tetrahedron is simply proportional to the fraction of atoms in the film available to complete that bond, i.e., $(1-x)$ for a Si—Si bond in a Si-centered tetrahedron or for C—Si bond in a C-centered tetrahedron. The total probability P_i for a given tetrahedron is then equal to the product of (1) the probability for starting with a Si or C atom at the center of the tetrahedron, (2) the probabilities for the individual bonds within the tetrahedron, and (3) a factor giving the number of possible ways of connecting the bonds within the tetrahedron. For example, for a Si-Si_3C tetrahedron, the resultant probability $P_i=4x(1-x)^4$ results from the product of four factors: $(1-x)$ for having the Si atom at the center of the tetrahedron, $(1-x)^3$ for having three Si atoms bonded to the central Si atom, x for having one C atom bonded to the central Si atom, and a factor of 4 for the possible ways of connecting the three Si and one C atoms to the four bonds available in the tetrahedron. The resulting probabilities P_i for the ten possible tetrahedra for the case of no chemical ordering are listed in the second column of Table I.

For the cases of complete chemical ordering with homogeneous dispersion and with phase separation, the tetrahedron probabilities P_i must take into account the fact that, in Si-rich alloys, for example, C atoms will be bonded only to Si atoms. To determine the P_i for Si-rich alloys, we begin by defining $f(\mathrm{Si})=(1-x)$ and $f(\mathrm{C})=x$ as the fractions of Si and C atoms in the film. Also,

$$f_1(\mathrm{Si})=f(\mathrm{Si})-f(\mathrm{C})=(1-x)-x=(1-2x)$$

is the fraction of Si atoms which can bond to a given Si atom and $f_1(\mathrm{C})=f(\mathrm{C})=x$ is the fraction of C atoms which can bond to a given Si atom. We note that $f_1(\mathrm{Si})$ is reduced below $f(\mathrm{Si})=(1-x)$ by an amount $f(\mathrm{C})=x$ since a fraction $f(\mathrm{C})$ of the Si atoms must have their bonds effectively tied up by C atoms and thus, as a result of the complete chemical ordering, are effectively unavailable to bond to other Si atoms. Finally,

$$\begin{aligned} f_2(\mathrm{Si})&=f_1(\mathrm{Si})/[f_1(\mathrm{Si})+f_1(\mathrm{C})] \\ &=(1-2x)/[(1-2x)+x]=(1-2x)/(1-x) \end{aligned}$$

is the fraction of *all* atoms which can bond to Si atoms which are *Si* atoms. Likewise,

$$f_2(\mathrm{C})=f_1(\mathrm{C})/[f_1(\mathrm{Si})+f_1(\mathrm{C})]=x/(1-x)$$

is the fraction of *all* atoms which can bond to Si atoms which are *C* atoms.

The probability P_i for a Si—Si_3C tetrahedron is now given by

$$\begin{aligned} P_i&=4f(\mathrm{Si})f_2^3(\mathrm{Si})f_2(\mathrm{C}) \\ &=4(1-x)[(1-2x)/(1-x)]^3[x/(1-x)] \end{aligned}$$

for the case of complete chemical ordering with homogeneous dispersion. The remaining P_i for Si-rich and C-rich alloys for the case of homogeneous dispersion are given in the third and fourth columns, respectively, of Table I.

For the case of complete chemical ordering with phase separation, the only possible tetrahedra in a Si-rich alloy are Si-Si_4, Si-C_4, and C-Si_4, where the first tetrahedron can be thought of as corresponding to a-Si and the remaining two as corresponding to a-SiC. The probability for the Si-Si_4 tetrahedron is given by

$$\begin{aligned} P_i&=f(\mathrm{Si})f_2(\mathrm{Si})(1)^3 \\ &=(1-x)[(1-2x)/(1-x)]=(1-2x) \end{aligned}$$

since if a single Si atom is bonded to the central Si atom, then all of the three remaining atoms *must* also be Si

TABLE I. Tetrahedron probabilities P_i for $\mathrm{Si}_{1-x}\mathrm{C}_x$.

Tetrahedron	No chemical ordering	Complete chemical ordering with homogeneous dispersion Si-rich $(0 \le x \le 0.5)$	C-rich $(0.5 \le x \le 1)$	Complete chemical ordering with phase separation Si-rich	C-rich
(1) $\mathrm{Si\text{-}Si_4}$	$(1-x)^5$	$(1-x)\left[\frac{1-2x}{1-x}\right]^4$	0	$(1-2x)$	0
(2) $\mathrm{Si\text{-}Si_3C}$	$4x(1-x)^4$	$4(1-x)\left[\frac{1-2x}{1-x}\right]^3\left[\frac{x}{1-x}\right]$	0	0	0
(3) $\mathrm{Si\text{-}Si_2C_2}$	$6x^2(1-x)^3$	$6(1-x)\left[\frac{1-2x}{1-x}\right]^2\left[\frac{x}{1-x}\right]^2$	0	0	0
(4) $\mathrm{Si\text{-}SiC_3}$	$4x^3(1-x)^2$	$4(1-x)\left[\frac{1-2x}{1-x}\right]\left[\frac{x}{1-x}\right]^3$	0	0	0
(5) $\mathrm{Si\text{-}C_4}$	$x^4(1-x)$	$(1-x)\left[\frac{x}{1-x}\right]^4$	$(1-x)$	x	$(1-x)$
(6) $\mathrm{C\text{-}Si_4}$	$x(1-x)^4$	x	$x\left[\frac{1-x}{x}\right]^4$	x	$(1-x)$
(7) $\mathrm{C\text{-}Si_3C}$	$4x^2(1-x)^3$	0	$4x\left[\frac{1-x}{x}\right]^3\left[\frac{2x-1}{x}\right]$	0	0
(8) $\mathrm{C\text{-}Si_2C_2}$	$6x^3(1-x)^2$	0	$6x\left[\frac{1-x}{x}\right]^2\left[\frac{2x-1}{x}\right]^2$	0	0
(9) $\mathrm{C\text{-}SiC_3}$	$4x^4(1-x)$	0	$4x\left[\frac{1-x}{x}\right]\left[\frac{2x-1}{x}\right]^3$	0	0
(10) $\mathrm{C\text{-}C_4}$	x^5	0	$x\left[\frac{2x-1}{x}\right]^4$	0	$(2x-1)$

