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Atomic bonding in amorphous hydrogenated silicon carbide alloys: A statistical thermodynamic approach

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The free-energy model (FEM) previously developed for predicting the bonding in amorphous covalent alloys has been extended to include tetrahedra, the fundamental structural units in the a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys under consideration. It is proven that the tetrahedron probabilities $P(i)$ can be obtained by randomly distributing, according to statistics, the bonds predicted by the FEM among the possible Si- and C-centered tetrahedra. The short-range order present in these alloys therefore corresponds, in general, to partial chemical ordering (CO) with a homogeneous dispersion of the bonds among the available tetrahedra. The nature of the CO predicted for these a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys is shown to vary with alloy composition. For example, Si-C bonds are favored over Si-Si and C-C bonds in stoichiometric alloys, Si-Si and C-H bonds are favored over Si-C and Si-H bonds in Si-rich alloys, while Si-C and C-H bonds are favored over C-C and Si-H bonds in C-rich alloys. Detailed predictions are presented for the bond fractions, tetrahedron probabilities, and tetrahedral and polymeric volume fractions in a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys and also in a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys with both high H content and lower H content. In the high-H-content alloys, C is predicted to be present primarily in CH_2 and CH_3 units, in good agreement with experiment, and a significant polymeric component is predicted to be present. In the lower-H-content alloys, on the other hand, more Si-C bonds and a smaller polymeric component are predicted. It is therefore demonstrated that the H content plays a dominant role in controlling the optical and electronic properties of these technologically important alloys. The simplest way of improving the usefulness of these alloys is to lower the H content, thereby promoting the random bonding of C and H atoms in the amorphous Si network.

I. INTRODUCTION

The most fundamental questions that can be asked concerning the properties of amorphous covalent alloys are related to their structure. Once the composition of an amorphous alloy such as hydrogenated silicon carbide, a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$, is known, it is natural to ask what atomic bonds are present and what are the resulting bond fractions, e.g., how many Si-C bonds are there, on the average, per Si or C atom. Once the bond fractions are known, one can then ask how the bonds are distributed among the fundamental structural units, namely the Si- and C-centered tetrahedra.[1] These questions concern the short-range order present in the alloy and their answers can be discussed in terms of the tendency for the structural properties of the alloy to be dominated by chemical ordering. In this paper the free-energy model (FEM) previously developed[2] for predicting the bond fractions in amorphous covalent alloys will be extended and applied to a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys. It will be shown that the predictions of this model for the bond fractions can be used to directly obtain the probabilities for the 30 possible Si- and C-centered tetrahedra present in these alloys simply by distributing the predicted bonds randomly among the possible tetrahedra. C-$\mathrm{Si}_2\mathrm{H}_2$ and C-SiH_3, for example, are the only two C-centered tetrahedra predicted to be present in Si-rich alloys with high H-content (defined below in Sec. II B). These two tetrahedra correspond to the CH_2 and CH_3 bonding units, respectively, which have been found from experiment to control the optoelectronic response of the technologically important Si-rich a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys which are widely used as p-type window layers in amorphous Si solar cells.[3]

This paper is organized as follows. Chemical ordering and random bonding in amorphous covalent alloys are defined in Sec. II, which also summarizes previous relevant results on the bonding in a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys. The FEM for bonds is presented in Sec. III, while the FEM for tetrahedra is developed in Sec. IV. The predictions of these two different versions of the FEM are also presented in Secs. III and IV and are discussed and compared with relevant experimental results in Sec. V. Finally, conclusions are presented in Sec. VI.

II. BACKGROUND

While amorphous covalent network alloys such as a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ are characterized by the absence of long-range order, they can possess a considerable degree of short-range order (SRO). This SRO is often referred to as chemical ordering (CO). In a previous study[1] of amorphous silicon-carbon alloys we have identified and described in detail three limiting forms of local atomic bonding which are in principle possible in these alloys, namely (1) random bonding, (2) chemical ordering with homogeneous dispersion (COHD), and (3) chemical ordering with phase separation (COPS). In addition, it has been shown[1,4] that Si- and C-centered tetrahedra, as opposed simply to Si-Si, Si-C, and C-C bonds, are the fundamental structural units which determine the optical response of these alloy films. The present study establishes the fact that it is possible to predict the form of local atomic bonding in a given alloy using the basic principles of statistical thermodynamics. It will be shown that CO corresponds to the local atomic bonding which minimizes the enthalpy of mixing H_M of the alloy in question, while random bonding corresponds to the local atomic bonding which maximizes the entropy of mixing S_M. In any given alloy, however, the actual atomic bonding present will correspond in general neither to perfect CO nor to completely random bonding, but will be that which minimizes the free energy of mixing, $G_M = H_M - TS_M$. This will be shown to correspond to partial COHD below.

The degree of CO present in a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys remains the most important outstanding question, both experimentally and theoretically. This has been emphasized in recent reviews[5,6] of amorphous silicon-carbon alloys. In Si-rich alloys with high H content early ir absorption studies[7] and subsequent studies[8] have clearly indicated that C atoms are almost exclusively incorporated into the network in the form of CH_2 and CH_3 bonding units, with the result that most of the H atoms are bonded to C atoms. It is clear from this observation that there must be a strong tendency for CO in these Si-rich alloys since if the H atoms were randomly bonded, most of them would be bonded to Si, not C. This will be discussed further in Sec. III B below. As a result of the dominance of CH_2 and CH_3 units, the C atoms are only weakly incorporated into the amorphous Si network and, as a result, tend to reside in a distinct polymeric phase. The presence of the network-terminating CH_3 units and the bridging CH_2 units thus leads to a microstructure consisting of microvoids and clustered hydrogen, with an increased defect density. These Si-rich a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys with high H content therefore have poorer optoelectronic properties than do high-quality a-$\mathrm{Si}_x\mathrm{H}_y$ alloys. To improve the usefulness of the Si-rich alloys it would therefore be desirable to promote the random bonding of C and H atoms within the amorphous Si network. It will be shown that the simplest way of achieving this is to lower the H content in the alloy.

In near-stoichiometric hydrogen-free a-$\mathrm{Si}_x\mathrm{C}_y$ alloys, early Raman studies[9] indicated that CO was not complete as evidence for like-atom bonds was found. Our previous experimental study[4] of the optical constants of a series of a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ films led us to propose that the films are macroscopically homogeneous while having a heterogeneous microstructure consisting of four components: (1) amorphous polymeric, (2) amorphous graphitic, (3) amorphous tetrahedral, and (4) void. The analysis of the results of these optical measurements provided evidence that COHD dominated in the amorphous tetrahedral component across the entire alloy series. From the results of a wide range of experimental studies[5,6] of the bonding in a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys it can be concluded that CO is in general not perfect and that the degree of CO depends sensitively on the deposition conditions. The issue of CO in C-rich alloys is far from simple or clear due to the additional complication[4] of the bonding of C atoms in both tetrahedral and trigonal or graphitic configurations.

III. FREE-ENERGY MODEL FOR BONDS

The FEM for predicting the bond fractions in amorphous covalent alloys has been developed in detail previously for the case of a-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloys,[2] where it has been shown that CO favors Si-N and Si-H bonds at the expense of Si-Si and N-H bonds. It has also been found that the predictions of the FEM are in good agreement with experimentally determined bond fractions in a-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloys. The FEM for bonds has also been outlined[10] for a-$\mathrm{Si}_x\mathrm{N}_y$, a-$\mathrm{Si}_x\mathrm{O}_y\mathrm{H}_z$, a-$\mathrm{Si}_w\mathrm{N}_x\mathrm{O}_y\mathrm{H}_z$, a-$\mathrm{Si}_x\mathrm{C}_y$, and a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys.

The FEM includes chemical bonding effects in the enthalpy and effects related to the statistics of bonding within local structural units, Si- and C-centered tetrahedra in this case, in the entropy. Although these alloys are clearly not in a state corresponding to thermodynamic equilibrium, the approach taken here is to determine the state of the amorphous alloy which has the lowest free energy. The FEM may be expected to be valid whenever good "atomic mixing" occurs at the surface of the growing film. This should be the case for plasma-enhanced chemical vapor deposition, for example, when all of the reactants are sufficiently excited.

There are five possible bonds in a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys, namely Si-Si, Si-C, C-C, Si-H, and C-H, where the single bond energies $E(X\text{-}Y)$ between atoms X and Y are listed in Table I. These bond energies have been calculated using standard thermodynamic heats of formation for the appropriate species,[11] except for E(C-H)= 4.60 eV, which instead has been determined as described below in Sec. III B. For simplicity, these bond energies are initially assumed to be independent of their local chemical and physical environment in the alloy.[12]

In an alloy of fixed composition $(x+y+z=1)$, the three possible reactions involving these five bonds can be expressed by the following bond reaction equations (BRE's):

$$\text{Si-Si} + \text{C-C} \leftrightarrow 2\text{Si-C} \ , \tag{1}$$

$$\text{Si-C} + \text{Si-H} \leftrightarrow \text{Si-Si} + \text{C-H} \ , \tag{2}$$

$$\text{C-C} + \text{Si-H} \leftrightarrow \text{Si-C} + \text{C-H} \ . \tag{3}$$

All three BRE's as written are exothermic in the forward direction, respectively, by

$$\Omega_1 = 2E(\text{Si-C}) - E(\text{Si-Si}) - E(\text{C-C}) = +0.38 \text{ eV} \ , \tag{4}$$

TABLE I. Atom and bond energies used in the FEM.

