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# Free-energy model for bonding in amorphous covalent alloys

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A free-energy model (FEM) for bonding in amorphous covalent alloys is developed and applied to the ternary $a$-Si$_x$N$_y$H$_z$ alloy system. The Gibbs free energy of mixing $G_M = H_M - TS_M$ is obtained with use of the quasichemical approach to the thermodynamics of regular solutions. The enthalpy of mixing, $H_M$, is expressed in terms of the nearest-neighbor bond energies, while the entropy of mixing, $S_M$, is given by the number of possible bonding configurations in Si-centered tetrahedra. Chemical ordering (CO) in these alloys is shown to correspond to the preference for Si—N and Si—H bonds at the expense of Si—Si and N—H bonds. The predictions of the FEM are shown to be in good agreement with experimentally determined bond concentrations in $a$-Si$_x$N$_y$H$_z$ alloy films where, in general, neither the CO ($T = 0$ K) nor random-bonding limits are valid.

Amorphous covalent network alloys such as $a$-Si$_x$H$_y$ and $a$-Si$_x$N$_y$H$_z$ are first and foremost characterized by the absence of long-range order (LRO). They can, nevertheless, possess a considerable degree of short-range order (SRO) which, in alloys, is generally referred to as chemical ordering[1,2] (CO). CO usually corresponds to a preference for unlike nearest-neighbor (NN) bonds and results from the tendency to maximize the chemical-bonding energy in the alloy. Random bonding, on the other hand, refers to a purely statistical distribution of NN bond types.[1] While the NN distribution of Si—Si and Si—H bonds in single phase $a$-Si$_x$H$_y$ alloys is fixed by the composition[3] and by the fact that H—H bonds cannot be considered to be part of the network, the distribution of bonds in $a$-Si$_x$N$_y$H$_z$ and similar ternary alloys cannot be determined from the composition alone even if bonds such as H—H and N—N are excluded. This is due to the fact that the division of H into Si—H and N—H bonds cannot be obtained solely from the composition, but must be specified separately. The ability to predict the NN bond distributions in amorphous covalent network alloys is clearly of fundamental importance as an aid in constructing realistic network models and is also of great practical significance since, for example, Si—Si and Si—H bonds have been proposed[4] to act as precursors for the Si dangling bonds, which are important defects in the $a$-Si$_x$N$_y$H$_z$ films currently used in a variety of device-related applications. We note that while Si—H bond concentrations can be obtained from ir absorption, there is no direct method available to determine the concentration of Si—Si bonds in these alloys.

We have developed a free-energy model (FEM) for bonding in amorphous covalent alloys which includes chemical-bonding effects in the enthalpy and effects due to the statistics of bonding within local structural units (in this case, Si-centered tetrahedra[5]) in the entropy. While recognizing the obvious fact that these alloys are not in thermodynamic equilibrium, our approach has been to determine the state of lowest free energy among the possible states of the amorphous alloy which lack LRO. The rationale for this approach is that even though the deposition processes typically used for these alloy films are not, strictly speaking, equilibrium processes, nevertheless the bonding in the film which corresponds to the greatest product stability should be favored. The absence of LRO in these amorphous films is clearly due to kinetic effects, i.e., insufficient atom mobility at the surface of the growing film. Nevertheless, the SRO which is typically present is controlled by nearest-neighbor bonding, and this is the focus of the FEM. An outline of the FEM for bonding as applied to $a$-Si$_x$N$_y$H$_x$ alloys will be given below. The predictions of the FEM for the distribution of bonds will then be presented and compared with the results of previous experimental studies of the bonding in $a$-Si$_x$N$_y$H$_z$ films, including our own recent results[6] for a series of N-rich films.

The FEM for bonding in amorphous covalent alloys is based on the quasichemical approach to the thermodynamics of regular solutions,[7] which is the simplest model that can be used to describe the free energy of mixing of the alloys of interest here. Although the usual assumption of atoms residing on a lattice does not apply, the more important assumptions of including only pairwise bonding energies and a specific coordination number for each type of atom given by the normal chemical valence ($8-N$ rule) are retained. The minimization of the Gibbs free energy of mixing, $G_M = H_M - TS_M$, where $H_M$ and $S_M$ are the enthalpy and entropy of mixing, respectively, will yield the normalized bond concentrations, i.e., bond fractions, for an alloy of fixed composition $x,y,z$.

