Band Tails, Entropy, and Equilibrium Defects in Hydrogenated Amorphous Silicon

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A method of calculation of the equilibrium defect concentration for a disordered semiconductor with exponential band tails is presented. For hydrogenated amorphous silicon, the entropy-of-mixing term in the expression for the free energy is found by consideration of the dangling bonds as an impurity in a system of bonding orbitals. These calculations are compared with experimental results.

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It has long been recognized that the entropy gained when a defect (structural or compositional) is introduced into a perfect solid leads to a lower limit on how free of defects the solid can be made. Two familiar examples are the minimum impurity density of "pure" materials,[1] and the minimum density of vacancies or interstitials (Schottky and Frenkel defects, respectively) in pure crystals.[2] Intuitively, we expect the gain in entropy to be large when we go from a completely ordered system to a slightly disordered one, with the gain diminishing as the system becomes increasingly disordered. Perhaps for this reason, the approaches taken thus far to the understanding of defects in a highly disordered solid such as hydrogenated amorphous silicon (*a*-Si:H) have never explicitly included entropy considerations. Recent experimental work indicates that defects (in particular, the density of neutral deep states usually identified as Si dangling bonds[3]) in both doped[4] and undoped[5] *a*-Si:H exhibit many of the characteristics of an equilibrium system. In this Letter, we will consider the equilibrium between these broken bonds and bonding (valence band) orbitals in *a*-Si:H. Including the entropy-of-mixing term in the expression for the free energy allows us to calculate values for the thermodynamic equilibrium dangling-bond density consistent with experimental results, given only the sharpness of the valence-band–tail density of states and the position of the dangling bond in the band gap.

Following the development of Kittel and Kroemer,[1] consider a system of N bonds, of which M are broken (producing $2M$ dangling bonds), such that the fraction of bonds which have been broken is $x \equiv M/N$. The system entropy S, computed from the number of possible arrangements of randomly distributed dangling bonds, is given by

$$S \cong -kNx\ln x \tag{1}$$

for $x \ll 1$, where k is Boltzmann's constant. If the breaking of a bond entails a cost to the system of energy U_B, the free energy is given by

$$F(x) = xNU_B + kTNx\ln x, \tag{2}$$

which is minimized at the concentration

$$x^*(T) = e^{-1}e^{-U_B/kT}. \tag{3}$$

Following the results of Heine,[6] we approximate the difference in total energy U_B as the difference in the sum over the occupied one-electron energy levels. We further assume that the Si core levels are essentially the same in the fourfold and threefold (but still sp^3) bonded states. Electron paramagnetic resonance hyperfine studies[7] indicate that the dangling bond in *a*-Si:H is strongly *p*-like in character and places only $\simeq 50\%$ of its charge density on the central atom; both results suggest that core-level shifts are small. Consequently, we approximate U_B as just the difference in electronic energy between the singly occupied dangling bonds and two electrons in the valence-band bonding orbital originally joining two Si atoms. Recently, Stutzmann[8] suggested that the light-induced creation of neutral dangling-bond defects[9] (with electronic states located at energy E_{D^0} above the valence-band mobility edge) associated with the Staebler-Wronski effect[10] is due to the conversion of band-tail orbitals $\simeq 0.3$ eV into the mobility gap; then $U_B = 2E_{D^0} - 0.6$ eV.

However, it is more plausible that the bonding orbitals which are most likely to be broken are those associated with valence-band–tail states highest in the mobility gap; these are the most strained bonds. This affects our determination of U_B. Consider a material with valence-band–tail density of states decaying exponentially from its mobility-edge value[11] $N_V^\mu \simeq 4\times 10^{21}$ cm^{-3} eV^{-1} with characteristic energy E_u, shown in Fig. 1. Starting with the highest energy states, we convert valence-band–tail states into dangling bonds until we have created N_{D^0} states; the conversion process stops at energy E^*, defined such that

$$N_{D^0} = \int_{E^*}^{\infty} N_V^\mu e^{-E/E_u}\,dE = N_V^\mu E_u e^{-E^*/E_u}. \tag{4}$$

We can solve Eq. (4) for E^*,

$$E^* = E_u \ln(N_V^\mu E_u/N_{D^0}). \tag{5}$$

Now U_B is negative for the valence-band–tail states with $E > E_{D^0}$ (region A in Fig. 1), and positive for $E < E_{D^0}$; but as the integral in Eq. (4) is dominated by the states within E_u of E^*, the value of U_B which ultimately determines the dangling-bond concentration is just

$$U_B \cong 2E_{D^0} - 2E^*. \tag{6}$$

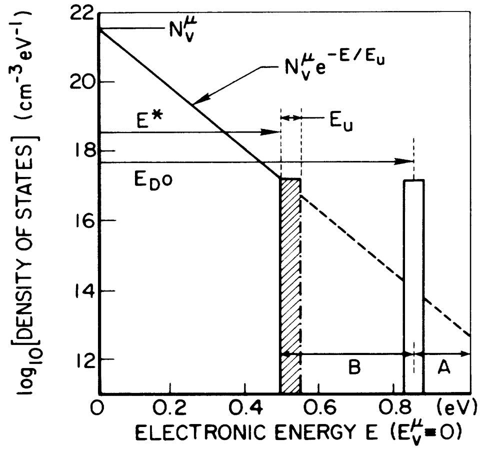

FIG. 1. Density of states in the valence-band–tail region. Weak bonding orbitals at one-electron state energies greater than E^* (regions A plus B, with area equal to the shaded region between E^* and E^*+E_u) are converted into dangling-bond states (at energy E_{D^0}).