Atom[a]	H_0 (eV)	Bond	$E(X-Y)$ (eV)
Si (4)	4.68	Si-Si	2.34
C (4)	7.40	Si-C	3.21
H (1)	2.27	C-C	3.70
		Si-H	3.34
		C-H	4.60
		(Ge-Ge)	(1.95)
		(Ge-C)	(2.74)

[a] The assumed valence (8-N rule) is given in parentheses.

$$\Omega_2 = E(\text{Si-Si}) + E(\text{C-H}) - E(\text{Si-C}) - E(\text{Si-H}) = +0.39\ \text{eV}\ , \tag{5}$$

$$\Omega_3 = E(\text{Si-C}) + E(\text{C-H}) - E(\text{C-C}) - E(\text{Si-H}) = +0.77\ \text{eV}\ . \tag{6}$$

Given the uncertainties in the bond energies, these values for the interaction parameters Ω_i should be considered to be only first approximations. It should also be noted that only two of the three BRE's are independent, and that $\Omega_3 = \Omega_1 + \Omega_2$. These BRE's are very useful as they indicate which bonds are favored by CO. For example, Eq. (1) with $\Omega_1 = +0.38$ eV indicates that Si-C bonds are favored by CO in near-stoichiometric a-Si$_x$C$_y$ alloys, Eq. (2) with $\Omega_2 = +0.39$ eV indicates that Si-Si and C-H bonds are favored by CO over Si-C and Si-H bonds in Si-rich alloys, while Eq. (3) with $\Omega_3 = +0.77$ eV shows that Si-C and C-H bonds are favored by CO over C-C and Si-H bonds in C-rich alloys. It is important to emphasize that Si-C bonds are not favored by CO in Si-rich alloys. The tendency for CO to actually dominate the bonding in these alloys is related to the magnitude of the interaction parameter Ω_i for the BRE in question. This statement will be made more quantitative below.

The FEM as developed here is based on the pair approximation and thus is related to the quasichemical approach to the thermodynamics of regular solutions. The enthalpy of mixing is given by $H_M = E_{\text{atoms}} - E_{\text{bonds}}$, where E_{atoms} is the sum of the energies of the isolated atoms and E_{bonds} is the sum of the energies of the nearest-neighbor bonds in the alloy. Note that exothermic mixing ($E_{\text{bonds}} > E_{\text{atoms}}$) corresponds to $H_M < 0$. We assume initially that the network is fully coordinated, with no defects such as broken bonds, and that Si and C atoms have their normal chemical valence of 4 (given by the 8-N rule). In terms of the atom concentrations $N(X)$, the bond concentrations $N(X\text{-}Y)$, the bond energies $E(X\text{-}Y)$, and the atom heats of formation $H_0(X)$, we can write

$$E_{\text{atoms}} = N(\text{Si})H_0(\text{Si}) + N(\text{C})H_0(\text{C}) + N(\text{H})H_0(\text{H})\ , \tag{7}$$

$$E_{\text{bonds}} = N(\text{Si-Si})E(\text{Si-Si}) + N(\text{Si-C})E(\text{Si-C}) + N(\text{C-C})E(\text{C-C}) + N(\text{Si-H})E(\text{Si-H}) + N(\text{C-H})E(\text{C-H})\ , \tag{8}$$

where[11] $H_0(\text{Si}) = 4.68$ eV, $H_0(\text{C}) = 7.40$ eV, and $H_0(\text{H}) = 2.27$ eV (Table I).

The mixing or configurational entropy S_M is given in the FEM by $k_B \ln\Gamma$, where k_B is the Boltzmann constant and Γ is the total number of distinct bonding configurations in the system of Si- and C-centered tetrahedra. We will approximate Γ by the product $\Gamma_{\text{Si}}\Gamma_{\text{C}}$, where Γ_{Si} and Γ_{C} refer to the numbers of possible configurations in the Si- and C-centered tetrahedra, respectively. The product $\Gamma_{\text{Si}}\Gamma_{\text{C}}$ overestimates the number of distinct bonding configurations in the pair approximation, but by a factor which is a function only of the alloy composition.[13] This overestimation therefore has no effect on the minimization of the Gibbs free energy of mixing which is carried out for an alloy of given composition.

Since all four tetrahedral sites are equivalent, it follows that $\Gamma_{\text{Si}} = \Gamma_{1,\text{Si}}^4$, where $\Gamma_{1,\text{Si}}$ represents any one of the four sites. Now

$$\Gamma_{1,\text{Si}} = N(\text{Si})!/(N_{\text{Si,Si}}!\ N_{\text{C,Si}}! N_{\text{H,Si}}!)\ , \tag{9}$$

with an analogous expression for $\Gamma_{1,\text{C}}$. Here, for example, $N_{\text{C,Si}}$ is the concentration of C atoms bonded at one of the four available Si-centered tetrahedral sites. Note that the concentration of Si atoms $N(\text{Si}) = N_{\text{Si,Si}} + N_{\text{C,Si}} + N_{\text{H,Si}}$ and that $N_{\text{C,Si}} = N_{\text{Si,C}}$. It is convenient to introduce the normalized bond concentrations $n_{\text{i,Si}} = N_{\text{i,Si}}/N(\text{Si})$ and $n_{\text{i,C}} = N_{\text{i,C}}/N(\text{Si})$, with $i = $ Si,C,H. When these are used in the expressions for $\Gamma_{1,\text{Si}}$ and $\Gamma_{1,\text{C}}$, and following the application of Stirling's rule, we obtain

$$S_M = -4k_B N(\text{Si}) \left[\sum_i n_{i,\text{Si}} \ln(n_{i,\text{Si}}) + \sum_i n_{i,\text{C}} \ln(x n_{i,\text{C}}/y) \right]\ , \tag{10}$$

where $\sum_i$ is the sum over the three atoms Si, C, and H. It should be noted that the factor of four which appears in Eq. (10) is present because we are dealing with tetrahedra with four available bondings sites. This factor of four would not be present in the regular solution model where atoms simply occupy random sites on a "lattice." Using standard relationships between bond and atom concentrations, the following three constraint equations are obtained:

$$\begin{aligned} 1 &= n_{\text{C,Si}} + n_{\text{H,Si}} + n_{\text{Si,Si}}\ , \\ y/x &= n_{\text{C,Si}} + n_{\text{H,C}} + n_{\text{C,C}}\ , \\ z/x &= 4n_{\text{H,Si}} + 4n_{\text{H,C}}\ . \end{aligned} \tag{11}$$

The enthalpy of mixing per total atom H_M can be expressed, using the normalized bond concentrations $n_{\text{i,Si}}$ and $n_{\text{i,C}}$, as

$$\begin{aligned} H_M = {} & xH_0(\text{Si}) + yH_0(\text{C}) + zH_0(\text{H}) - 2xn_{\text{Si,Si}}E(\text{Si-Si}) \\ & - 4xn_{\text{C,Si}}E(\text{Si-C}) - 2xn_{\text{C,C}}E(\text{C-C}) \\ & - 4xn_{\text{H,Si}}E(\text{Si-H}) - 4xn_{\text{H,C}}E(\text{C-H})\ . \end{aligned} \tag{12}$$

The Gibbs free energy of mixing per total atom $G_M = H_M - TS_M$ can thus be expressed using Eqs. (10) and (12) as a function of the five normalized bond concentrations $n_{\text{Si,Si}}$, $n_{\text{C,Si}} = n_{\text{Si,C}}$, $n_{\text{H,Si}}$, $n_{\text{C,C}}$, and $n_{\text{H,C}}$, as well as the alloy composition x,y,z, the bond energies, and the temperature T. These normalized bond concentrations will be obtained by minimizing G_M for an alloy of given composition. Equation (11) already provides three relationships between the normalized bond concentrations and the composition so that only two more are needed. These can be obtained by setting the partial derivatives of G_M with respect to $n_{\text{Si,Si}}$ and $n_{\text{H,Si}}$ equal to 0. From $\partial G_M/\partial n_{\text{Si,Si}} = 0$, we obtain

$$n_{\text{C,Si}}^2/n_{\text{Si,Si}}n_{\text{C,C}} = \exp(\Omega_1/2k_B T)\ , \tag{13}$$

while from $\partial G_M/\partial n_{\mathrm{H,Si}}=0$ we obtain

$$(n^2_{\mathrm{C,Si}}n_{\mathrm{H,C}})/(n^2_{\mathrm{C,C}}n_{\mathrm{H,Si}})=\exp(\Omega_3/k_BT)\ . \qquad (14)$$

The predictions of the FEM for bonds will now be presented separately for hydrogen-free a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys and for a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys.

A. Predictions for a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys

For these alloys $n_{\mathrm{H,Si}}$ and $n_{\mathrm{H,C}}$ are identically zero. Combining Eqs. (11) and (13) then yields the following quadratic equation for $n_{\mathrm{Si,Si}}$, where $a=\exp(\Omega_1/2k_BT)$:

$$(a-1)n^2_{\mathrm{Si,Si}}+[a(1-x)/x-a+2]n_{\mathrm{Si,Si}}-1=0\ . \qquad (15)$$

We now examine the solutions to Eq. (15) for a range of values of $\Omega_1/2k_BT$. These results are also summarized in Table II. It should be noted that these results apply to all tetrahedrally coordinated binary amorphous alloys, including a-$\mathrm{Si}_x\mathrm{Ge}_{1-x}$ and a-$\mathrm{Ge}_x\mathrm{C}_{1-x}$, see below.