atoms (i.e., with unit probability). For the $\mathrm{Si\text{-}C_4}$ tetrahedron, we have

$$P_i = f(\mathrm{Si}) f_2(\mathrm{C})(1)^3 = (1-x)[x/(1-x)] = x$$

for similar reasons, while for the $\mathrm{C\text{-}Si_4}$ tetrahedron, we have $P_i = f(\mathrm{C})(1)^4 = x$ due to the existence of complete chemical ordering. These P_i and those for C-rich alloys for the case of phase separation are listed in the fifth and sixth columns of Table I, respectively.

In Figs. 1–3 the tetrahedron probabilities P_i for the cases of no chemical ordering, complete chemical ordering with homogeneous dispersion, and complete chemical ordering with phase separation, respectively, are shown as functions of x for a-$\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys. The largest differences occur near $x = 0.5$, at which composition only $\mathrm{Si\text{-}C_4}$ and $\mathrm{C\text{-}Si_4}$ tetrahedra are present for the two types of complete chemical ordering considered. For the case of no chemical ordering, all ten tetrahedra are present for $x = 0.5$.

The contribution of each tetrahedron to the optical response of an a-$\mathrm{Si}_{1-x}\mathrm{C}_x$ alloy film is determined both by its dielectric function ϵ_i and its volume fraction in the film, v_i. The individual v_i are given by $v_i = P_i V_i / \sum P_i V_i$, where V_i is the volume associated with the ith tetrahedron. For a tetrahedron with all like atoms, e.g., $\mathrm{Si\text{-}Si_4}$, the

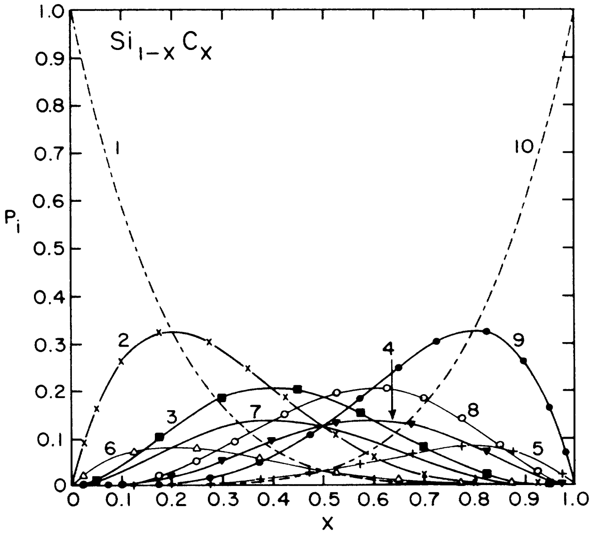

FIG. 1. Probabilities P_i for Si- and C-centered tetrahedra in $\mathrm{Si}_{1-x}\mathrm{C}_x$ alloys as functions of composition x for the case of no chemical ordering. See Table I or II for numbering of the tetrahedra; e.g., tetrahedron 1 is $\mathrm{Si\text{-}Si_4}$.

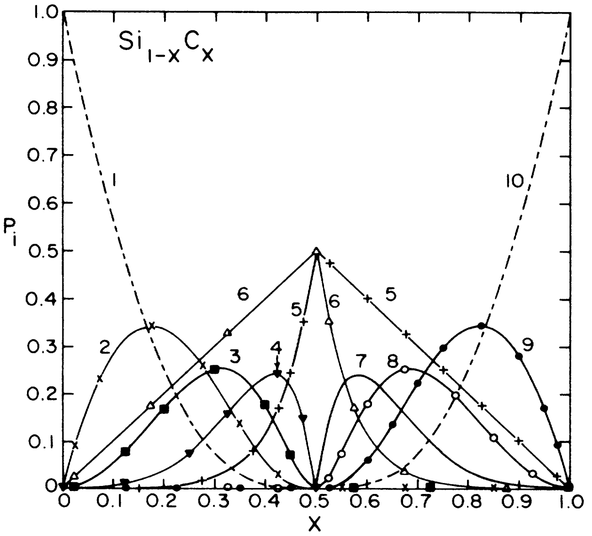

FIG. 2. Probabilities P_i for Si- and C-centered tetrahedra in $Si_{1-x}C_x$ alloys as functions of composition x for the case of complete chemical ordering with homogeneous dispersion. See Table I or II for numbering of the tetrahedra; e.g., tetrahedron 1 is $Si\text{-}Si_4$.

