

## Structure and Electronic States in Disordered Systems

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We adopt the view that the structure of disordered systems is itself determined by the formation energy of structural deviations from an ideally bonded network. By developing an equilibrium statistical mechanical model for disorder we predict properties of electronic band tails, defects, defect densities of states, and impurity doping.

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In the study of solids the usual approach has been to obtain or assume a structure and then determine electronic states. This is particularly true in the case of disordered solids<sup>1</sup> even though the actual structure of these materials is not known in detail.

In this paper we present an equilibrium statistical mechanical model for disordered systems with covalent bonding. The central point is that the structure itself is determined by the formation free energy of deviations from an ideally bonded network and of local deviations in alloy composition. Such deviations induce features of the electronic density of states (DOS). We consider major features of the electronic structure—band tails, defect density of states, and doping—and compare with experimental results on *a*-Si:H and chalcogenide glasses.

We describe the effective ground state of an amorphous material as a perfectly bonded network, having optimal coordination, ideal bond lengths and bond angles, and uniform alloy composition. The networks of interest are taken to lie in three-dimensional manifolds and generally do not fit into flat three-dimensional space. However, at any finite temperature the thermally excited structural deviations enable a particular class of ideal networks to lie flat. This class of networks (temperature dependent) is the effective (degenerate) ground state of the material.<sup>2</sup> The elementary excitations of the amorphous ground state are both electronic and structural in nature. Generally there exists a temperature ( $T^*$ ) below which structural deviations are frozen. We assume that properties of material deposited or processed above  $T^*$  can be described by equilibrium statistical mechanics. We confine our discussion here to such material.

We assume the electronic density of states of the amorphous ground state (perfect networks) to have well-defined energy bands and gaps. This forms the background on which the contribution of structural deviations must be added.

**Electronic band tails.**—In the usual understanding of electronic band tails, the structure of the amorphous material is assumed given. Disorder causes local fluctuations in the potential experienced by electrons. These local fluctuations combine through random

statistics to form electronic bound states with a distribution of binding energies. Direct analysis of this model yields band tails having the form<sup>3</sup>  $\exp(a\epsilon^{1/2})$ , not the experimentally observed<sup>4,5</sup> simple exponential band tails. Modifications<sup>6</sup> of the theory have been developed to account for the discrepancy with experiment.

In our model, where the material structure is responsive to electronic states, the density of electronic states above the valence-band edge is determined by the energy required by the system to make a filled electronic state at an energy  $\epsilon - \epsilon_v$  from the valence band. Let this energy be  $F_v(\epsilon - \epsilon_v)$ ; then the valence-band tail decays as  $\exp[-F_v(\epsilon - \epsilon_v)/kT^*]$ . We can estimate the behavior of  $F_v(\epsilon - \epsilon_v)$  by using the relationship  $\epsilon = F[n] - F[n-1]$ , where  $F$  is the system energy and  $n$  is the number of electrons. We obtain

$$F_v(\epsilon - \epsilon_v) = (1 + s_v)(\epsilon - \epsilon_v),$$

where  $s_v$  is the fractional change in  $F[n-1]$  due to a structural deviation which raises the energy of the unoccupied state by  $\epsilon - \epsilon_v$ . While  $s_v$  need not be zero or independent of  $\epsilon - \epsilon_v$ , it is likely to have a magnitude less than or of order 1 and higher-order terms in  $\epsilon - \epsilon_v$  do not contribute over decades in the density of states for small values of  $kT^*$ . We thus obtain the valence-band DOS as

$$D_v(\epsilon) = \exp[-(\epsilon - \epsilon_v)/kT_v]; \quad T_v = T^*/(1 + s_v).$$

Similarly, the energy to make an unfilled state below the conduction band is  $F_c(\epsilon - \epsilon_c) = s_c(\epsilon_c - \epsilon)$ , leading to a conduction-band tail  $\exp[(\epsilon - \epsilon_c)/kT_c]$ , where  $T_c = T^*/s_c$ . For many systems, the same structural deviations are responsible for lowering of antibonding states and raising of bonding states. Thus, we write  $T_c = \alpha T_v$ , where  $\alpha$  is the proportionality between energy differences,  $\delta\epsilon_c = \alpha\delta\epsilon_v$ .

While the microscopic structure of amorphous materials is not known, the parameters  $s$  and  $\alpha$  are likely to be characteristic of structural variations in general and thus may be obtained from theoretical calculations such as of the electron-phonon coupling or electron-alloy composition coupling. For the case of *a*-Si:H, us-

ing a tight-binding model, we studied the effect of simple distortions on the band edges of crystalline silicon yielding  $\alpha \sim 0.5$ . The experimental exponential decay parameters of the valence and conduction bands in  $a$ -Si:H are<sup>4</sup>  $T_v = 500$  K,  $T_c = 300$  K, the ratio of which is reasonably correctly given by our result.