1. $\Omega_l/2k_BT=0$

Since the driving force for CO is zero, this is the limit of perfectly random bonding discussed previously.[1] Now $a=1$ and Eq. (15) simplifies to $[(1-x)/x+1]n_{\mathrm{Si,Si}}-1=0$, which yields $n_{\mathrm{Si,Si}}=N_{\mathrm{Si,Si}}/N(\mathrm{Si})=x$ and $n_{\mathrm{C,Si}}=N_{\mathrm{C,Si}}/N(\mathrm{Si})=1-x$. Finally, we have $n_{\mathrm{C,C}}=N_{\mathrm{C,C}}/N(\mathrm{Si})=(1-x)^2/x$, which corresponds to $N_{\mathrm{C,C}}/N(C)=1-x$. Also given in Table II are the total bond fractions f(Si-Si), f(Si-C), and f(C-C). This limit of random bonding is known to correspond quite well to the case of a-$\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys[14,15] since E(Si-Ge) is very close to the average of E(Si-Si) and E(Ge-Ge).

2. $\Omega_l/2k_BT\gg1$

Here the driving force for CO is strong and $a\gg1$. Equation (15) simplifies to $n_{\mathrm{Si,Si}}[n_{\mathrm{Si,Si}}+(1-2x)/x]=0$. The results for $x>\frac{1}{2}$ (Si-rich alloys) and for $x<\frac{1}{2}$ (C-rich alloys) are presented in Table II. This limit corresponds exactly to COHD discussed previously.[1]

For a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ with $\Omega_1=0.38$ eV [Eq. (4)], we obtain $a=67.76$ at a typical deposition temperature of $T=523$ K (250 °C). For the stoichiometric case of $x=1-x=\frac{1}{2}$, Eq. (15) then yields $n_{\mathrm{Si,Si}}=n_{\mathrm{C,C}}=0.108$ and $n_{\mathrm{C,Si}}=1-n_{\mathrm{Si,Si}}=0.892$. Thus, while CO clearly dominates, it is not perfect in a-$\mathrm{Si}_{0.5}\mathrm{C}_{0.5}$ as only 89% of all bonds are Si-C bonds, with about 5% each of Si-Si and C-C bonds also present (see Table II). Figure 1 shows the atom bond fractions predicted for a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ with $\Omega_1=0.38$ eV and $T=523$ K for $0<x<1$. The distribution of these bonds among the Si- and C-centered tetrahedra will be discussed below in Sec. IV.

3. $\Omega_l/2k_BT\ll0$

Now $a=0$ and Eq. (15) becomes $(n_{\mathrm{Si,Si}}-1)^2=0$. Hence $n_{\mathrm{Si,Si}}=1$, $n_{\mathrm{C,Si}}=0$, and $n_{\mathrm{C,C}}=(1-x)/x$. This is the limit of complete phase separation in which there is no atomic mixing at all. The "alloy" separates into regions of pure Si and pure C for all values of x. Note that this form of phase separation is not the same as the COPS discussed previously.[1] COPS corresponds to the existence for Si-rich alloys of phase-separated regions of pure Si and of stoichiometric SiC.

Although this limit of complete phase separation is not appropriate for a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys, it apparently does apply to a-$\mathrm{Ge}_x\mathrm{C}_{1-x}$ alloys.[14] The relevant bond energies (see Table I) are E(Ge-Ge) = 1.95 eV, E(C-C)=3.70 eV, and E(Ge-C) approximately[16] equal to 2.74 eV. With these values, $\Omega_1=2E(\text{Ge-C})-E(\text{Ge-Ge})-E(\text{C-C})=-0.17$ eV, which explains quite naturally the observed complete phase separation and lack of compound formation.[17]

B. Predictions for a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys

For plasma-deposited a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ films, an increase of the hydrocarbon fraction [e.g, $\mathrm{CH_4/(CH_4+SiH_4)}$] in the discharge leads to a steady increase in the incorporation

TABLE II. Predictions for a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys.

	$n_{\mathrm{Si,Si}}$[a]	$n_{\mathrm{C,Si}}$[b] $(=n_{\mathrm{Si,C}})$	$xn_{\mathrm{C,C}}/(1-x)$[c]	f(Si-Si)[d]	f(Si-C)[d]	f(C-C)[d]
(1) $\Omega_1/2k_bT=0$	x	$(1-x)$	$(1-x)$	x^2	$2x(1-x)$	$(1-x)^2$
(2) $\Omega_1/2k_bT\gg1$						
(a) $x>1/2$	$(2x-1)/x$	$(1-x)/x$	0	$2x-1$	$2(1-x)$	0
(b) $x<1/2$	0	1	$(1-2x)/(1-x)$	0	$2x$	$(1-2x)$
(3) $\Omega_1/2k_bT=+4.22$[e] $x=(1-x)=1/2$	0.108	0.892	0.108	0.054	0.892	0.054
(4) $\Omega_1/2k_bT\ll0$	1	0	1	x	0	$(1-x)$

[a] $n_{\mathrm{Si,Si}}=N_{\mathrm{Si,Si}}/N(\mathrm{Si})$.

[b] $n_{\mathrm{C,Si}}=N_{\mathrm{C,Si}}/N(\mathrm{Si})$.

[c] $xn_{\mathrm{C,C}}/(1-x)=N_{\mathrm{C,C}}/N(\mathrm{C})$.

[d] $f(\text{Si-Si})=xn_{\mathrm{Si,Si}}$, $f(\text{Si-C})=2xn_{\mathrm{C,Si}}$, and $f(\text{C-C})=xn_{\mathrm{C,C}}$ are the fractions of all bonds which are Si-Si, Si-C, and C-C bonds, respectively.

[e] $\Omega_1/2k_bT=+4.22$ corresponds to $\Omega_1=+0.38$ eV [see Eq. (4)] and $T=523$ K.

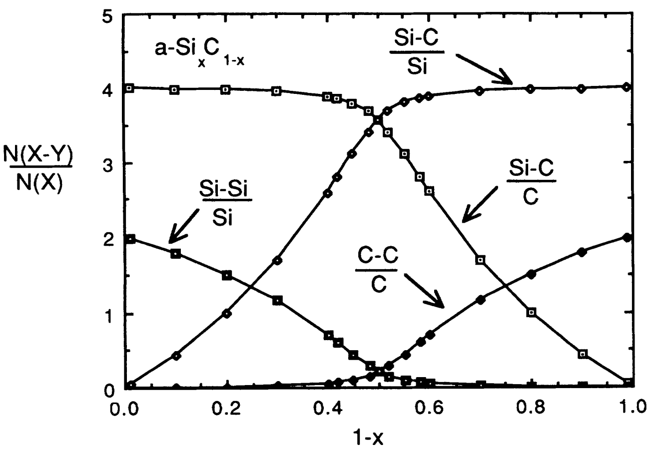

FIG. 1. Predicted atom bond fractions $N(X\text{-}Y)/N(X)$ for a-$\mathrm{Si}_x\mathrm{C}_{1-x}$ alloys vs C content $1-x$, with interaction parameter $\Omega_1=2E(\text{Si-C})\text{-}E(\text{Si-Si})\text{-}E(\text{C-C})=+0.38$ eV and $T=523$ K. The labeling of the curves indicates the average number of bonds per atom, e.g., Si-C/Si refers to Si-C bonds per Si atom.

of both C and H in the film. The dependence of the H fraction z on the C/(Si+C) ratio observed[18,19] for Si-rich alloy films with high H-content deposited, for example, from $\mathrm{CH_4/SiH_4}$ plasmas has been sumarized recently by Robertson.[6] These alloy films with high H contents correspond approximately to $z=2.5y+0.1x$, or about 2.5 H atoms per C atom and about 0.1 H atoms per Si atom. We will focus on Si-rich films for a test of the FEM for bonds since these films are technologically important and also are not as likely to be complicated by the presence of a graphitic component.[4]

As the first test of the FEM, the average number of C-H bonds per C atom $N(\text{C-H})/N(\text{C})$ has been calculated for Si-rich alloys with high H contents. When the average energy of the four C-H bonds in the $\mathrm{CH_4}$ molecule, $E(\text{C-H})=4.31$ eV, is used, the FEM predicts that $N(\text{C-H})/N(\text{C})=0.15$, instead of the two or three H atoms observed experimentally.[7,8] As $E(\text{C-H})$ is varied in the FEM, $N(\text{C-H})/N(\text{C})$ remains constant at 0.15 up to $E(\text{C-H})=4.5$ eV. It then increases steadily up to 3.0 (the maximum value allowed in the FEM) for $E(\text{C-H})=4.7$ eV. We have therefore decided to use $E(\text{C-H})=4.6$ eV, which in fact is close to the average energy required to break the first three bonds in the $\mathrm{CH_4}$ molecule.