volume of the tetrahedron is given by $V_{\rm tet}=8a^3/9\sqrt{3}$, where $a=d(\rm SiSi)$ is the Si—Si bond length equal to 2.35 Å. However, in crystalline Si, in order to account for the entire volume of the crystal, the volume associated with each $Si\text{-}Si_4$ tetrahedron is actually $V_i=3V_{\rm tet}$. This extra factor of 3 is necessary, for example, in calculating atomic densities. Similarly, for tetrahedra such as $Si\text{-}Si_3C$, we have $V_{\rm tet}=2a^2(a+3b)/9\sqrt{3}$, where $a=d(\rm SiSi)$ and $b=d(\rm SiC)=1.884$ Å. Finally, for tetrahedra such as $Si\text{-}Si_2C_2$, we have $V_{\rm tet}=4ab(a+b)/9\sqrt{3}$, with $a=d(\rm SiSi)$ and $b=d(\rm SiC)$. Note that $d(\rm CC)=1.542$ Å. Using these expressions for $V_{\rm tet}$, and including the necessary factor of three as discussed above, the volumes V_i associated with each of the ten tetrahedra are listed in Table II.

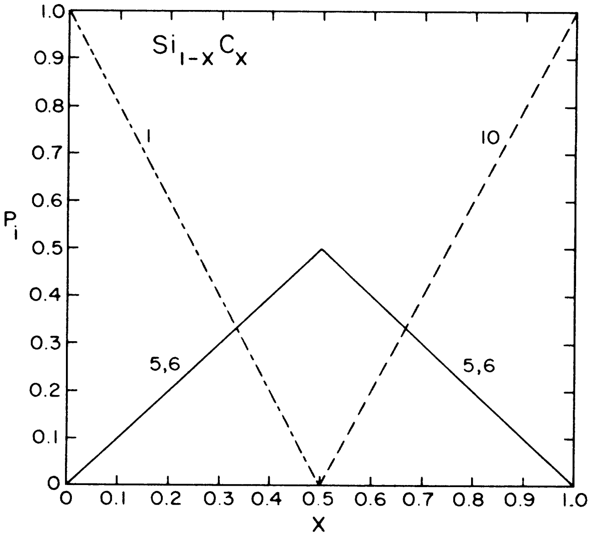

FIG. 3. Probabilities P_i for Si- and C-centered tetrahedra in $Si_{1-x}C_x$ alloys as functions of composition x for the case of complete chemical ordering with phase separation. See Table I or II for numbering of the tetrahedra; e.g., tetrahedron 1 is $Si\text{-}Si_4$.

B. Scaling of ϵ_1 and ϵ_2

The dielectric responses ϵ_i of the tetrahedra which are listed in Table I are, in general, not directly available from experiment. Aspnes and Theeten[5] have shown, however, that it is possible to determine $\epsilon_i=\epsilon_{1i}+i\epsilon_{2i}$ for each tetrahedron by scaling from the measured ϵ for amorphous Si. The measured ϵ for amorphous Si will in fact be taken to be the ϵ_i for the $Si\text{-}Si_4$ tetrahedron. This scaling approach is based on the expression

$$\epsilon_i(E)-1=C_{1i}[\epsilon_{a\text{-Si:H}}(C_{2i}E)-1]\ , \tag{2}$$

where E is the photon energy and C_{1i} and C_{2i} are scaling parameters appropriate to the ith tetrahedron, to be defined below using the plasma sum rule and the Phillips—Van Vechten—Levine (PVVL) dielectric model.[9–11] Note that, as indicated by Eq. (2), we will scale from the measured ϵ for a-Si:H,[12] so that the scaled ϵ_i spectra for the tetrahedra will indirectly include the effect of the hydrogen as incorporated in a-Si:H.

Aspnes and Theeten[5] have indicated that when Eq. (2) and the plasma sum rule given by

$$n_{\rm eff}(E)=(m/2\pi^2e^2\hbar^2)\int_0^E E'\epsilon_2(E')dE'\ , \tag{3}$$

are taken together, then the following relationship between the scaling parameters C_{1i} and C_{2i} can be obtained:

$$C_{1i}=[n(i)/n(a\text{-Si:H})]C_{2i}^2\ . \tag{4}$$

Here $n(i)$ and $n(a\text{-Si:H})$ are the density of bonding electrons associated with the ith tetrahedron and with a-Si:H, respectively.

The scaling parameter C_{2i} for the energy will now be shown to be simply related to E_g, the average energy-gap parameter in the PVVL dielectric model.[9–11] We note that the real part of Eq. (2), when evaluated at zero energy, can be written as

$$\epsilon_{1i}(0)-1=C_{1i}[\epsilon_{1,a\text{-Si:H}}(0)-1]\ . \tag{5}$$

By using the expression[13] $\epsilon_1(0)-1=A(\hbar\omega_p/E_g)^2$, where A is a constant and $\hbar\omega_p$ is the plasma energy ($\omega_p^2=4\pi ne^2/m$), Eq. (5) can be written in the form

$$A(\hbar\omega_p/E_g)_i^2=C_{1i}A(\hbar\omega_p/E_g)_{a\text{-Si:H}}^2\ . \tag{6}$$

Given that $(\hbar\omega_p)_i^2\propto n(i)$ and $(\hbar\omega_p)_{a\text{-Si:H}}^2\propto n(a\text{-Si:H})$, Eq. (6) can be rearranged to yield

$$C_{1i}=[n(i)/n(a\text{-Si:H})][E_g(a\text{-Si:H})/E_{gi}]^2\ . \tag{7}$$

Comparing Eq. (7) with Eq. (4), we can see that the energy scaling parameter C_{2i} is given simply by

$$C_{2i}=E_g(a\text{-Si:H})/E_{gi}\ . \tag{8}$$

TABLE II. Parameters for Si- and C-centered tetrahedra (defined in text).

