Invited

The Role of Thermodynamics in Determining the Short Range Order in Amorphous Insulating Films

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The physical properties of amorphous insulating thin films are controlled by short range order, i.e. by the local atomic bonding configurations. From the thermodynamic point of view, the factors determining the atomic bonding are the energy of the bonds and the entropy associated with the number of possible bonding configurations. The free energy model developed for the prediction of the bonding in amorphous alloys will be applied here to diamond-like carbon alloys and to fluorinated silicon dioxide, $a\text{-}SiO_2\text{:}F$.

1. INTRODUCTION

Amorphous covalent alloys such as diamond-like carbon, a-C:H, and $a\text{-}SiO_2$ are examples of amorphous network alloys[1] in which long range order (LRO) is absent but in which a considerable degree of short range order (SRO) and even intermediate range order (IRO) can still exist.

The free energy model (FEM) to be applied here to a-C:H and $a\text{-}SiO_2\text{:}F$ alloys has been developed previously for the thermodynamic analysis of the bonding in several amorphous Si-based network alloys[2-6]. The basic approach used in the FEM begins by assuming that the alloys lack LRO but otherwise have structures which correspond to the lowest possible Gibbs free energy $G_M = H_M - TS_M$ of the network. Here $H_M = E_{atoms} - E_{bonds}$ is the enthalpy of mixing and $S_M = \ln\Gamma$ is the entropy of mixing associated with the number of possible bonding configurations which in the case of a-C:H includes both tetrahedral and trigonal carbon-centered bonding units.

Interest in fluorinated silicon dioxide, $a\text{-}SiO_2\text{:}F$, has developed recently[7] due to the desire to obtain low ε interlayer dielectrics for use in advanced VLSI. The addition of F to $a\text{-}SiO_2$ results in a modest decrease in ε and the retention of many of the desirable properties of $a\text{-}SiO_2$. Predictions for the bonding in $a\text{-}SiO_2\text{:}F$ will also be presented below.

2. PREDICTIONS FOR DIAMOND-LIKE CARBON ALLOYS

a-C:H alloys are considerably more complicated structurally and chemically than a-Si:H and a-Ge:H due to the fact that C atoms can exist in three states of hybridization, sp^3, sp^2, or sp^1. $C(sp^3)$, $C(sp^2)$, and $C(sp^1)$ atoms will be four-fold, three-fold, and two-fold coordinated, respectively. In the a-C:H films of technological interest the bonding is dominated by $C(sp^3)$ and $C(sp^2)$ atoms and so $C(sp^1)$ atoms have not been included in the FEM.

The bonds which are possible in these alloys include five single bonds and one double bond, with the following energies,

Table I   Bonds and Bond Energies

bond (X-Y)	bond energy E(X-Y)
$C(sp^3)\text{-}C(sp^3)$	3,61 eV
$C(sp^3)\text{-}C(sp^2)$	3.70 eV
$C(sp^2)\text{-}C(sp^2)$	3.92 eV
$C(sp^2)=C(sp^2)$	6.72 eV
$C(sp^3)\text{-}H$	4.31 eV
$C(sp^2)\text{-}H$	4.35 eV
(H-H	4.52 eV)

The important bond reactions and the corresponding interaction parameters Ω which involve these bonds and which help to determine the bond concentrations in these alloys can be written as follows:

$$2C(sp^3)\text{-}C(sp^2) \leftrightarrow C(sp^3)\text{-}C(sp^3) + C(sp^2)\text{-}C(sp^2) \qquad \Omega = +0.12 \text{ eV} \quad (1)$$

$$C(sp^3)\text{-}C(sp^3) + C(sp^2)\text{-}H \leftrightarrow C(sp^3)\text{-}C(sp^2) + C(sp^3)\text{-}H \qquad \Omega = +0.05 \text{ eV} \quad (2)$$

$$C(sp^3)\text{-}C(sp^2) + C(sp^2)\text{-}H \leftrightarrow C(sp^2)\text{-}C(sp^2) + C(sp^3)\text{-}H \qquad \Omega = +0.17 \text{ eV} \quad (3)$$

$$H\text{-}H + C(sp^2)=C(sp^2) + 4C(sp^3)\text{-}C(sp^2) \leftrightarrow 2C(sp^3)\text{-}H + 5C(sp^3)\text{-}C(sp^3) \qquad \Omega = +0.63 \text{ eV} \quad (4)$$

$$2C(sp^3)\text{-}C(sp^3) \leftrightarrow C(sp^2)=C(sp^2)/2 + C(sp^2)\text{-}C(sp^2) \qquad \Omega = +0.05 \text{ eV} \quad (5)$$
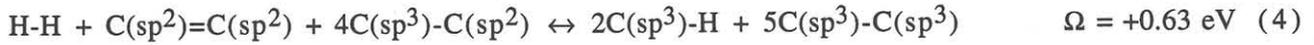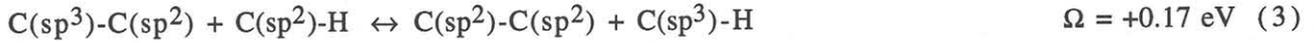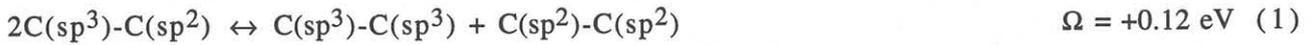
The limit of chemical ordering (CO) in the network corresponds to $G_M = H_M$, i.e. $T = 0$ K, and therefore to the maximum energy of bonding. In the limit of CO the reaction equations listed above may be interpreted as follows: Eq. (1) indicates that total phase separation into diamond-like regions containing only $C(sp^3)$ atoms and graphitic regions containing only $C(sp^2)$ atoms is predicted. Eqs. (2) and (3) predict that H atoms are preferentially bonded to $C(sp^3)$ atoms while Eq. (4) shows that the incorporation of H in the alloys removes isolated double bonds and therefore leads to an increasing sp^3/sp^2 ratio. Eq. (5) describes the conversion of $C(sp^3)$ to $C(sp^2)$ atoms in the alloy (in the absence of H) and confirms that at $T = 0$ K the graphitic form of bonding is preferred to the diamond-like form, but only by 0.05 eV per C atom.