For a typical deposition temperature of 523 K (250 °C) and using the bond energies listed in Table I, the FEM predicts the atom bond fractions given in Table III for two distinct sets of Si-rich alloys: high H content,[18,19] as defined above, and lower H content.[4] Lower H-content alloys are defined to be any alloys which have a significantly lower z, for a given $y/(x+y)$ ratio, than do the high H-content alloys. Figure 2 presents the H-content z versus the C/(Si+C) ratio $y/(x+y)$ for these two sets of alloys, as well as for some additional alloys to be discussed below. The results for the high H-content films are also presented in Fig. 3 as functions of $y/(x+y)$. It is interesting to note that the Si-rich alloy with the lowest C content, $y=0.01$, is predicted to have the lowest number of C-H bonds per C atom, 1.956. This prediction indicates that CO is not complete in very Si-rich alloys, in agreement with a recent extended-x-ray-absorption fine-structure (EXAFS) study.[20] We have shown[21] that the SRO parameter σ drops from 1 to about 0.8 as y approaches 0. As y increases to 0.07, CO begins to dominate, with $N(\text{C-H})/N(\text{C})$ quickly reaching a value of 3.0.

It is clear from Table III and Fig. 3 that essentially all of the C and H atoms incorporated in the high H-content Si-rich films are predicted to enter as $\mathrm{CH_3}$ units, in very good agreement with the observation[8] that films with high H contents can be called "methylated amorphous silicon," a-$\mathrm{Si}_x(\mathrm{CH_3})_{1-x}$:H. For such films only a single Si-C bond per C atom is predicted. As a result, the Si-Si atom bond fraction is not significantly affected by alloying with C and the films can be expected to be similar to a-$\mathrm{Si}_x\mathrm{H}_z$ in their optical and electronic properties. It is interesting to note that $N(\text{Si-H})/N(\text{Si})$ remains almost constant at a value of about 0.11 from $y=0$ (a-$\mathrm{Si_{0.88}H_{0.12}}$) up to a-$\mathrm{Si_{0.36}C_{0.15}H_{0.49}}$ for these high H-content alloys.

In contrast to the high H-content Si-rich alloy films, films with much lower H contents have been deposited[4] from $\mathrm{C_2H_2/SiH_4}$ plasmas. The predicted atom bond fractions for three such films are also given in Table III

TABLE III. Predicted atom bond fractions $N(X-Y)/N(X)$ for Si-rich a-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$ alloys ($T=523$ K).

	High H content[a]							Lower H content[b]		
x	0.88	0.87	0.65	0.47	0.36	0.29	0.235	0.77	0.65	0.55
y	0	0.01	0.07	0.12	0.15	0.20	0.235	0.14	0.25	0.33
z	0.12	0.12	0.28	0.41	0.49	0.51	0.53	0.09	0.10	0.12
$y/(x+y)$	0	0.011	0.097	0.203	0.294	0.408	0.500	0.154	0.278	0.375
N(Si-Si)/N(Si)	1.932	1.931	1.893	1.819	1.736	1.498	1.137	1.695	1.313	0.927
N(Si-C)/N(Si)	0	0.024	0.107	0.255	0.417	1.000	1.726	0.609	1.374	2.145
N(Si-H)/N(Si)	0.136	0.115	0.108	0.106	0.111	0.004	0.000	0.000	0.000	0.000
N(C-C)/N(C)		0.015	0.004	0.000	0.000	0.003	0.009	0.003	0.013	0.031
N(Si-C)/N(C)		2.041	0.992	1.000	1.000	1.450	1.726	3.350	3.573	3.575
N(C-H)/N(C)		1.956	3.000	3.000	3.000	2.544	2.255	0.643	0.400	0.364

[a] These compositions correspond to Si-rich films deposited from $\mathrm{CH_4/SiH_4}$ plasmas (Refs. 18 and 19; also see Fig. 7 of Ref. 6).

[b] These compositions correspond to Si-rich films deposited from $\mathrm{C_2H_2/SiH_4}$ plasmas (Ref. 4).

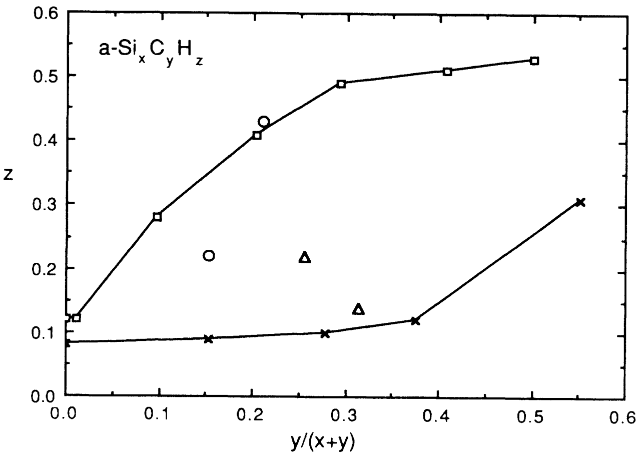

FIG. 2. Hydrogen content z vs the C/(Si+C) ratio $y/(x+y)$, as measured for Si-rich a-Si$_x$C$_y$H$_z$ alloys. Upper curve, high H-content alloys, Refs. 18 and 19; lower curve, lower H-content alloys, Ref. 4; circles, Ref. 25; triangles, Ref. 3.

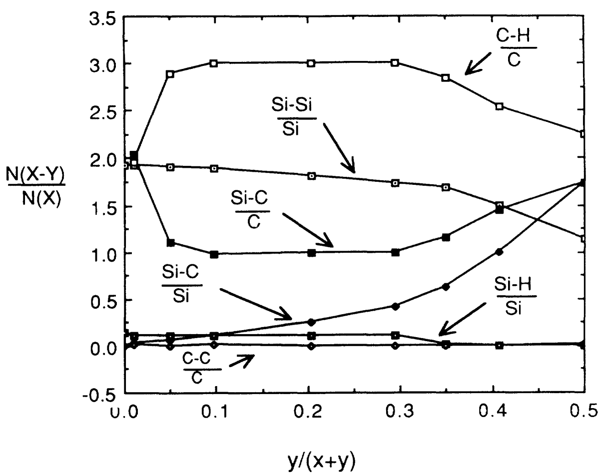

FIG. 3. Predicted atom bond fractions $N(X-Y)/N(X)$ for high H-content Si-rich a-Si$_x$C$_y$H$_z$ alloys (see upper curve in Fig. 2) vs the C/(Si+C) ratio $y/(x+y)$, at $T=523$ K. The labeling of the curves indicates the average number of bonds per atom, e.g., Si-C/Si refers to Si-C bonds per Si atoms.

and it is apparent that the bonding is quite different from that found in high H-content films. In particular, much higher fractions of Si-C bonds per Si atom and per C atom are predicted and, correspondingly, the fraction of Si-Si bonds is predicted to be much lower. As a result, for a given $y/(x+y)$ ratio, these lower H-content films can be expected to have properties corresponding to a random silicon-carbon alloy.

The question of how these predicted bonds are distributed among the possible Si- and C-centered tetrahedra in the alloy will now be addressed. Comparisons with experiment will follow in Sec. V.

IV. FREE-ENERGY MODEL FOR TETRAHEDRA

In order to completely specify the SRO present in these amorphous covalent alloys it is necessary to predict how the bonds will be distributed among the Si- and C-centered tetrahedra. In general there is no unique answer to this question. Our approach will be to reformulate the FEM for bonds by explicitly using tetrahedron probabilities to define the possible configurations in the entropy of mixing S_M. This approach will first be developed for a-Si$_x$C$_{1-x}$ alloys.

A. Predictions for a-Si$_x$C$_{1-x}$ alloys

There are ten possible tetrahedra in these alloys, namely Si-Si$_{4-n}$C$_n$ and C-Si$_{4-n}$C$_n$ with $n=0-4$, as discussed previously.[1] These ten tetrahedra ($i=1-10$) are listed in Table IV, where the number of possible distinct arrangements of bonds within each tetrahedron is included in the corresponding tetrahedron probability $P(i)$. For example, there are six distinct ways in which two Si and two C atoms can bond to the four available sites in the Si-Si$_2$C$_2$ tetrahedron. There has been disagreement recently[1,22]

TABLE IV. Tetrahedra and tetrahedron probabilities $P(i)$ in a-Si$_x$C$_{1-x}$ alloys.