Tetrahedron	$\langle r \rangle$ (Å)	k_F (Å^{-1})	k_s (Å^{-1})	E_H (eV)	C (eV)	E_g (eV)	C_2	C_1	V_i (Å^3)
(1) Si-Si$_4$	1.176	1.809	2.085	4.76	0	4.76	1	1	20.02
(2) Si-Si$_3$C	1.118	1.910	2.142	5.40	0.84	5.46	0.871	0.893	17.01
(3) Si-Si$_2$C$_2$	1.059	2.016	2.201	6.18	1.78	6.43	0.740	0.759	14.45
(4) Si-SiC$_3$	1.001	2.133	2.264	7.11	2.85	7.66	0.621	0.632	12.21
(5) Si-C$_4$	0.942	2.257	2.329	8.26	4.08	9.21	0.517	0.520	10.30
(6) C-Si$_4$	0.942	2.257	2.329	8.26	4.08	9.21	0.517	0.520	10.30
(7) C-Si$_3$C	0.899	2.371	2.387	9.28	3.21	9.82	0.485	0.530	8.88
(8) C-Si$_2$C$_2$	0.856	2.492	2.447	10.47	2.26	10.71	0.444	0.516	7.65
(9) C-SiC$_3$	0.813	2.623	2.510	11.90	1.13	11.95	0.398	0.483	6.56
(10) C-C$_4$	0.771	2.762	2.576	13.62	0	13.62	0.349	0.434	5.62

We note that this expression for C_{2i} differs from that used previously by Aspnes and Theeten[5] [Eq. (10) of Ref. 5]. Instead of $E_g(a\text{-Si:H})$ in the numerator of Eq. (8), they used a weighted average of $E_g(a\text{-Si:H})$ and E_{gi}. We believe, however, that our expression for C_{2i} is more consistent with the PVVL dielectric model,[9–11] which will now be used to determine values for E_{gi}, and hence C_{2i}, for the individual tetrahedra.

C. Dielectric model for the average energy-gap parameter E_g

The average energy-gap parameter E_g of the dielectric model of PVVL does not correspond to any particular energy gap in the band structure, but rather is an average over all the bands. As such, E_g can be calculated from the PVVL dielectric model using the following relationships which have been generalized to and are appropriate for the Si-centered tetrahedra listed in Table I (using the notation Si-Si$_{4-v}$C$_v$):

$$E_g^2 = E_H^2 + C^2 , \tag{9a}$$

$$E_H = (7.123 \text{ eV})(\langle r \rangle)^{-2.48} \tag{9b}$$

$$\langle r \rangle = (4-v)r(\text{SiSi})/4 + vr(\text{SiC})/4 , \tag{9c}$$

$$C = (14.4 \text{ eV})b \exp(-k_s \langle r \rangle) \times [Z_{\text{Si}}/r(\text{SiSi}) - \langle Z_i/r_i \rangle] , \tag{9d}$$

$$b = 0.089 N_{\text{C}}^2 , \tag{9e}$$

$$k_s = (4k_f/\pi a_b)^{1/2} , \tag{9f}$$

and

$$k_F = [3\pi^2 n(i)]^{1/3} . \tag{9g}$$

Here E_H and C are the homopolar (covalent) and heteropolar (ionic) parts of E_g. $\langle r \rangle$ is one half of the average bond length between the central (Si) atom and the four other atoms in the tetrahedron, with $r(\text{SiSi}) = d(\text{SiSi})/2 = 1.176$ Å, $r(\text{SiC}) = 0.942$ Å, and $r(\text{CC}) = 0.771$ Å. In Eq. (9d) for C, $Z_{\text{Si}} = 4$ and $Z_i = Z_{\text{Si}}$ or $Z_{\text{C}} = 4$ (as appropriate). The average $\langle Z_i/r_i \rangle$ in Eq. (9d) is taken over the four atoms surrounding the central (Si) atom in the tetrahedron, with $r_i = r(\text{SiSi})$ or $r(\text{CC})$, as appropriate. Finally, N_{C} is the average coordination number of the atoms in the crystal (equal to 4 for Si$_{1-x}$C$_x$ alloys), a_B is the Bohr radius, and $n(i)$ is the density of bonding electrons in the ith tetrahedron, given by $n(i) = 4/V_i$, where the V_i are the volumes associated with the tetrahedra and listed in Table II. Equations (9a)–(9g) are also appropriate for C-centered tetrahedra (C-Si$_{4-v}$C$_v$, $v = 0$–4), when r(SiSi) and Z_{Si} are replaced by r(CC) and Z_{C}, respectively.