Once U_B is known, Eq. (3) can be used to find x^*, and then the dangling-bond concentration is given by

$$N_{D^0}^{\mathrm{eq}}(T)=4N_{\mathrm{Si}}x^*(T), \tag{7}$$

where $N_{\mathrm{Si}}\cong 4\times 10^{22}$ cm^{-3} is the atomic density of Si. Combining Eqs. (3)–(7) yields

$$N_{D^0}=[4N_{\mathrm{Si}}e^{-1}\exp(-2E_{D^0}/kT)]^{kT/(2E_u+kT)}[N_V^\mu E_u]^{2E_u/(kT+2E_u)}. \tag{8}$$

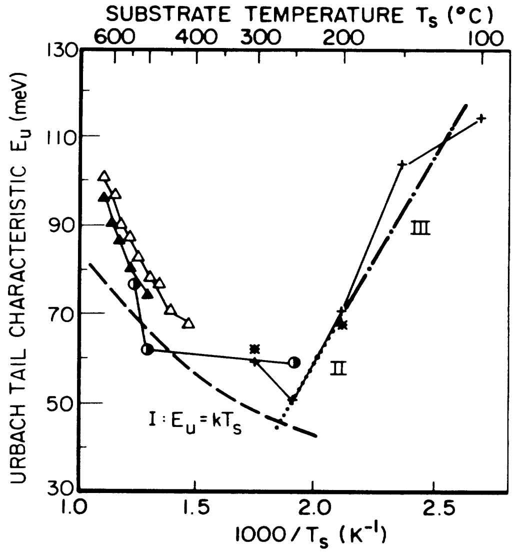

FIG. 2. Valence-tail (Urbach) parameter E_u vs sample preparation temperature T_s. Experimental data from Refs. 16 (crosses), 17 (asterisks), 18 (half-filled circles), and 19 (open and filled triangles). Curves marked I, II, and III represent the three regions used in the calculation of Fig. 3.

E_u, the valence-band–tail parameter, is approximately equal to the characteristic (Urbach) energy of optical absorption[12]; for good-quality a-Si:H, $E_u\cong 50$ meV. If we take[13] $E_{D^0}\cong 0.85$ eV (all energies hereafter are referenced to the valence-band mobility edge $E_V^\mu\equiv 0$), then Eq. (8) predicts that the dangling-bond density at the growth temperature ($T_s\cong 520$ K) is 1.2×10^{16} cm^{-3}. The defect density observed at room temperature, for many systems, reflects the "freeze in" of defects present at growth,[2] and depends on the rate at which the sample is cooled from the growth.[14] In a-Si:H, calculations[5] suggest that commonly used cooling rates lead to $N_{D^0}(300\ \mathrm{K})\cong \frac{1}{2}N_{D^0}(T_s)$. Put another way, the T to be used in Eq. (8) should be the "fictive" or freeze-in temperature T_F; data indicate that T_F is approximately 500 K in undoped films (grown at 540 K)[5] and lower in doped films.[4] Thus Eq. (8) predicts a room-temperature observed dangling-bond density of approximately 6×10^{15} cm^{-3}, in excellent agreement with experiment.

It has recently been suggested[15] that the band-tail densities of states themselves reflect a structural equilibrium such that $E_u\propto kT_F$. Indeed, in the case of the best a-Si:H (grown at $T_s\simeq 540$ K), $E_u\cong kT_F$. If this is substituted into Eq. (8), a particularly simple expression results:

$$N_{D^0}(T_F)=C_1(kT_F)^{2/3}\exp(-2E_{D^0}/3kT_F), \tag{9}$$

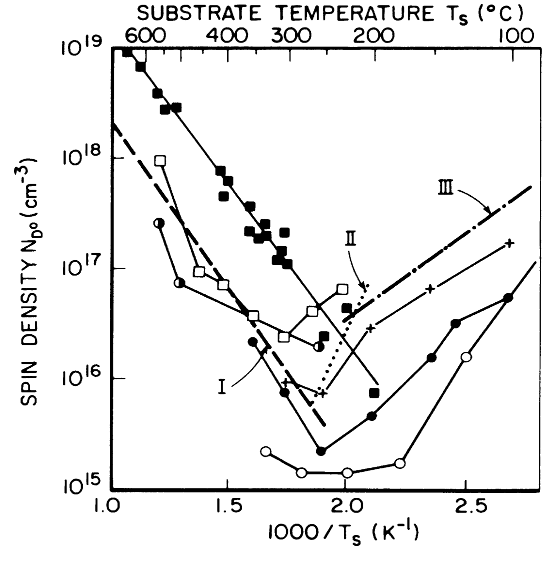

FIG. 3. Neutral dangling-bond density measured at room temperature vs sample preparation temperature T_s. Experimental data from Ref. 16 (crosses), 18 (half-filled circles), 20 (filled squares), 23 (open and filled circles), and 24 (open squares). Lines I (dashed), II (dotted), and III (dashed-dotted) are calculated with use of the E_u of Fig. 2.