				$P(i)$			
i	Tetrahedron	$\Omega_1/2k_bT=0$	$\Omega_1/2k_bT>>1$ $x>\frac{1}{2}$	$\Omega_1/2k_bT>>1$ $x<\frac{1}{2}$	$\Omega_1/2k_bT<<0$	$\Omega_1/2k_bT=4.22$[a]	for all $\Omega_1/2k_bT$[b]
1	Si-Si$_4$	x^5	$(2x-1)^4/x^3$	0	x	0.000 07	$xf^4_{\rm Si}({\rm Si})$
2	Si-Si$_3$C	$4x^4(1-x)$	$4(2x-1)^3(1-x)/x^3$	0	0	0.002	$4xf^3_{\rm Si}({\rm Si})f_{\rm Si}({\rm C})$
3	Si-Si$_2$C$_2$	$6x^3(1-x)^2$	$6(2x-1)^2(1-x)^2/x^3$	0	0	0.028	$6xf^2_{\rm Si}({\rm Si})f^2_{\rm Si}({\rm C})$
4	Si-SiC$_3$	$4x^2(1-x)^3$	$4(2x-1)(1-x)^3/x^3$	0	0	0.154	$4xf_{\rm Si}({\rm Si})f^3_{\rm Si}({\rm C})$
5	Si-C$_4$	$x(1-x)^4$	$(1-x)^4/x^3$	x	0	0.316	$xf^4_{\rm Si}({\rm C})$
6	C-Si$_4$	$x^4(1-x)$	$(1-x)$	$x^4/(1-x)^3$	0	0.316	$(1-x)f^4_{\rm C}({\rm Si})$
7	C-Si$_3$C	$4x^3(1-x)^2$	0	$4x^3(1-2x)/(1-x)^3$	0	0.154	$4(1-x)f^3_{\rm C}({\rm Si})f_{\rm C}({\rm C})$
8	C-Si$_2$C$_2$	$6x^2(1-x)^3$	0	$6x^2(1-2x)^2/(1-x)^3$	0	0.028	$6(1-x)f^2_{\rm C}({\rm Si})f^2_{\rm C}(C)$
9	C-SiC$_3$	$4x(1-x)^4$	0	$4x(1-2x)^3/(1-x)^3$	0	0.002	$4(1-x)f_{\rm C}({\rm Si})f^3_{\rm C}({\rm C})$
10	C-C$_4$	$(1-x)^5$	0	$(1-2x)^4/(1-x)^3$	$(1-x)$	0.000 07	$(1-x)f^4_{\rm C}({\rm C})$

[a] $P(i)$ for stoichiometric a-Si$_x$C$_{1-x}$, $x=(1-x)=\frac{1}{2}$, with $\Omega_1=+0.38$ eV [see Eq. (4)] at $T=523$ K.

[b] Here $f_{\rm Si}({\rm Si})=n_{\rm Si,Si}, f_{\rm Si}({\rm C})=n_{\rm C,Si}$, $f_{\rm C}({\rm Si})=xn_{\rm Si,C}/(1-x)$, and $f_{\rm C}({\rm C})=xn_{\rm C,C}/(1-x)$, where $n_{\rm Si,Si}, n_{\rm C,Si}=n_{\rm Si,C}$, and $n_{\rm C,C}$ are given in Table II.

over the question of whether or not it is necessary to include all of these distinct arrangements of the bonds within tetrahedra when determining the number of allowed configurations needed to obtain the entropy S_M. We have shown that it is in fact necessary, with the proof of this assertion for a square lattice presented in Appendix A.

The enthalpy H_M and entropy S_M of mixing per total atom, as derived in Appendix B, are given, respectively, by

$$\begin{aligned} H_M = {} & xH_0(\mathrm{Si})+(1-x)H_0(\mathrm{C})-2(P_1+3P_2+3P_3+P_4)E(\text{Si-Si}) \\ & -4(P_2+3P_3+3P_4+P_5)E(\text{Si-C})-2(P_7+3P_8+3P_9+P_{10})E(\text{C-C}) \,, \end{aligned} \tag{16}$$

$$\begin{aligned} S_M = {} & -k_B[-x\ln x-(1-x)\ln(1-x)+P_1\ln P_1+4P_2\ln P_2+6P_3\ln P_3 \\ & +4P_4\ln P_4+P_5\ln P_5+P_6\ln P_6+4P_7\ln P_7+6P_8\ln P_8+4P_9\ln P_9+P_{10}\ln P_{10}] \,, \end{aligned} \tag{17}$$

where P_3, for example, refers to any of the six equal probabilities for the six distinct arrangements of the bonds in the Si-Si_2C_2 tetrahedron. Note that the total probability for the Si-Si_2C_2 tetrahedron is therefore given by $P(3)=6P_3$.

The Gibbs free energy of mixing $G_M=H_M-TS_M$ for tetrahedra is thus a function of the composition x, the ten tetrahedron probabilities $P(i)$, the bond energies, and the temperature T. The constraint equations (B3)–(B5) have been used to eliminate P_1, P_2, and P_{10} from G_M. By setting $\partial G_M/\partial P_i=0$ for $i=3$–9, and again letting $a=\exp(\Omega_1/2k_BT)$, the following quadratic equation in $r=P_2/P_1$ is obtained, with details of the derivation given in Appendix B:

$$xr^2+a(2x-1)r+a(x-1)=0 \,. \tag{18}$$

It is straightforward to solve Eq. (18) for $r=P_2/P_1$ for a given composition x. Three limiting cases are (1) for $\Omega_1/2k_BT=0$ ($a=1$), Eq. (18) becomes $xr^2+(2x-1)r+(x-1)=0$, which yields $r=(1-x)/x$ as the only allowed solution; (2) for $\Omega_1/2k_BT\gg 1$ ($a\gg 1$), Eq. (18) becomes $(2x-1)r+(x-1)=0$ or $r=(1-x)/(2x-1)$; and (3) for $\Omega_1/2k_BT\ll 0$ ($a=0$) Eq. (18) becomes $xr^2=0$ or $r=0$. The resulting tetrahedron probabiities $P(i)$ for these three cases are presented in Table IV. Note that $a=1$ ($\Omega_1=0$) corresponds to random bonding, $a\gg 1$ to COHD, and $a=0$ to complete phase separation into pure Si and pure C. The $P(i)$ for the first two cases agree exactly with previous results obtained for random bonding and for COHD, respectively (see Table I of Ref. 1, where the notation a-$Si_{1-x}C_x$ was used). Also shown in Table IV are the $P(i)$ predicted for stoichiometric a-Si_xC_{1-x} ($x=1-x=\frac{1}{2}$) for the case of $\Omega_1=+0.38$ eV [see Eq. (4)] at $T=523$ K.

We will now show that the $P(i)$ presented in Table IV can in fact be directly determined from the normalized bond concentrations predicted using the FEM for bonds in Sec. III. We proceed by assuming that the predicted bonds will be distributed randomly, according to statistics, among the ten possible tetrahedra. The justification for this assumption is that, since the predicted bonds already completely determine the enthalpy H_M, the free energy $G_M=H_M-TS_M$ will therefore be minimized when the entropy S_M is maximized. This clearly corresponds to a random distribution of the predicted bonds among the available tetrahedra. The resulting general expressions for the $P(i)$ are given in the last column of Table IV where, for example, $P(3)=6P_3=6f_{\mathrm{Si}}(\mathrm{Si})^2 f_{\mathrm{Si}}(\mathrm{C})^2$ with $f_{\mathrm{Si}}(\mathrm{Si})=n_{\mathrm{Si,Si}}/(n_{\mathrm{Si,Si}}+n_{\mathrm{C,Si}})=n_{\mathrm{Si,Si}}$, $f_{\mathrm{Si}}(\mathrm{C})=n_{\mathrm{C,Si}}/(n_{\mathrm{Si,Si}}+n_{\mathrm{C,Si}})=n_{\mathrm{C,Si}}$, etc., using $n_{\mathrm{Si,Si}}+n_{\mathrm{C,Si}}=1$. When the values of $n_{\mathrm{Si,Si}}$, $n_{\mathrm{C,Si}}$, etc., from Table II are used in these general expressions for the $P(i)$, exactly the same results are obtained for the three limiting cases ($a=1$, $a\gg 1$, and $a=0$) as have already been predicted using the FEM for tetrahedra developed in this section. As an example, using the normalized bond concentrations from Table II for $\Omega_1=0.38$ eV and $x=(1-x)=\frac{1}{2}$, the prediction for the Si-Si_2C_2 tetrahedron is $P(3)=6(\frac{1}{2})(0.108)^2(0.892)^2=0.028$. This agrees exactly with the prediction for $P(3)$ in the next-to-the-last column of Table IV and proves the validity of our initial assumption concerning the distribution of the bonds. We have in fact already used this approach for a-Si_xH_z alloys.[23]

We conclude therefore that it is in fact not necessary to develop a separate FEM for tetrahedra since the normalized bond concentrations predicted by the FEM for bonds can be used to obtain the $P(i)$ for tetrahedra. This leads to the important additional conclusion that the distribution of bonds in amorphous covalent alloys corresponds in general to partial chemical ordering with homogeneous dispersion, i.e, partial COHD. On this basis, we can assert that COPS will not occur in these alloys unless bond energies vary according to their local environment. For example, if Si-C bonds are stronger in Si-centered tetrahedra in which other Si-C bonds are present, then COPS can occur in Si-rich a-Si_xC_y alloys, with only Si-Si_4, Si-C_4, and C-Si_4 tetrahedra predicted to be present.

B. Predictions for a-$Si_xC_yH_z$ alloys

The 30 possible Si- and C-centered tetrahedra in these a-$Si_xC_yH_z$ alloys are listed in Table V. Also given in Table V are the tetrahedron probabilities $P(i)$, $i=1$–30, expressed in terms of $f_{\mathrm{Si}}(\mathrm{Si})$, $f_{\mathrm{Si}}(\mathrm{H})$, etc., where these factors represent the atom fractions available for bonding at a given site in a given tetrahedron. For example, $f_{\mathrm{Si}}(\mathrm{H})$ is the fraction of all atoms which can bond to Si which are H atoms, and is just equal to the normalized bond

TABLE V. Tetrahedra and tetrahedron probabilities $P(i)$ and volumes $V(i)$ for a-$Si_xC_yH_z$ alloys.