Values of E_{gi} for the ten Si- and C-centered tetrahedra, along with some of the other parameters which appear in Eq. (9), are presented in Table II. We note that the expression which we use for C in Eq. (9d) above differs from that used by Aspnes and Theeten[5] [their Eq. (8c)]. The use of Eq. (9d) is necessary for silicon-carbon alloys, as noted by Levine,[11] due to a coincidental cancellation which occurs in the two terms contributing to C in Eq. (8c) of Aspnes and Theeten.[5]

In addition to the results for E_{gi} appearing in Table II, the results obtained for C_{2i} and C_{1i} from Eqs. (8) and (4) are also presented. In Eq. (8) for C_{2i}, we use E_g for the Si-Si$_4$ tetrahedron from Table II in place of $E_g(a\text{-Si:H})$. In Eq. (4) we set $n(i) = 4/V_i$ as mentioned above and $n(a\text{-Si:H}) = 4/20.02$ Å^3 where 20.02 Å^3 is the volume of the Si-Si$_4$ tetrahedron from Table II. We note that $n(a\text{-Si:H})$ can alternatively be equated to the actual value of n determined for the particular a-Si:H sample used for scaling. Note that C_{1i} and C_{2i} for the Si-C$_4$ and C-Si$_4$ tetrahedra listed in Table II are identical, indicating that these two tetrahedra have the same dielectric response, as expected.

III. TETRAHEDRON MODEL—PREDICTIONS

Making use of the values of C_{1i} and C_{2i} for the individual tetrahedra listed in Table II and measured dielectric function data[12] for a-Si:H, $\epsilon_{a\text{-Si:H}}$, we have used Eq. (2) to generate scaled ϵ_i spectra for the Si- and C-centered tetrahedra. These are displayed in Figs. 4 and 5 where ϵ_{1i} and ϵ_{2i} are shown as functions of energy from 0 to 6 eV. As stated above, the values of ϵ_{1i} and ϵ_{2i} shown for the Si-Si$_4$ tetrahedron in Figs. 4 and 5 correspond to the measured values of $\epsilon_{a\text{-Si:H}}$ for a-Si:H. The results[12] which we have used for $\epsilon_{a\text{-Si:H}}$ in the range 1.5–6 eV have been ex-

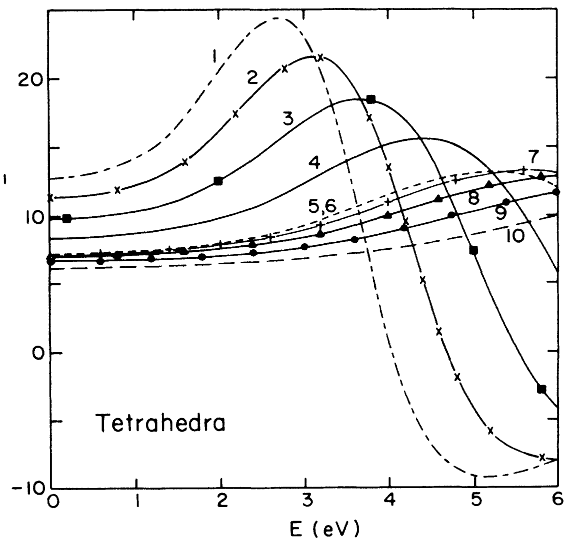

FIG. 4. Real part ϵ_1 of the dielectric function vs energy E for Si- and C-centered tetrahedra, obtained by scaling from amorphous silicon (see text). See Table I or II for numbering of the tetrahedra.

trapolated down to 0 eV using the single oscillator expression for $\epsilon(E)$, see Eq. (A14) of Ref. 14.

It can be seen from Figs. 4 and 5 that the predicted maxima in ϵ_{1i} and ϵ_{2i} decrease in magnitude and shift to higher energies as Si—Si bonds are replaced in the Si-centered tetrahedra by stronger Si—C bonds. The ϵ_{1i} and ϵ_{2i} spectra for the Si-C_4 and C-Si_4 tetrahedra are identical, as expected, and represent the dielectric constant of chemically ordered stoichiometric amorphous silicon carbide, a-$Si_{0.5}C_{0.5}$:H.

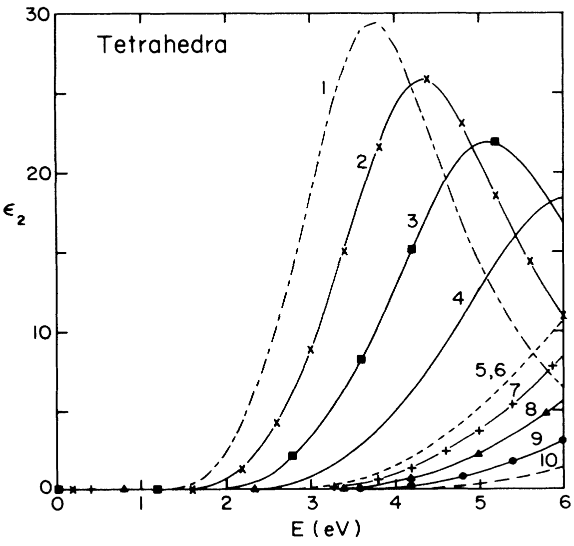

FIG. 5. Imaginary part ϵ_2 of the dielectric function vs energy E for Si- and C-centered tetrahedra, obtained by scaling from amorphous silicon (see text). See Table I or II for numbering of the tetrahedra.