**Defect density of states.**—The density of electronic states introduced by defects such as wrongly coordinated atoms depends on their microscopic nature. Here we focus on the dangling bond in  $a$ -Si:H which is expected to have three charge states (+, 0, -). Because defects can be charged, the number of defects in equilibrium depends on the position of the Fermi energy ( $\mu$ ) at  $T^*$ .  $\mu$  is determined by material composition and the value of  $T^*$ . In this section we treat  $\mu$  as a parameter; in the following section its value is determined.

The contribution of dangling bonds to the DOS depends on their formation energy as a function of thermodynamic transition energies:  $F(\text{Si}_3, \epsilon(+/0), \epsilon(0/-))$ , where  $\epsilon(p/q)$  is the defect thermodynamic transition from charge  $p$  to  $q$ . Specifically the concentration of a particular dangling-bond type is

$$n(\text{Si}_3, \epsilon(+/0), \epsilon(0/-)) = n(\text{Si}) (2e^{-F/kT^*} + e^{-[F+\mu-\epsilon(+/0)]/kT^*} + e^{-[F-\mu+\epsilon(0/-)]/kT^*}),$$

where the second and third terms arise from defects which, at  $T^*$ , are charged positively and negatively, respectively. To illustrate simply the nature of the resulting density of states, we let the formation energy be weakly dependent on the transition energies, and let the effective correlation energy be small. The resulting density of states is shown in Fig. 1. This looks like an ordinary density of states with transition energies separated by an effective correlation energy. However, the two peaks arise from different dangling bonds, and material properties differ from positive- and negative-correlation-energy models. For example, defects with transitions below  $\mu$  are negatively charged and those above  $\mu$  are positively charged; however, the DOS does not change with occupation or excitation as a negative-correlation-energy system.<sup>7</sup>

A long-standing controversy<sup>7-9</sup> on the sign of the effective correlation energy of dangling bonds in  $a$ -Si:H has centered on seemingly contradictory detection of neutral dangling bonds while measurements show negative dangling bonds with transition energies below those of positive dangling bonds.<sup>7</sup> Thus, as described above, our model explains and is consistent with both experimental results. According to our model, it is also possible that two different defects with transitions (+/0) and (-/0) lead to different DOS below and above  $\mu$ . This may explain experiments on chalcogenide glasses which suggest an exponential DOS below  $\mu$  but also a peak 0.35 eV from  $\mu$ .<sup>5</sup> Finally, the exponential DOS below  $\mu$  may arise from conventional band tail states discussed above, or defect states, or both.

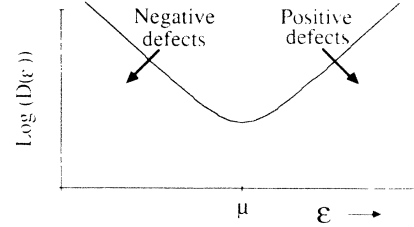


FIG. 1. Contribution of a single defect type to the electronic density of states in amorphous systems according to the model presented here for the case described in the text.

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**Doping.**—The discovery of doping<sup>10</sup> in  $a$ -Si:H was unexpected because of a random network's ability to satisfy local bonding requirements.<sup>1</sup> Suggestions for explaining the formation of fourfold-coordinated (incorrectly bonded) impurities have included defect interactions,<sup>11</sup> amorphous-network structural constraints,<sup>12</sup> and charged impurity deposition paired to dangling-bond formation.<sup>13</sup> Several of the ideas of Adler<sup>11</sup> and, particularly, Street,<sup>13</sup> discussed below, are suggestive of thermodynamic processes.

The equilibrium statistical-mechanics model we present provides explicit predictions of the functional behavior of the doping efficiency and the Fermi-energy shift and places definite restrictions on defect formation energies consistent with experiment.

The concentration of defects in equilibrium is

$$n(A_p^q) = n(A) \exp\{-[F(A_p^q) + q(\mu - \mu_0)]/kT\},$$

where  $n(A_p^q)$  is the concentration of atom  $A$  with coordination  $p$  and charge  $q$ ,  $n(A)$  is the total concentration of atom  $A$  assumed to be much larger than the defect concentration, and  $F(A_p^q)$  is the formation free energy at the reference Fermi energy  $\mu_0$ . The chemical potential is determined by charge neutrality:

$$\sum qn(A_p^q) = n(e^-) - n(h^+).$$

We assume for simplicity that above  $T^*$  the Fermi energy is far enough from the valence or conduction bands [with DOS  $D_v(\epsilon), D_c(\epsilon)$ ] to approximate electron occupation by the Boltzmann distribution. The Fermi energy and the defect concentrations are (assuming charges  $q = 0, \pm 1$ )