		Si centered				C centered	
i	Tetrahedron	$P(i)^a$	$V(i)^b$ (Å^3)	i	Tetrahedron	$P(i)^a$	$V(i)^b$ (Å^3)
1	$Si\text{-}Si_4$	$xf_{Si}^4(Si)/(x+y)$	19.98	16	$C\text{-}C_4$	$yf_C^4(C)/(x+y)$	5.64
2	$Si\text{-}Si_3H$	$4xf_{Si}^3(Si)f_{Si}(H)/(x+y)$	17.81	17	$C\text{-}C_3H$	$4yf_C^3(C)f_C(H)/(x+y)$	5.86
3	$Si\text{-}Si_2H_2$	$6xf_{Si}^2(Si)f_{Si}^2(H)/(x+y)$	15.84	18	$C\text{-}C_2H_2$	$6yf_C^2(C)f_C^2(H)/(x+y)$	6.07
4	$Si\text{-}SiH_3$	$4xf_{Si}(Si)f_{Si}^3(H)/(x+y)$	14.07	19	$C\text{-}CH_3$	$4yf_C(C)f_C^3(H)/(x+y)$	6.30
5	$Si\text{-}H_4$	$xf_{Si}^4(H)/(x+y)$	12.48	20	$C\text{-}H_4$	$yf_C^4(H)/(x+y)$	6.53
6	$Si\text{-}Si_3C$	$4xf_{Si}^3(Si)f_{Si}(C)/(x+y)$	17.01	21	$C\text{-}SiC_3$	$4yf_C(Si)f_C^3(C)/(x+y)$	6.58
7	$Si\text{-}Si_2CH$	$12xf_{Si}^2(Si)f_{Si}(C)f_{Si}(H)/(x+y)$	15.12	22	$C\text{-}SiC_2H$	$12yf_C(Si)f_C^2(C)f_C(H)/(x+y)$	6.83
8	$Si\text{-}SiCH_2$	$12xf_{Si}(Si)f_{Si}(C)f_{Si}^2(H)/(x+y)$	13.42	23	$C\text{-}SiCH_2$	$12yf_C(Si)f_C(C)f_C^2(H)/(x+y)$	7.08
9	$Si\text{-}CH_3$	$4xf_{Si}(C)f_{Si}^3(H)/(x+y)$	11.90	24	$C\text{-}SiH_3$	$4yf_C(Si)f_C^3(H)/(x+y)$	7.34
10	$Si\text{-}Si_2C_2$	$6xf_{Si}^2(Si)f_{Si}^2(C)/(x+y)$	14.43	25	$C\text{-}Si_2C_2$	$6yf_C^2(Si)f_C^2(C)/(x+y)$	7.66
11	$Si\text{-}SiC_2H$	$12xf_{Si}(Si)f_{Si}^2(C)f_{Si}(H)/(x+y)$	12.80	26	$C\text{-}Si_2CH$	$12yf_C^2(Si)f_C(C)f_C(H)/(x+y)$	7.94
12	$Si\text{-}C_2H_2$	$6xf_{Si}^2(C)f_{Si}^2(H)/(x+y)$	11.34	27	$C\text{-}Si_2H_2$	$6yf_C^2(Si)f_C^2(H)/(x+y)$	8.23
13	$Si\text{-}SiC_3$	$4xf_{Si}(Si)f_{Si}^3(C)/(x+y)$	12.21	28	$C\text{-}Si_3C$	$4yf_C^3(Si)f_C(C)/(x+y)$	8.89
14	$Si\text{-}C_3H$	$4xf_{Si}^3(C)f_{Si}(H)/(x+y)$	10.81	29	$C\text{-}Si_3H$	$4yf_C^3(Si)f_C(H)/(x+y)$	9.21
15	$Si\text{-}C_4$	$xf_{Si}^4(C)/(x+y)$	10.30	30	$C\text{-}Si_4$	$yf_C^4(Si)/(x+y)$	10.30

[a] The $P(i)$ are defined in terms of the atom fractions available for bonding at a given site in a tetrahedron (see text) where $f_{Si}(Si)=n_{Si,Si}$, $f_{Si}(C)=n_{C,Si}$, $f_{Si}(H)=n_{H,Si}$, $f_C(Si)=xn_{Si,C}/y$, $f_C(H)=xn_{H,C}/y$, and $f_C(C)=xn_{C,C}/y$.

[b] $V(i)$ is the volume associated with the ith tetrahedron. The bond lengths used for these calculations are d(Si-Si)=2.35 Å, d(Si-C)=1.884 Å, d(C-C)=1.542 Å, d(Si-H)=2.009 Å, and d(C-H)=1.619 Å. Note that we have added the Bohr radius, 0.529 Å, to the usual values of the Si-H and C-H bond lengths (see Ref. 23).

concentration $n_{H,Si}$ defined previously. Thus the $P(i)$ can be calculated directly from the predicted results of the FEM for bonds represented in Sec. III, as discussed above. These $P(i)$ can be used in the calculations of a variety of alloy properties which are dependent on the distribution of atoms among the Si- and C-centered tetrahedra. For example, the optical dielectric function ε can be calculated using the effective medium approximation.[1] The volume $V(i)$ associated with each tetrahedron are also given in Table V. The procedures used for calculating the $V(i)$ have been discussed previously for a-Si_xC_y alloys[1] and a-Si_xH_z alloys.[23]

The resulting predictions for the $P(i)$ for the high H-content Si-rich alloys listed in Table III are given in Table VI(a), while those for the lower H-content alloys listed in Table III are presented in Table VI(b). Only the tetrahedra predicted to have $P(i)>0.001$ are presented in these tables. Also included are the predictions for P_{tet} and P_{polym} which are the total probabilities, respectively, for tetrahedra in the amorphous tetrahedral and polymeric components[4] in the films, along with the corresponding volume fractions v_{tet} and v_{polym}. P_{tet} and v_{tet} include all tetrahedra containing zero or one H atom while P_{polym} and v_{polym} include those containing two or more H atoms. It should be noted that, for simplicity, the CH_4 "tetrahedron" has been retained in the model. If it were excluded, the probabilities $P(24)$, $P(27)$, and $P(29)$ for the other C-centered tetrahedra containing H atoms would increase correspondingly.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

From the predictions of the FEM presented in Tables VI(a) and (b), it can be seen quite clearly that the $P(i)$ for tetrahedra containing only Si-Si and Si-C bonds, e.g., $Si\text{-}Si_2C_2$, are much higher for the lower H-content alloys. As a result, these alloys have much lower polymeric components, again for a given $y/(x+y)$ ratio, than do the high H-content alloys. The fact that the polymeric component is controlled primarily by the H-content z is demonstrated in Fig. 4 where the volume fraction v_{polym} is plotted versus z for these two sets of alloys and also for additional alloys to be discussed below. The predicted v_{polym} increases rapidly above $z=0.2$ and is actually higher for the lower H-content alloys since, for a given z, these have higher C contents.

We will now compare the predictions of the FEM with some experimental results obtained for Si-rich alloy films. It has been demonstrated that Si-rich films can be prepared with enhanced optoelectronic properties, e.g., lower Urbach edge parameters E_0, by using either (1) CH_4 in the discharge[3] instead of C_2H_4, or (2) H_2 dilution[24,25] of the plasma gases. We propose that these techniques in fact have been successful because of a resulting lower H content in the deposited films and, hence, a lower polymeric component. This is demonstrated in Table VII where the FEM predictions for v_{tet} and v_{polym} are presented for the films in question. The CH_4-based film[3] with $z=0.22$ has $v_{polym}=0.04$ while the C_2H_4-based film with $z=0.43$ has $v_{polym}=0.09$. The former film has been characterized[3] as a rather ideal amorphous silicon-carbon alloy, in contrast to the latter which has an organosilanelike structure. These descriptions are in fact consistent with the local atomic bonding predicted by the FEM.

Likewise, the film prepared[25] with H_2 dilution $[H_2/(CH_4+SiH_4)=10]$ has $z=0.14$ and $v_{polym}=0.02$ while the film prepared without H_2 diluton has $z=0.22$ and $v_{polym}=0.04$. It can be inferred from these observations that one key to achieving enhanced optoelectronic properties is to deposit films with lower H contents and corresponding smaller polymeric components. This is consistent with a previous suggestion of Beyer.[26] There thus seems to be little point in alloying C into a-Si_xH_z if it enters primarily in CH_2 and CH_3 units. The effectiveness of H_2 dilution for this purpose has been proposed[24] to be due to the occurrence of energetically favorable reactions such as $-CH_2+2H\rightarrow CH_4$ and $-CH_3+H\rightarrow CH_4$, which remove CH_2 and CH_3 units from the surface of the growing film via the formation of CH_4 which desorbs. These surface reactions reduce both the H-content z of the film and v_{polym} simultaneously.

The optical dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ in Si-rich alloy films has been found to depend sensitively on the local atomic bonding, with significant differences observed for films with high[18] and lower[4] H content. Films prepared from $C_2H_2+SiH_4$ mixtures with lower H content show a

TABLE VI. (a) Predicted tetrahedron probabilities $P(i)$ for high H-content Si-rich a-$Si_xC_yH_z$ alloys. (b) Predicted tetrahedron probabilities $P(i)$ for lower H-content Si-rich a-$Si_xC_yH_z$ alloys.