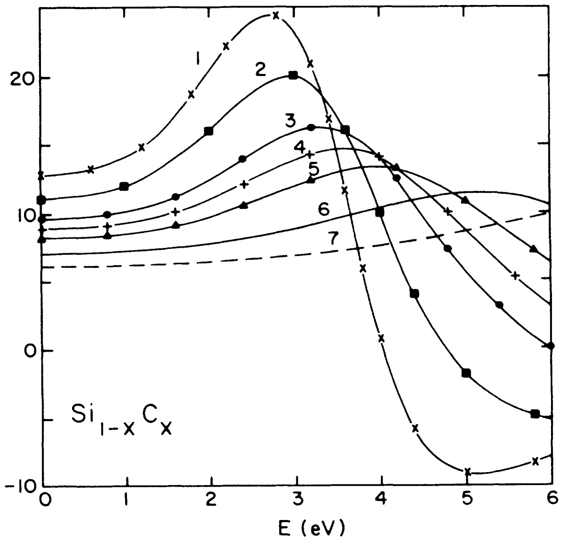

FIG. 6. Real part ϵ_1 of the dielectric function versus energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of no chemical ordering (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

As Si—C bonds are, in turn, replaced by C—C bonds in the C-centered tetrahedra, the ϵ_{1i} and ϵ_{2i} spectra continue to shift to higher energies, although not as rapidly as when Si—Si bonds were replaced by Si—C bonds in the Si-centered tetrahedra. Finally, for the C-C_4 tetrahedron, representing tetrahedrally coordinated amorphous diamond, little dispersion in ϵ_1 or absorption corresponding to ϵ_2 are observed up to 6 eV.

ϵ_1 and ϵ_2 spectra for a-$Si_{1-x}C_x$:H alloys will now be generated by using the Si- and C-centered tetrahedra as

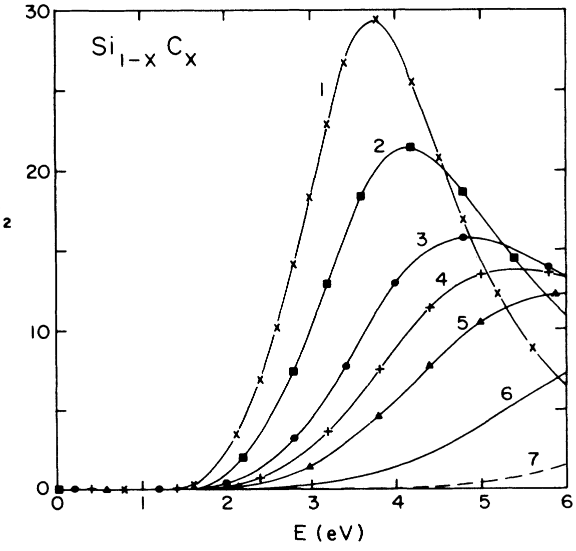

FIG. 7. Imaginary part ϵ_2 of the dielectric function vs energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of no chemical ordering (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

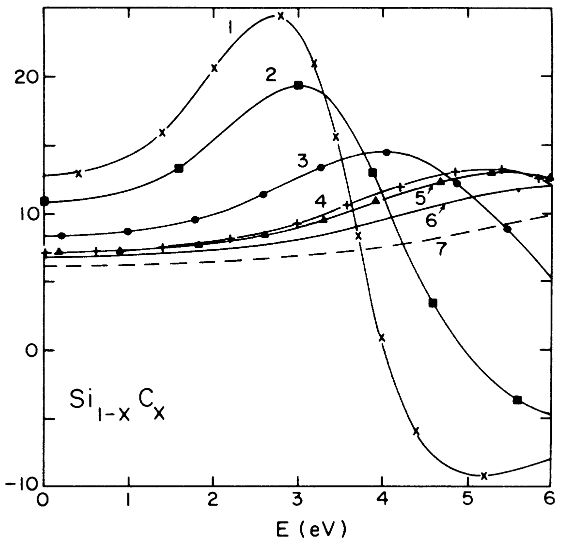

FIG. 8. Real part ϵ_1 of the dielectric function vs energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of complete chemical ordering with homogeneous dispersion (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

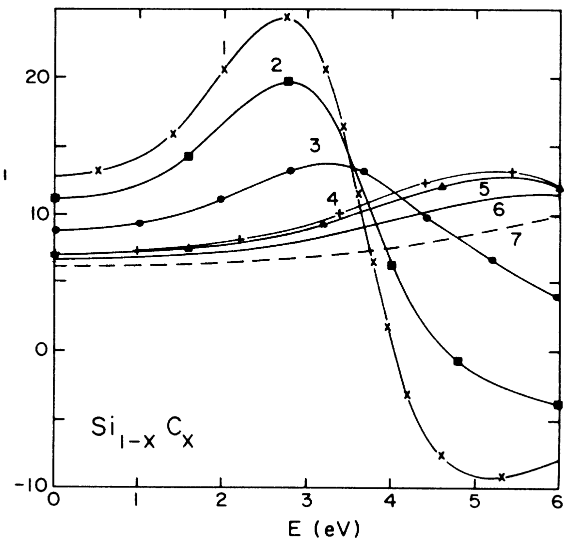

FIG. 10. Real part ϵ_1 of the dielectric function vs energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of complete chemical ordering with phase separation (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

the components in the EMA as expressed by Eq. (1). The procedure for obtaining ϵ_1 and ϵ_2 for a given composition x involves (1) choosing which type of chemical ordering is to be considered, (2) calculating the appropriate probabilities $P_i(x)$ from Table I, (3) calculating the volume fractions $v_i(x)$ for each tetrahedron according to

$$v_i(x)=P_i(x)V_i/\sum P_i(x)V_i \ ,$$

where the V_i are the tetrahedron volumes listed in Table II and the sum in the denominator is over all the possible tetrahedra, and (4) substituting the $v_i(x)$ from above and the appropriate ϵ_{1i} and ϵ_{2i} from Figs. 4 and 5 into Eq. (1)