$H_M$ will be taken here to be equal to $E_{\text{atoms}} - E_{\text{bonds}}$, where $E_{\text{atoms}}$ is the sum of the energies of the isolated atoms and $E_{\text{bonds}}$ is the sum of the NN bond energies in the alloy. With three constituents present in the $a$-Si$_x$N$_y$H$_z$ alloys of interest, there are in principle six possible NN bond pairs. H—H bonds can be excluded as not being part of the network, while N—N bonds will be excluded due to their low binding energy,[8] 1.7 eV. In addition, broken (or dangling) bonds will not be considered.

$E_{\text{bonds}}$ can then be expressed in terms of the four bond concentrations $N(X\text{—}Y)$ and corresponding NN bond energies[8] $E(X\text{—}Y)$ via

$$E_{\text{bonds}} = N(\text{Si—Si})E(\text{Si—Si}) + N(\text{Si—H})E(\text{Si—H}) + N(\text{Si—N})E(\text{Si—N}) + N(\text{N—H})E(\text{N—H}) , \tag{1}$$

where $E(\text{Si—Si}) = 2.34$ eV, $E(\text{Si—H}) = 3.34$ eV, $E(\text{Si—N}) = 3.45$ eV, and $E(\text{N—H}) = 4.05$ eV. Although these NN bond energies are initially assumed to be independent of the local environment of the bonds in the alloy, i.e., the identity of the second nearest neighbors and strain effects due to deviations of bond lengths and angles from their "ideal" values, possible variations of $E(\text{Si—N})$ with composition will be discussed below. Extensions of the model to explicitly account for the effects of strain will be desirable.

$H_M$ is minimized for a given alloy when the chemical bonding energy $E_{\text{bonds}}$ is maximized. This limit corresponds to the maximum possible CO and it will be shown below for $a\text{-Si}_x\text{N}_y\text{H}_z$ that this is equivalent to maximizing $N(\text{Si—N})$ and $N(\text{Si—H})$. This result is consistent with the following network bond reaction equation:

$$\text{Si—Si} + \text{N—H} \leftrightarrow \text{Si—N} + \text{Si—H} , \tag{2}$$

for which the change in chemical-bonding energy is exothermic in the forward direction. The driving force for CO is given by the generalized interaction parameter $\Omega$, which for $a\text{-Si}_x\text{N}_y\text{H}_z$ can be expressed by

$$\Omega = E(\text{Si—N}) + E(\text{Si—H}) - E(\text{Si—Si}) - E(\text{N—H}) . \tag{3}$$

When the bond energies listed above are used, a value of $\Omega = +0.40$ eV is obtained. Better estimates for $\Omega$ are obtained below from comparisons of the predictions of the FEM with the results of experiments on $a\text{-Si}_x\text{N}_y\text{H}_z$ alloys.

The mixing or configurational entropy $S_M$ is given by $k_b \ln\Gamma$, where $\Gamma$ will be taken in the FEM to be the number of possible bonding configurations in Si-centered tetrahedra. The five distinct atomic units[9] in $a\text{-Si}_x\text{N}_y\text{H}_z$ that can bond to the four bonds on a central Si atom are Si(4), H(1), N(3), NH(2), and $\text{NH}_2$(1). The number of valence electrons that each unit has available for bonding to the network is indicated in parentheses. Their probabilities of bonding to a Si atom can be expressed in terms of the composition $x,y,z$ and two additional parameters $y_1$ and $y_2$, which are defined to be the fractions of N atoms bonded to one or two H atoms, respectively. We note that with this notation $N(\text{Si—H})/N(\text{N—H}) = (z - y_1 - 2y_2)/(y_1 + 2y_2)$.

It is assumed in the FEM that all four bonding sites in a Si-centered tetrahedron are equivalent, so that $S_M = k_B \ln\Gamma = k_B \ln(\Gamma_1\Gamma_2\Gamma_3\Gamma_4) = 4k_B \ln\Gamma_1$, with $\Gamma_1$ for a single site given by

$$\Gamma_1 = N(\text{Si})!/(N_{\text{Si}}!\,N_{\text{H}}!\,N_{\text{N}}!\,N_{\text{NH}}!\,N_{\text{NH}_2}!) . \tag{4}$$

Here $N(\text{Si})$ is the concentration of Si atoms in the alloy and $N_{\text{Si}}$, for example, is the concentration of Si atoms bonded at one of the tetrahedral sites. We note that the bond concentrations are given by $N(\text{Si—Si}) = 2N_{\text{Si}}$, $N(\text{Si—H}) = 4N_{\text{H}}$, $N(\text{Si—N}) = 4(N_{\text{N}} + N_{\text{NH}} + N_{\text{NH}_2})$, and $N(\text{N—H}) = 2N_{\text{NH}} + 8N_{\text{NH}_2}$.