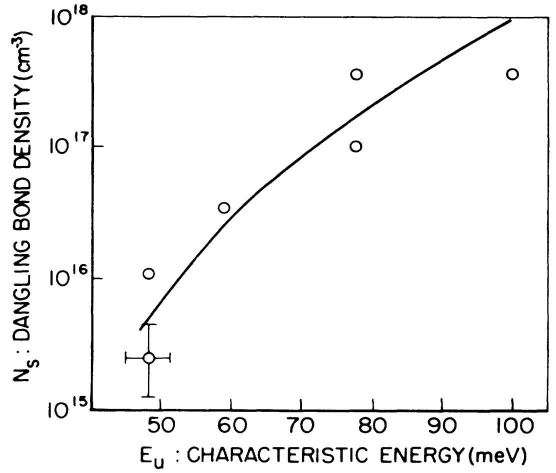

FIG. 4. Dangling-bond density N_s vs valence-band–tail parameter E_u at $T=503$ K. Data are for a series of a-Si:H films grown at this substrate temperature with a range of glow-discharge deposition powers (Ref. 25); solid curve is the theoretical curve [Eq. (8)] assuming nearly complete freeze-in of the defect density present at the growth temperature.

have linked the motion of hydrogen to the rate at which equilibrium is established, and so it is reasonable to assume that as hydrogen content is reduced (by evolution of H or growth at elevated temperatures), T_F rises. In Fig. 2 we show E_u vs $1/T$ data from several authors.[16-19] For $T_s > 250\,°\mathrm{C}$, it is seen that $E_u \cong kT_F \cong kT_s$. This is consistent with the theoretical result of Cody *et al.*[19] In such a regime, Eq. (9) predicts that a plot of $N_{D^0}(T_s)$ should be exponentially activated with an activation energy of $\frac{2}{3} E_{D^0} = 0.57$ eV. This is exactly the experimental result of Branz *et al.*,[20] and agrees with the result (0.55 eV) from kinetics arguments[5] as well.

a-Si:H films produced at $T_s < 250\,°\mathrm{C}$ are usually strongly inhomogeneous,[21] and $E_u \gg kT_s$. In terms of the film growth processes, the growth constituents lack the surface mobility to find the optimal sites to minimize total energy—not all possible arrangements can be explored.[22] In this situation, only the valence states with $E > E_{D^0}$ (shown in Fig. 1 as region A) can be guaranteed to convert into dangling bonds. Then we expect

$$N_{D^0} \geq E_u N_V^{\mu} \exp(-E_{D^0}/E_u). \qquad (10)$$

Thus we can identify three regimes of growth temperature and the corresponding expression for $N_{D^0}(T_s)$: region I ($T_s > 300\,°\mathrm{C}$)—Eq. (9); region II ($300 > T_s > 200\,°\mathrm{C}$)—Eq. (8); and region III ($T_s < 200\,°\mathrm{C}$)—Eq. (10). Calculated N_{D^0} values are shown in Fig. 3, and compared with published room-temperature measurements.[16,18,20,23,24] Deposition temperature is, of course, not the only parameter affecting film properties. For example, sitting at one deposition temperature and increasing the deposition power (and hence growth rate) has the effect of reducing adatom surface range; hence the bonds are more strained, the band tails are wider, and the deep-defect density is increased.[25] Published results for a series of samples grown at 230 °C are compared with the prediction of Eq. (8) in Fig. 4.

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[1] See, for example, C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, San Francisco, 1980), 2nd ed., pp. 78–80.

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[3] We adopt the conventional identification of the paramagnetic deep defect as a dangling Si bond; the work presented here could be adapted to the suggestion [S. Pantelides, Phys. Rev. Lett. **57**, 2979 (1986)] that this defect be identified as an *over*coordinated Si atom in just the same way that the analysis of Schottky defects is applied to this understanding of Frenkel defects.

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[22] In the preceding discussion (for $T \gtrsim 200\,^\circ\mathrm{C}$), we have assumed that the weak bonds which are broken to make pairs of dangling bonds are randomly distributed. In inhomogeneous material, these sites would presumably not be randomly distributed. Lacking unambiguous experimental evidence to the contrary, our analysis for homogeneous material assumes that the dangling bonds remain in pairs; should they be able to diffuse away from one another, the entropy term [Eq. (1)] is doubled and the resulting equations adjusted by replacing "kT" with "$2kT$."

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