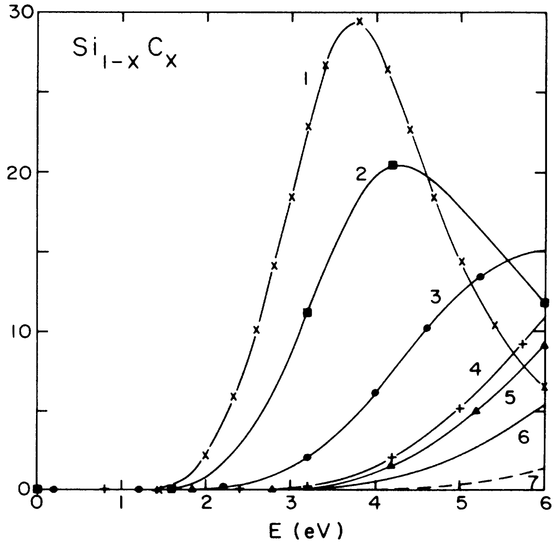

FIG. 9. Imaginary part ϵ_2 of the dielectric function vs energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of complete chemical ordering with homogeneous dispersion (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

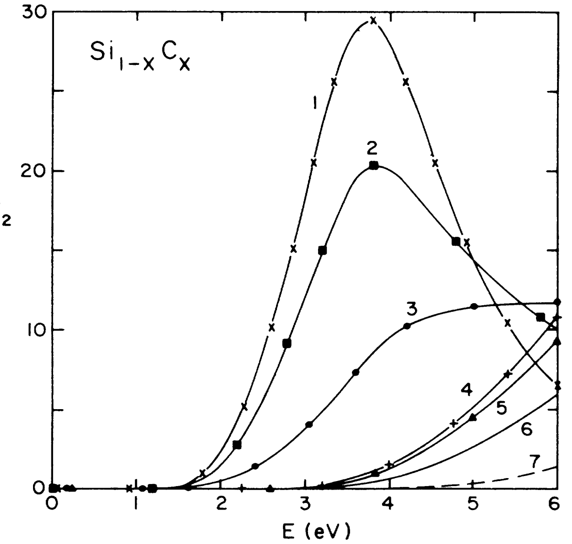

FIG. 11. Imaginary part ϵ_2 of the dielectric function vs energy E for $Si_{1-x}C_x$ alloys, obtained using the EMA for the case of complete chemical ordering with phase separation (see text). Curve 1: $x=0.0$; 2: $x=0.2$; 3: $x=0.4$; 4: $x=0.5$; 5: $x=0.6$; 6: $x=0.8$; 7: $x=1.0$.

and solving for the resulting ϵ_1 and ϵ_2 corresponding to the alloy of composition x. We note that we have not considered voids as a possible component of the alloys at this point. In any real alloy film, however, the presence of voids must be considered and has been so in the following paper[3] where experimental results for ϵ_1 and ϵ_2 for a-$Si_{1-x}C_x$:H films are presented.

Predictions for ϵ_1 and ϵ_2 for the alloy compositions $x=0$, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 and for the three types of chemical ordering considered (no chemical ordering, complete chemical ordering with homogeneous dispersion, and complete chemical ordering with phase separation) as obtained using the above procedure are shown in Figs. 6–11. Considering first the case of no chemical ordering (Figs. 6 and 7), we see that the ϵ_1 and ϵ_2 spectra for this case evolve smoothly with increasing x, reflecting the fact that the tetrahedron probabilities P_i vary smoothly across the entire composition range from $x=0$ to 1 (see Fig. 1). For the two kinds of complete chemical ordering considered (Figs. 8–11), however, ϵ_1 and ϵ_2 evolve much more rapidly for $x<0.5$ (Si-rich alloys) than for $x>0.5$. This is due to the fact that for complete chemical ordering, the probabilities P_i for Si-centered tetrahedra all must equal zero for $x>0.5$ (except for Si-C_4), while for C-centered tetrahedra the P_i must all equal zero for $x<0.5$ (except for C-Si_4). The more rapid variation of ϵ_1 and ϵ_2 for $x<0.5$ for complete chemical ordering is thus directly due to the fact that the weaker Si—Si bonds in Si-centered tetrahedra, which absorb at lower energies that either Si—C or C—C bonds, fall from 100% of the bonds in the film for $x=0$ to 0% as x increases to 0.5.

The main differences between the ϵ_1 and ϵ_2 spectra for the cases of complete chemical ordering with homogeneous dispersion and with phase separation appear to occur for Si-rich alloys with compositions in the range $x=0.2$–0.4. We note that these two types of chemical ordering must yield identical ϵ_1 and ϵ_2 spectra for $x=0.5$, where only Si-C_4 and C-Si_4 tetrahedra are present in the films. Figures 8–11 also serve to indicate that bonds alone (i.e., Si—Si, Si—C, and C—C bonds) are not the proper structural units determining the optical response of the alloys since, although the two forms of complete chemical ordering considered (homogeneous dispersion and phase separation) correspond to the same fractions of Si—Si, Si—C, and C—C bonds present in the alloys, the distribution of these bonds in the tetrahedra is very different. This leads to the different predictions for ϵ_1 and ϵ_2 for these two forms of complete chemical ordering.

The tetrahedron model as developed above can also be employed to obtain predictions for the optical energy gap parameter E_{opt} defined by[15]

$$\epsilon_2(E)=B(E-E_{\text{opt}})^2/E^2 \ , \tag{10}$$

where B is a constant. We have fitted our predicted results for ϵ_2 from Figs. 7, 9, and 11 to the above expression and have obtained the values of E_{opt} shown in Fig. 12 as a function of composition x for the three types of chemical ordering considered. We note that where necessary, particularly for C-centered tetrahedra, predicted values for ϵ_2 have been obtained for energies well above 6 eV in order to reach the energy region where Eq. (10) is applicable.