					(a)			
	x	0.88	0.87	0.65	0.47	0.36	0.29	0.235
	y	0.00	0.01	0.07	0.12	0.15	0.20	0.235
	z	0.12	0.12	0.28	0.41	0.49	0.51	0.53
	$y/(x+y)$	0.00	0.011	0.097	0.203	0.294	0.408	0.500
i	Tetrahedron				$P(i)$			
1	Si-Si_4	0.870	0.858	0.724	0.545	0.401	0.186	0.052
2	Si-Si_3H	0.124	0.103	0.082	0.064	0.051	0.001	
3	Si-Si_2H_2	0.006	0.005	0.004	0.003	0.002		
6	Si-Si_3C		0.021	0.082	0.153	0.192	0.249	0.159
7	Si-Si_2CH		0.002	0.007	0.013	0.018	0.001	
10	Si-Si_2C_2			0.003	0.016	0.035	0.125	0.181
13	Si-SiC_3				0.001	0.003	0.028	0.091
15	Si-C_4						0.002	0.017
20	C-H_4		0.001	0.031	0.064	0.093	0.067	0.051
24	C-SiH_3		0.003	0.041	0.086	0.124	0.152	0.155
27	C-Si_2H_2		0.004	0.020	0.043	0.062	0.130	0.178
29	C-Si_3H		0.003	0.004	0.010	0.014	0.049	0.091
30	C-Si_4				0.001	0.001	0.007	0.017
	P_{tet} [a]	0.99	0.99	0.91	0.80	0.72	0.65	0.62
	P_{polym} [a]	0.01	0.01	0.09	0.20	0.28	0.35	0.38
	v_{tet} [b]	0.99	0.99	0.96	0.91	0.86	0.80	0.75
	v_{polym} [b]	0.01	0.01	0.04	0.09	0.14	0.20	0.25

			(b)	
	x	0.77	0.65	0.55
	y	0.14	0.25	0.33
	z	0.09	0.10	0.12
	$y/(x+y)$	0.154	0.278	0.375
i	Tetrahedron		$P(i)$	
1	Si-Si_4	0.437	0.134	0.029
6	Si-Si_3C	0.314	0.281	0.134
10	Si-Si_2C_2	0.085	0.220	0.232
13	Si-SiC_3	0.010	0.077	0.179
15	Si-C_4		0.010	0.052
24	C-SiH_3	0.002	0.001	0.001
26	C-Si_2CH		0.002	0.005
27	C-Si_2H_2	0.017	0.013	0.015
28	C-Si_3C	0.001	0.005	0.016
29	C-Si_3H	0.058	0.079	0.097
30	C-Si_4	0.076	0.177	0.239
	P_{tet} [a]	0.98	0.98	0.98
	P_{polym} [a]	0.02	0.02	0.02
	v_{tet} [b]	0.99	0.99	0.99
	v_{polym} [b]	0.01	0.01	0.01

[a] P_{tet} and P_{polym} are the total probabilities for tetrahedra in the amorphous tetrahedral and polymeric components, respectively.

[b] v_{tet} and v_{polym} are the volume fractions of the amorphous tetrahedral and polymeric components, respectively.

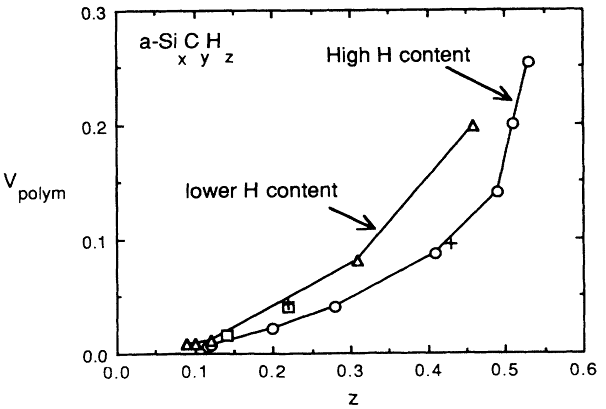

FIG. 4. Predicted polymeric volume fraction v_{polym} vs H content z for a-$\text{Si}_x\text{C}_y\text{H}_z$ alloys. Specific alloys: circles, high H-content alloys, Refs. 18 and 19; triangles, lower H-content alloys, Ref. 4; squares, Ref. 25; +, Ref. 3.

steady shift of ϵ_2 to higher energies with increasing C content.[4] These films are predicted by the FEM and are found experimentally[4] to have lower polymeric contents, $v_{\text{polym}}=0.01$, and higher fractions of Si-C bonds than are predicted to be found in the high H-content films prepared from CH_4+SiH_4 mixtures.[18] In these latter films few Si-C bonds are formed since CO favors Si-Si and C-H bonds and therefore the ϵ_2 peak remains essentially constant in energy until the C fraction $y/(x+y)$ reaches about 0.4. The observed shifts[4,18] energy of ϵ_2 can be correlated quite well with a gradual transition from a network dominated by Si-Si bonds to one dominated by Si-C bonds. The FEM predicts that Si-Si_4 remains the most probable tetrahedron up to $y/(x+y)=0.4$ in high H-content alloys while only up to 0.2 in lower H-content alloys. This dominance of the Si-Si_4 tetrahedron can thus explain the observed absence of a shift in energy for the ϵ_2 peak in high H-content films.[18] Thus it is clear that, for a given C/(Si+C) fraction, high H-content films not only have a higher v_{polym} but also have a tetrahedral component which is even more Si-rich than the alloy as a whole, in agreement with recent EXAFS studies.[20]

While the preferential bonding of H to C is favored by CO in Si-rich alloys, it is nevertheless found that the N(Si-H)/N(Si) ratio observed experimentally is often higher than that predicted by the FEM. For example, Mui *et al.*[4] found $N(\text{Si-H})/N(\text{Si})=0.4$ and $N(\text{C-H})/N(\text{C})=1.3$ in an a-$\text{Si}_{0.27}\text{C}_{0.27}\text{H}_{0.46}$ alloy for which the FEM predicts values of 0.0 and 1.7, respectively, using the bond energies listed in Table I. Similar discrepancies are observed between the experimental results of other researchers[3,27,28] and the predictions of the FEM. If, as suggested,[12] Si-H bonds become stronger and C-H bonds weaker as the fraction of Si-C bonds in the alloy increases, then the concentration of Si-H bonds will increase relative to that of C-H bonds as the C content in Si-rich alloys increases. Such effects of the local environment on E(Si-H) and E(C-H) can be included in the FEM either by explicitly allowing these bond energies to be composition dependent[29] or by assigning different values of the bond energies to each distinct tetrahedron in the alloy. Either approach would clearly lead to a more realistic, and much more complicated, FEM. In order to test the predictions of a more realistic FEM, a careful experimental study of the relative bonding of H to Si and C atoms in a well-characterized series of a-$\text{Si}_x\text{C}_y\text{H}_z$ alloys, similar to those carried out on a-$\text{Si}_x\text{N}_y\text{H}_z$ alloys,[30] is necessary.

TABLE VII. Dependence of v_{tet} and v_{polym} on H content.

	Tawada *et al.*[a]		H_2 dilution[b]	
	CH_4	C_2H_2	yes ($R=10$)	no ($R=0$)
x	0.66	0.45	0.59	0.58
y	0.12	0.12	0.27	0.20
z	0.22	0.43	0.14	0.22
$y/(x+y)$	0.154	0.211	0.31	0.256
v_{tet}[c]	0.96	0.91	0.98	0.96
v_{polym}[c]	0.04	0.09	0.02	0.04

[a] See Ref. 3.

[b] See Ref. 25; $R=\text{H}_2/(\text{CH}_4+\text{SiH}_4)$.

[c] v_{tet} and v_{polym} are the volume fractions for the amorphous tetrahedral and polymeric components, respectively.

VI. CONCLUSIONS

The free-energy model for bonding in amorphous covalent alloys has been extended to include tetrahedra, the fundamental structural units in the a-$\text{Si}_x\text{C}_y\text{H}_z$ alloys under consideration. It has been proven that the tetrahedron probabilities $P(i)$ can be obtained from a random distribution, according to statistics, of the bonds predicted by the FEM among the possible Si- and C-centered tetrahedra. As a result, the short-range order present in these alloys corresponds, in general, to partial chemical ordering with a homogeneous dispersion of the bonds among the available tetrahedra.

The degree and nature of the CO predicted for these a-$\text{Si}_x\text{C}_y\text{H}_z$ alloys has been shown to vary with alloy composition and also with the magnitude (and sign) of the interaction parameters Ω_i. For example, Si-C bonds are favored over Si-Si and C-C bonds in stoichiometric alloys, Si-Si and C-H bonds are favored over Si-C and Si-H bonds in Si-rich alloys, while Si-C and C-H bonds are favored over C-C and Si-H bonds in C-rich alloys.