$$\begin{aligned} \mu - \mu_0 &= (kT/2) \ln\left[\frac{\sum n_0(A_p^+) + n_0(h^+)}{\sum n_0(A_p^-) + n_0(e^-)}\right], \\ n(A_p^q) &= \left[\frac{\sum n_0(A_p^+) + n_0(h^+)}{\sum n_0(A_p^-) + n_0(e^-)}\right]^{-q/2} n_0(A_p^q), \\ n(e^-) &= \left\{\left[\frac{\sum n_0(A_p^+) + n_0(h^+)}{\sum n_0(A_p^-) + n_0(e^-)}\right]^{1/2} n_0(e^-)\right\}, \end{aligned} \quad (1)$$

where a 0 subscript indicates concentrations at a reference Fermi energy  $\mu_0$ :

$$n_0(A_p^q) = n(A) \exp\{-[F(A_p^q)]/kT\},$$

$$n_0(e^-) = \int d\epsilon D_c(\epsilon) e^{-(\epsilon - \mu_0)/kT}.$$

*Dependence on dopant concentrations.*—For definiteness we consider *n*-type phosphorus doping,<sup>14</sup> which is the most studied. A Fermi-energy shift [Eq. (1)] occurs only if the number of positively charged fourfold-coordinated phosphorus atoms is greater than the number of positively charged dangling bonds and holes:  $F(P_4^+) < F(Si_3^+), \mu_0 - e_v$ . Thus, the dependence of the defect and electron concentration on dopant is

$$n(Si_3^-), n(e^-), n(P_4^+) \sim n(P)^{1/2}. \quad (2)$$

An experimentally observed square-root dependence of defect concentration on dopant concentration has been described by Street,<sup>13</sup> and is consistent also with the doping model he presented. However, according to our model, the creation of dangling bonds or other structural defects is not fundamentally necessary for the doping of amorphous material. Two limiting cases are possible: (1)  $n(Si_3^-) < n(e^-)$ , and (2)  $n(Si_3^-) > n(e^-)$ . Case (1) corresponds to  $F(Si_3^-) > e_c - \mu_0$  and is reminiscent of a more usual doping mechanism where equilibrium is reached between electron concentration and ionized-impurity concentration. However, because of the defect formation energy, the Fermi energy does not follow the behavior of crystalline systems. The functional dependence of the Fermi-level shift on dopant is similar for both electron- and defect-dominant cases. Case (2) involves equilibrium primarily between charged impurities and intrinsic charged defects and parallels the model of Street.<sup>13</sup> Recent measurements of excess electrons<sup>13</sup> indeed favor a larger concentration of dangling bonds than of excess electrons.

Like the defect concentration, the Fermi-energy dependence on dopant concentration is determined explicitly:

$$\mu - \mu_0 \sim (kT/2) \ln n(P). \quad (3)$$

To compare with experiment we must include the temperature dependence of  $\mu$  below the freezing temperature ( $T^*$ ). Below  $T^*$  only electronic equilibrium can be achieved (DOS is fixed). The contribution of defects to the DOS is determined by defect densities at  $T^*$ . As a function of impurity concentration three regimes occur. At low doping levels,  $n(e^-) < n(Si_3^0)$ ,  $\mu$  rises as  $\sim n(P)^{1/2}$  due to the neutral dangling-bond DOS. At intermediate doping levels  $\mu$  rises logarithmically as  $(kT/2) \ln[n(P)]$  (the coefficient varies with

TABLE I. Defect formation energies from thermodynamic model analysis of experimental results.  $\mu_0$  is 0.6 eV below the conduction band.

Defect	Formation energy (eV)
$Si_3^0$	0.7
$Si_3^-$	$0.7 - (\mu - \mu_0)$
$P_4^0$	0.5
$P_4^+$	$0.0 + (\mu - \mu_0)$

temperature as  $kT/2$  and is not fixed at  $kT^*/2$ . At high doping levels  $\mu$  saturates because it rises into the  $P_4$  transition (+/0) and  $n(P_4^+) \sim n(P)^{1/2}$  [Eq. (2)]. These results are consistent with measurements of LeComber and Spear<sup>10</sup> on the dependence of conductivity on doping.

*Compensation.*—In the model presented here, counterdoping always increases doping efficiency. A partially or totally compensated semiconductor, where doping concentrations are controlled to maintain a particular Fermi energy, has constant doping efficiency independent of concentration. For the minority dopant, the approximation of small defect concentration can break down and appropriately corrected formulas apply (yielding nearly 100% counterdoping efficiency). Several experimental results on compensated systems<sup>13</sup> confirm the greater doping efficiency predicted by our model. Directly changing the Fermi energy at  $T^*$  by annealing under applied voltage improves doping efficiency<sup>15</sup> and device performance,<sup>16</sup> consistent with our predictions for changes in defect concentration and doping efficiency.