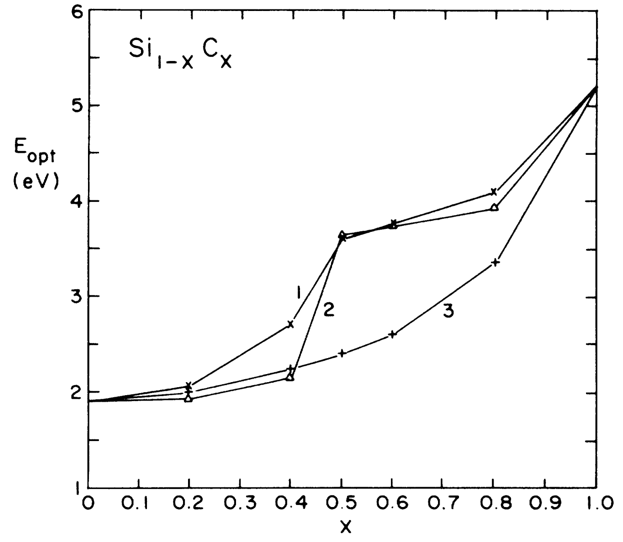

FIG. 12. Optical energy gap E_{opt} vs carbon fraction x for disordered $Si_{1-x}C_x$ alloys as predicted by the EMA (see text). Curve 1: prediction for the complete chemical ordering with homogeneous dispersion; curve 2: complete chemical ordering with phase separation; curve 3: no chemical ordering.

It is clear from Fig. (12) that the three types of chemical ordering yield significantly different predictions for E_{opt}. For the case of no chemical ordering, E_{opt} increases smoothly as a function of x, from 1.9 eV for amorphous silicon ($x=0$) to 5.2 eV for amorphous carbon ($x=1$). This smooth variation of E_{opt} with x reflects the smooth variations in the predicted values of ϵ_1 and ϵ_2 for this case as displayed in Figs. 6 and 7. For the two cases of chemical ordering considered, E_{opt} initially increases more rapidly with x, reaching the value of 3.6 eV at $x=0.5$, which is thus the prediction of the model for chemically ordered amorphous silicon carbide. At this composition ($x=0.5$), only Si-C_4 and C-Si_4 tetrahedra are present in the films and homogeneous dispersion and phase separation yield identical predictions. At $x=1$ all three predictions coincide, as expected, and yield a value of 5.2 eV for E_{opt}. That such a value has not yet been observed for amorphous carbon films is due to the presence of non-tetrahedrally-coordinated carbon, i.e., a graphitic component, in the films prepared so far.[16] Such a graphitic component has been included in the analysis of our measured ϵ_1 and ϵ_2 spectra obtained for a series of a-$Si_{1-x}C_x$:H alloy films and presented in the following paper.[3]

IV. CONCLUSIONS

We have developed a Si- and C-centered tetrahedron model for the determination of the dielectric function of disordered silicon-carbon alloys. This model has been shown to provide a useful formalism for calculating ϵ_1 and ϵ_2 for such alloys as functions of composition x and different types of chemical ordering. In addition, the model has been used to predict the behavior of the optical energy gap as a function of the above variables. The predictions of this model are compared with experimental results for ϵ_1, ϵ_2, and E_{opt} for a series of a-Si$_{1-x}$C$_x$:H alloys in the following paper.[3]

ACKNOWLEDGMENTS

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[1] Y. Tawada, H. Okamoto, and Y. Hamakawa, Appl. Phys. Lett. **39**, 237 (1981); Y. Tawada, K. Tsuge, M. Kondo, H. Okamoto, and Y. Hamakawa, J. Appl. Phys. **53**, 5273 (1982).

[2] D. R. McKenzie, N. Savvides, D. R. Mills, R. C. McPhedran, and L. C. Botten, Solar Energy Mater. **9**, 113 (1983).

[3] K. Mui, D. K. Basa, F. W. Smith, and R. Corderman, following paper, Phys. Rev. B **35**, 8089 (1987).

[4] H. R. Philipp, J. Phys. Chem. Solids **32**, 1935 (1971); J. Electrochem. Soc. **120**, 295 (1973).

[5] D. E. Aspnes and J. B. Theeten, J. Appl. Phys. **50**, 4928 (1979).

[6] D. A. G. Bruggemann, Ann. Phys. (Leipzig) **24**, 636 (1935).

[7] G. Lucovsky, Solid State Commun. **29**, 571 (1979).

[8] R. Kärcher, L. Ley, and R. L. Johnson, Phys. Rev. B **30**, 1896 (1984).

[9] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968); Rev. Mod. Phys. **42**, 317 (1970).

[10] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969); **187**, 1007 (1969).

[11] B. F. Levine, J. Chem. Phys. **59**, 1463 (1973).

[12] D. E. Aspnes, A. S. Studna, and E. Kinsbron, Phys. Rev. B **29**, 768 (1984).

[13] D. Penn, Phys. Rev. **128**, 2093 (1962).

[14] S. H. Wemple, J. Chem. Phys. **67**, 2151 (1977).

[15] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi **15**, 627 (1966).

[16] F. W. Smith, J. Appl. Phys. **55**, 764 (1984).