Using standard relationships between the bond and atom concentrations,[9] the Gibbs free energy of mixing, $G_M$, of $a\text{-Si}_x\text{N}_y\text{H}_z$ can thus be expressed as a function of the composition $x,y,z$, the two parameters $y_1$ and $y_2$, the NN bond energies, and the temperature $T$. For given $x,y,z$, and $T$, the predicted bond concentrations can be calculated once the values of $y_1$ and $y_2$ that minimize $G_M$ are found. We note that the $T = 0$ K limit of the FEM which corresponds to $G_M = H_M$ yields the maximum possible CO. The $\Omega = 0$ (or $T \rightarrow \infty$) limit, on the other hand, corresponds to the maximum possible bonding disorder, or simply the random limit.

The predictions of the FEM for the bond fractions, i.e., $N(\text{Si—}X)/N(\text{Si})$ with $X = \text{Si}$, H, or N, and $N(\text{N—H})/N(\text{N})$, are shown in Fig. 1 as functions of the [N]/[Si] ratio $y/x$ for $z = 0.4$, $\Omega = +0.40$ eV, and $T = 300\,^\circ\text{C}$, a typical film deposition temperature. Also included for comparison are the predictions corresponding to maximum CO ($T = 0$ K) and maximum disorder ($\Omega = 0$). Since the interaction parameter $\Omega$ for $a\text{-Si}_x\text{N}_y\text{H}_z$ is relatively large, it is not surprising that the $T = 300\,^\circ\text{C}$ prediction lies close to the CO limit over the entire composition range, a result that is observed for $z = 0.2$ as well. The random limit can be seen from Fig. 1 to correspond to significant concentrations of Si—Si bonds even in N-rich alloys and of N—H bonds even in Si-rich alloys. The CO limit, on the other hand, yields no Si—Si or N—H bonds for the same alloys, which, as mentioned before, is

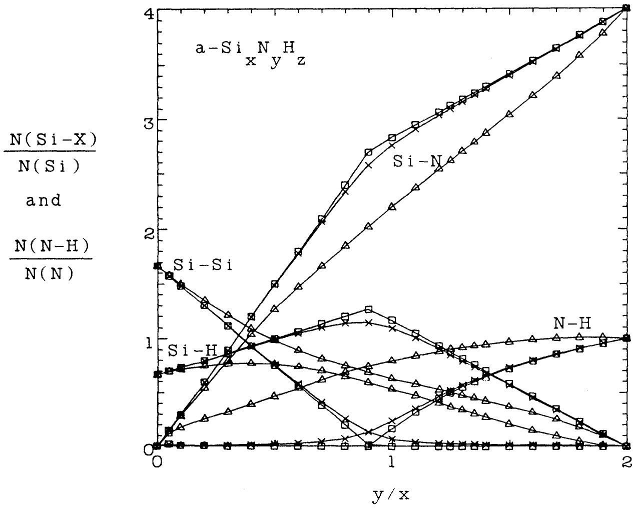


FIG. 1. Predicted bond fractions $N(\text{Si—}X)/N(\text{Si})$, with $X = \text{Si}$, H, or N, and $N(\text{N—H})/N(\text{N})$ as functions of the [N]/[Si] ratio $y/x$ for $a\text{-Si}_x\text{N}_y\text{H}_z$ alloys with $z = 0.4$. Predictions of the FEM are shown for $T = 300\,^\circ\text{C}$ with $\Omega + 0.40$ eV (see text) (×××) and also for the random ($\Omega = 0$, △△△) and CO ($T = 0$ K, □□□) limits.

equivalent to maximizing $N$(Si—N) and $N$(Si—H). The dividing line between what are referred to here as Si-rich and N-rich alloys is a function of $z$ and is given by $y/x = (4-5z)/(3-2z) = 0.91$ for $z=0.4$. This expression has been obtained using $x+y+z=1$ and $4x-3y-z=0$. Neither the random nor the CO predictions of the FEM have been found to be valid for plasma-deposited $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ films where small but nonzero concentrations of Si—Si (N—H) bonds are found in N-rich (Si-rich) films.[6] It can be seen from Fig. 1 that the FEM does in fact predict the presence of Si—Si bonds in N-rich films (and N—H bonds in Si-rich films) at 300 °C, in agreement with experiment. We will return to this important point below.