For $T > 0$ K, the effects of entropy play a critical role in determining the bonding in a-C:H alloys due to the small difference in bonding energy between graphite and diamond. At $T = 523$ K the predictions of the FEM are as follows: H atoms are still preferentially bonded to $C(sp^3)$ but there is no longer any phase separation into separate graphitic and diamond-like regions. No six-fold graphitic or aromatic rings of $C(sp^2)$ atoms are present at $T = 523$ K and instead $C(sp^2)$ atoms are present in isolated double bonds, i.e. olefinic units. Finally, the sp^3/sp^2 ratio is predicted to increase up to ~2 for the a-$C_{0.6}H_{0.4}$ alloy.

a-C:H alloys have been modeled previously as composite media consisting of amorphous diamond-like, amorphous graphitic, amorphous polymeric, and void components[8,9]. A similar approach has been taken here but with two more components introduced: an olefinic and an amorphous mixed diamond-graphitic (d-g) component in which $C(sp^3)$ and $C(sp^2)$ atoms are bonded to each other.

The predicted probabilities P_i for the five amorphous components are shown listed in Table II for four alloys, starting with the a-$C_{0.6}H_{0.4}$ alloy at $T = 523$ K and following its simulated annealing up to a H-free a-C alloy at $T = 823$ K. For a-$C_{0.6}H_{0.4}$ at $T = 523$ K the dominant components are predicted to be polymeric and mixed d-g. The predicted probability P_{dia} for a C atom to be in the diamond-like component is ~9% while the olefinic and graphitic components have predicted probabilities of ~4% and ~1%, respectively. As the alloy is annealed, the polymeric component is converted to the d-g component as H is evolved, while the probabilities for the diamond-like, the graphitic, and the olefinic components remain almost constant. For the annealed a-C alloy at $T = 823$K the mixed d-g component is still dominant with the diamond-like component having the next highest probability. This annealed alloy is predicted to have $sp^3/sp^2 = 0.85$.

It is important to emphasize that, for $T > 0$ K, essentially no true graphitic component is predicted to be present, in disagreement with the predictions of Robertson et al[10]. Instead, the $C(sp^2)$ atoms are predicted to be present either in isolated olefinic pairs or in a non-aromatic mixed sp^3-sp^2 diamond-graphitic (d-g) phase. The mixed d-g phase corresponds to the type of bonding between $C(sp^3)$ and $C(sp^2)$ atoms which would occur in the interfaces between diamond-like and graphitic regions. These predictions are consistent with recent Monte Carlo calculations[11,12] which indicate that few of the rings in an a-C alloy consist of pure sp^2 carbon and instead that most of the rings contain both $C(sp^2)$ and $C(sp^3)$ atoms and are not flat. Also, the polymeric phase is predicted to be composed of essentially only $C(sp^3)$ atoms in typical a-C:H alloys.

Table II   Predicted probabilities P_i for C atoms to be in the five amorphous components present in four a-$C_x H_{1-x}$ alloys at different temperatures T.

Temp. (K)	x	$\frac{sp^3}{sp^2}$	P_{dia}	P_{gr}	P_{olef}	P_{polym}	P_{d-g}
523	0.60	2.02	0.092	0.011	0.035	0.456	0.405
623	0.65	1.83	0.099	0.008	0.049	0.393	0.451
723	0.80	1.26	0.109	0.016	0.044	0.211	0.620
823	1.00	0.85	0.112	0.032	0.036	0.000	0.821

3. PREDICTIONS FOR a-SiO_2:F

The possible bonds in a-SiO_2:F alloys (with bond energies in eV) include Si-O (4.82), Si-F (6.17), Si-Si (2.34), and O-F (1.98). The only possible reaction involving these four bonds is

$$Si-Si + O-F \leftrightarrow Si-F + Si-O, \qquad (6)$$
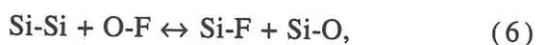
which has an interaction parameter $\Omega = +6.67$ eV and hence is highly exothermic in the forward direction. This result of the FEM shows clearly that Si-F and Si-O bonds are strongly favored by CO, that essentially no Si-Si or O-F bonds can be expected in typical a-SiO_2:F alloys, and that these alloys will typically be Si-rich, i.e. a-SiO_{2-x}:F.

The FEM also predicts that H and F atoms when present together in a-SiO_2 can eliminate each other from the network via the formation of HF(g), as expressed below in Eq. (7). When retained in the network, H and F will appear in Si-F and O-H bonds; see Eq. (8). Both of these reactions are strongly exothermic in the forward direction.

$$Si-H + O-F \leftrightarrow Si-O + H-F \qquad \Omega = +5.36 \text{ eV} \quad (7)$$

$$Si-H + O-F \leftrightarrow Si-F + O-H \qquad \Omega = +5.66 \text{ eV} \quad (8)$$

4. CONCLUSIONS

The FEM has been shown to provide a useful framework for predicting the bonds which are favored thermodynamically in amorphous network alloys. The effects of entropy are critical in a-C:H alloys while chemical ordering will dominate the bonding in a-SiO_2:F alloys.

5. ACKNOWLEDGEMENTS
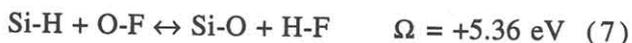
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