Detailed predictions have been presented for the bond fractions, tetrahedron probabilities, and tetrahedral and polymeric volume fractions in a-$\text{Si}_x\text{C}_{1-x}$ alloys and also in a-$\text{Si}_x\text{C}_y\text{H}_z$ alloys with both high H content and lower H content. In the high H-content alloys C has been predicted to be present primarily in CH_2 and CH_3 units, in good agreement with experiment, and a significant polymeric component has been predicted to be present. In the lower H-content alloys, on the other hand, more Si-C bonds and a smaller polymeric component have been predicted. It has therefore been concluded that the H content plays a dominant role in controlling the optical and electronic properties of these technologically important alloys. The simplest way to improve the usefulness of these alloys is to lower the H content, thereby promoting the random bonding of C and H atoms in the amorphous Si network.

Finally, evidence for the variation of the strengths of Si-H and C-H bonds with increasing C content in these alloys has been found. The FEM will be extended to take these variations into account.

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APPENDIX A: BOND ARRANGEMENTS IN TETRAHEDRA

In amorphous covalent alloys such as a-Si_xC_{1-x} there are ten possible tetrahedra, Si-$Si_{4-n}C_n$ and C-$Si_{4-n}C_n$, with $n=0$–4 (see Table IV). In order to calculate the entropy of mixing S_M for such alloys it is necessary to write down Γ, the number of distinct configurations of the alloy involving distributions of these ten tetrahedra. There has been disagreement recently[1,22] over whether or not it is necessary to count all of the possible arrangements of bonds within tetrahedra as distinct configurations. For example, a statistical weight of six has been assigned to tetrahedra such as Si-Si_2C_2 in our previous work,[1] while Gurman[22] states that such a factor of 6 is incorrect on the basis of the concept of "split atoms."

To illustrate, for the case of random bonding in a stoichiometric a-$Si_{0.5}C_{0.5}$ alloy Gurman predicts[22] that the ten tetrahedra listed in Table IV have equal probabilities of 0.1; see Table VIII. Our predictions which include the statistical weights of 1, 4, 6, 4, and 1 are also shown in Table VIII. In order to confirm that our prediction is correct, we have generated a disordered binary "alloy" of 10^6 "atoms" on a square lattice of 10^3 by 10^3 sites. This lattice has been created using a random number generator to assign a 0 (Si atom) or a 1 (C atom) to each site. This process resulted in 500 482 0's and 499 518 1's being assigned. The total probability $P(3)$ for the equivalent of a Si-Si_2C_2 tetrahedron, for example, was then calculated by counting the number of 0's (Si atoms) whose four nearest neighbors included two 0's and two 1's, in any arrangement relative to the central 0, and then dividing by 10^6, the total number of atoms. These results are also presented in Table VIII and indicate quite clearly the validity of the use of the statistical weights of 1, 4, 6, 4, and 1.

TABLE VIII. Tetrahedron probabilities $P(i)$ for the a $Si_{0.5}C_{0.5}$ alloy with random bonding.

i	Tetrahedron	$P(i)$[a]	$P(i)$[b]	$P(i)$[c]
1	Si-Si_4	$\frac{1}{32}=0.031\,25$	0.031 202	0.1
2	Si-Si_3C	$\frac{4}{32}=0.125\,0$	0.125 239	0.1
3	Si-Si_2C_2	$\frac{6}{32}=0.187\,5$	0.187 659	0.1
4	Si-SiC_3	$\frac{4}{32}=0.125\,0$	0.124 560	0.1
5	Si-C_4	$\frac{1}{32}=0.031\,25$	0.030 858	0.1
6	C-Si_4	$\frac{1}{32}=0.031\,25$	0.031 554	0.1
7	C-Si_3C	$\frac{4}{32}=0.125\,0$	0.124 982	0.1
8	C-Si_2C_2	$\frac{6}{32}=0.187\,5$	0.187 553	0.1
9	C-SiC_3	$\frac{4}{32}=0.125\,0$	0.125 253	0.1
10	C-C_4	$\frac{1}{32}=0.031\,25$	0.031 140	0.1

[a] $P(i)$ for random bonding ($\Omega_1/2k_bT=0$); from first column of Table IV, with $x=\frac{1}{2}$.

[b] $P(i)$ calculated for lattice for 10^6 "atoms"; see text.

[c] $P(i)$ according to Gurman, Ref. 22.

APPENDIX B: ENTHALPY H_M AND ENTROPY S_M OF MIXING FOR TETRAHEDRA

The concentration N(Si-Si) of Si-Si bonds which appears in the enthalpy of mixing H_M for a-Si_xC_{1-x} alloys can be expressed in terms of the probabilities P_i for distinct arrangement of bonds in the five Si-centered tetrahedra which are listed in Table IV. The contribution to N(Si-Si) from the Si-Si_2C_2 tetrahedron, for example, is given by $(\frac{1}{2})(2)(6)(P_3)N_{\text{tot}}=(6P_3)N_{\text{tot}}=P(3)N_{\text{tot}}$, where $N_{\text{tot}}=N(\text{Si})+N(\text{C})$. Here the factor $(\frac{1}{2})$ appears because the tetrahedron is credited with only $\frac{1}{2}$ of each bond, the factor (2) appears because there are two Si-Si bonds in this tetrahedron, and the factor (6) appears because this is the statistical weight for this tetrahedron. When the other three tetrahedra containing Si-Si bonds are included, the following result is obtained:

$$N(\text{Si-Si})=2(P_1+3P_2+3P_3+P_4)N_{\text{tot}}\ . \tag{B1}$$

The expressions for N(Si-C) and N(C-C) are obtained in a similar way. Using these bond concentrations, the expression for H_M presented as Eq. (16) in Sec. IV follows immediately.

The entropy of mixing S_M for tetrahedra is again equal to $k_B\ln\Gamma_{\text{Si}}\Gamma_{\text{C}}$, but with Γ_{Si} now given by

$$\Gamma_{\text{Si}}=N(\text{Si})!/[N_1!(N_2!)^4(N_3!)^6(N_4!)^4N_5!]\ , \tag{B2}$$

where, for example, $N_3=P_3N_{\text{tot}}$ is the concentration of any one of the six distinct arrangements of Si-centered tetrahedra containing two Si and two C atoms. Note that $N(\text{Si})=N_1+4N_2+6N_3+4N_4+N_5$. Finally, after using Stirling's rule and a similar expression for $\ln\Gamma_{\text{C}}$, we can obtain Eq. (17) of Sec. IV for S_M.

Three constraint equations involving the P_i are

$$x=N(\text{Si})/N_{\text{tot}}=P_1+4P_2+6P_3+4P_4+P_5\ , \tag{B3}$$

$$(1-x)=N(\text{C})/N_{\text{tot}}=P_6+4P_7+6P_8+4P_9+P_{10}\ , \tag{B4}$$

$$P_2+3P_3+3P_4+P_5=P_6+3P_7+3P_8+P_9\ . \tag{B5}$$

Equation (B5) simply states that the number of Si-C bonds must be the same whether counted in Si- or C-centered tetrahedra.

After P_1, P_2, and P_{10} are eliminated from $G_M=H_M-TS_M$, the following equations result from setting the partial derivatives of G_M with respect to P_i, $i=3$–9, equal to zero:

$$\begin{gathered} P_1P_3/P_2^2=P_1^2P_4/P_2^3=P_1^3P_5/P_2^4=1\ , \\ P_1^4P_{10}/P_2^4P_6=\exp(-2\Omega_1/k_BT)\ , \\ P_1^6P_{10}^2/P_2^6P_7^2=\exp(-3\Omega_1/k_BT)\ , \\ P_1^2P_{10}/P_2^2P_8=\exp(-\Omega_1/k_BT)\ , \\ P_1^2P_{10}^2/P_2^2P_9^2=\exp(-\Omega_1/k_BT)\ . \end{gathered} \tag{B6}$$

These equations, along with the constraint equations (B3)–(B5), can be combined to yield

$$P_1=x/(1+r)^4\ , \tag{B7}$$

$$P_{10}=(1-x)r^4/[r+\exp(\Omega_1/2k_BT)]^4\ , \tag{B8}$$

where $r=P_2/P_1$. When Eqs. (B6)–(B8) are used in Eq. (B5), Eq. (18) in Sec. IV can finally be obtained.

The results presented in Eq. (B6) have straightforward interpretations in terms of "tetrahedron reactions." Consider, for example,

$$P_1P_3/P_2^2=1 \quad \text{or} \quad P_1P_3=P_2^2\ , \tag{B9}$$

which corresponds to

$$\text{Si-Si}_4+\text{Si-Si}_2\text{C}_2\leftrightarrow 2\text{Si-Si}_3\text{C}\ . \tag{B10}$$

This tetrahedron reaction is neither exo- nor endothermic in our model since there is no net change in the numbers of Si-Si or Si-C bonds. Consider, on the other hand, the reaction

$$P_1^2P_{10}^2/P_2^2P_9^2=\exp(-\Omega_1/k_BT)\ , \tag{B11}$$

which corresponds to

$$2\text{Si-Si}_4+2\text{C-C}_4\leftrightarrow 2\text{Si-Si}_3\text{C}+2\text{C-SiC}_3\ . \tag{B12}$$

This can be expressed in terms of a net bond reaction equation as

$$\text{Si-Si}+\text{C-C}\leftrightarrow 2\text{Si-C}\ , \tag{B13}$$

which is exothermic and identical to Eq. (1). This is consistent with the appearance of the factor $\exp(-\Omega_1/k_BT)$ in Eq. (B11) since Ω_1 is the interaction energy for this BRE.

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