The prediction of the FEM for the fraction of H atoms bonded to Si, $N$(Si—H)/$N$(H), is shown in Fig. 2 as a function of $y/x$ for $z=0.3$ and $T=300\,^\circ\mathrm{C}$. Also shown are our own experimental results[6] and those of Claassen *et al.*[10] for $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ films with values of $z$ between 0.2 and 0.4. The experimental results are seen to be quite consistent with the FEM prediction when the value of $\Omega$ is taken to be $+0.25$ eV. The predictions corresponding to maximum CO and to random bonding are shown in Fig. 2 to be in poor agreement with experiment. In the limit of maximum CO Si—H (and Si—N) bonds are favored and no N—H bonds are predicted to be present for $y/x < 1.04$, while for random bonding N—H bonds are predicted to be present for all $y/x > 0$. Although $\Omega = +0.40$ eV was obtained using the bond energies listed previously, the lower value of $+0.25$ eV, which has been found here to give the best agreement with experiment, may be understood as follows. If it is assumed that Si—H and N—H bond energies are to a first approximation independent of their environment, then either Si—Si bonds must be stronger or Si—N bonds weaker than expected to explain this lower value for $\Omega$. Since the former situation seems very unlikely, we tentatively attribute the decrease in $\Omega$ from $+0.40$ to $+0.25$ eV to a decrease in $E$(Si—N) from 3.45 eV, the average bond energy in $\mathrm{Si_3N_4}$, to 3.30 eV in these $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloys. This decrease may be due either to strain or to the fact that most Si—N bonds have between one and four NN H atoms in these alloys.

Si—Si bonds have been proposed to be potentially harmful defects in the $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ films currently used in device applications.[4] We have obtained estimates[6] for $N$(Si—Si) for four N-rich films from measurements of the optical dielectric function $\epsilon$ by means of an effective-medium-approximation (EMA) analysis based on the optical response of Si-centered tetrahedra. The analysis yielding $N$(Si—Si) has focused on the region of the absorption edge where the absorption is dominated by the weak Si—Si bonds. Our EMA results[6] for $N$(Si—Si)/$N$(Si) are given in Fig. 3 for the four films studied, which were prepared via plasma-enhanced chemical vapor deposition at 400 °C using $R=[\mathrm{NH_3}]/[\mathrm{SiH_4}]$ ratios of 10, 20, and 40 at $P=0.5$ Torr and $R=40$ at 0.15 Torr. Also included are the FEM predictions for these films for $T=400\,^\circ\mathrm{C}$ with $\Omega=+0.25$ eV and for the random ($\Omega=0$) and CO ($T=0$ K) limits. For the $R=10$ ($y/x=1.31$, $z=0.19$) and $R=20$ ($y/x=1.64$, $z=0.34$)

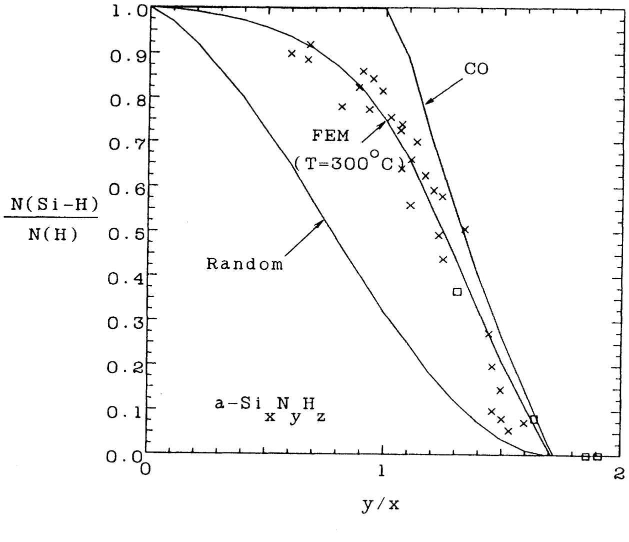


FIG. 2. Fraction of H bonded to Si, $N$(Si—H)/$N$(H), as a function of $y/x$ for $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloys with $z=0.3$. The predictions of the FEM are shown for $T=300\,^\circ\mathrm{C}$ with $\Omega=+0.25$ eV (see text) and also for the random ($\Omega=0$) and CO ($T=0$ K) limits. The experimental results of Claassen *et al.* (Ref. 10, ××× ) and Yin and Smith (Ref. 6, □□□) are also shown.