*Defect formation energies.*—Interpreted through our model, experimental measurements of a variety of doped- and undoped-material properties yield values for sums or differences of defect formation energies and electron excitation energies. Results are summarized in Table I. The following measurements were used to determine the formation energies of  $Si_3^0, Si_3^-, P_4^+, P_4^0$ , assuming a freezing temperature of<sup>15</sup>  $\sim 425$  K: (1) neutral dangling-bond concentration<sup>17</sup> (in intrinsic material)  $n(Si_3^0)/n(Si) \sim 10^{-7}$ , (2) ratio of concentrations of doping-induced electrons and dangling bonds<sup>12</sup>  $n(e^-)/n(Si_3^-) = 10^{-1}$ , (3) doping efficiency<sup>13</sup>  $n(Si_3^-)^2/n(P)n(Si) \sim 10^{-7}$ , and (4)  $P_4$  electron transition energy<sup>13</sup>  $\epsilon(P_4; +/0) \sim \epsilon_c - 0.1$  eV. We note that the formation energy of the neutral dangling bond is not too far from simple model estimates<sup>18</sup> of 1.3 eV or realistic calculations of 0.9 eV per dangling bond for a vacancy in crystalline silicon.<sup>19</sup>

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*Note added.*—Additional evidence for defect reactions has been recently found in undoped *a*-Si:H.<sup>20</sup>

<sup>1</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979), 2nd ed.

<sup>2</sup>The "effective ground state" is a convenient construction which is ultimately not essential to our ensemble theory. While one possible image is a continuous random network, this is not at all required; energetics determine both the finite-temperature and extrapolated "ground-state" ensembles. Aside from the continuous random network, other models are possible and should be relevant for a variety of materials. Examples include a restricted-microstructure ensemble or a unique ground state. Even in cases of a unique "effective ground state" it may not lie in a flat manifold. See also D. R. Nelson and M. Widom, *Nucl. Phys. B* **240** [FS12], 113 (1984); R. Mosseri, D. P. DiVincenzo, J. F. Sadoc, and M. H. Brodsky, *Phys. Rev. B* **32**, 3974 (1985).

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<sup>7</sup>David Adler, *Sol. Cells* **9**, 133 (1983), and in *Optical Effects in Amorphous Semiconductors*, edited by P. C. Taylor and S. G. Bishop, AIP Conference Proceedings No. 120 (American Institute of Physics, New York, 1984), p. 70.

<sup>8</sup>See R. A. Street and D. K. Biegelsen, in *The Physics of Hydrogenated Amorphous Silicon*, edited by J. D. Joannopoulos and G. Lucovsky, Springer Topics in Applied Physics Vol. 55 (Springer-Verlag, New York, 1984), p. 195; Z. Vardeny and J. Tauc, *Phys. Rev. Lett.* **54**, 1844 (1985).

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<sup>10</sup>P. G. LeComber and W. E. Spear, in *Amorphous Semiconductors*, edited by M. H. Brodsky, Springer Topics in Applied Physics Vol. 36 (Springer-Verlag, New York, 1979), p. 251.

<sup>11</sup>David Adler, *Phys. Rev. Lett.* **41**, 1755 (1978).

<sup>12</sup>J. C. Phillips, *Phys. Rev. Lett.* **42**, 1151 (1979).

<sup>13</sup>R. A. Street, *Phys. Rev. Lett.* **49**, 1187 (1982), and *J. Non-Cryst. Solids* **77**, 1 (1985); R. A. Street, J. Kakalios, and T. M. Hayes, to be published.

<sup>14</sup>Interesting differences between arsenic and phosphorus doping (Ref. 11) suggest that different doping mechanisms apply. It would be interesting to see whether a higher deposition temperature would lead to equilibration of arsenic and change its doping behavior. We also note that the difficulty in the doping of chalcogenides can be explained by the low formation energies (Ref. 4) of intrinsic charged defects, in addition to the standard negative-correlation-energy argument.

<sup>15</sup>D. V. Lang, J. D. Cohen, and J. P. Harbison, *Phys. Rev. Lett.* **48**, 421 (1982).

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<sup>17</sup>Z. E. Smith and S. Wagner, *Phys. Rev. B* **32**, 5510 (1985); this is consistent with their analysis only for the monomolecular recombination model so that  $F(\text{Si}_3) \sim e_g - 1.0$  eV describes the dynamical equilibrium generation and annealing kinetics.

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