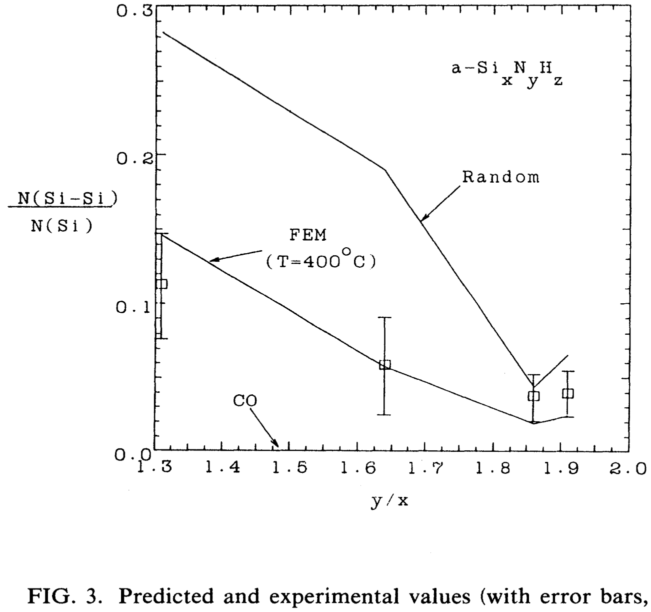
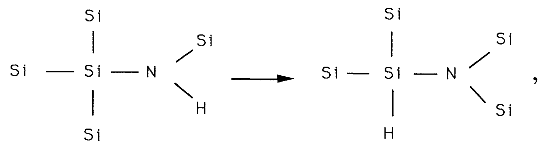


FIG. 3. Predicted and experimental values (with error bars, Ref. 6) of $N$(Si—Si)/$N$(Si) for four N-rich $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ films as functions of $y/x$. The predictions of the FEM for these films are shown for $T=400\,^\circ\mathrm{C}$ (the film deposition temperature) with $\Omega=+0.25$ eV, and also for the random ($\Omega=0$) and CO ($T=0$ K) limits.

films, the EMA results for $N$(Si—Si) agree, to within experimental error, with the $T=400\,^{\circ}\mathrm{C}$ predictions of the FEM, and can be seen to well below the prediction for the random limit and well above the prediction for the CO limit, which is $N(\mathrm{Si—Si})=0$ for these films.

For the two $R=40$ films ($y/x=1.86$, $z=0.37$ for 0.5 Torr; $y/x=1.91$, $z=0.39$ for 0.15 Torr) we find instead that the values of $N$(Si—Si) obtained from the EMA analysis are about a factor of 2 higher than the $T=400\,^{\circ}\mathrm{C}$ FEM prediction and thus are somewhat more consistent with the random limit prediction. The fact that no Si—H bonds have been observed[6] in these two films is also in agreement with random bonding. A possible explanation for this result is that $\Omega \rightarrow 0$ for these two films which are quite close in composition to silicon diimide, $\mathrm{Si(NH)_2}$, with $y/x=2$ and $z=0.4$. An additional reduction in $E$(Si—N) to 3.05 eV would in fact yield $\Omega \simeq 0$, although this is not a unique explanation. In $\mathrm{Si(NH)_2}$ each N atom is bonded to two Si atoms and one H atom. The presence of more electronegative H atoms may well lead to weakening of adjacent Si—N bonds.

Recent experimental analyses[11] of bonding in $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ films have indicated that each N atom in Si-rich films has at least one monohydrogenated Si nearest neighbor. These observations can be shown to be consistent with the tendency for CO in these alloys whereby Si—N and Si—H bonds are favored at the expense of Si—Si and N—H bonds. A specific example of a network bond reaction involving nearest-neighbor Si and N atoms which yields an N atom with one monohydrogenated Si nearest neighbor can be illustrated as follows:



, (5)

where, for simplicity, only the bonds of the NN Si and N atoms are shown. We note that the change in network bonding expressed in this diagram [Eq. (5)] is the same as that given by the simpler bond reaction Eq. (2).

In summary, we have presented a free-energy model for bonding in amorphous covalent alloys whose predictions have been shown to be in good agreement with the measured bond concentrations in $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloy films. These comparisons have enabled us to determine values for the generalized interaction parameter $\Omega$ for these alloys. It has been shown that chemical ordering in $a$-$\mathrm{Si}_x\mathrm{N}_y\mathrm{H}_z$ alloys corresponds to the preference for Si—N and Si—H bonds over Si—Si and N—H bonds, as expressed by the bond reaction equation Si—Si+N—H $\rightarrow$Si—N+Si—H. The FEM thus provides a simple and convenient framework for understanding and expressing the competition between chemical ordering and random bonding in amorphous covalent alloys and will be useful in constructing realistic network models for a wide range of important alloy systems, including $a$-$\mathrm{Si}_x\mathrm{O}_y\mathrm{H}_z$, $a$-$\mathrm{Si}_x\mathrm{C}_y$, $a$-$\mathrm{Si}_x\mathrm{C}_y\mathrm{H}_z$, and also certain amorphous chalcogenide alloy glasses.

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