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## Band Tails in Hydrogenated Amorphous Silicon and Silicon-Germanium Alloys

Samer Aljishi,<sup>(a)</sup> J. David Cohen,<sup>(b)</sup> Shu Jin,<sup>(c)</sup> and Lothar Ley<sup>(c)</sup>

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1,  
7000 Stuttgart 80, Federal Republic of Germany*

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The temperature dependence of the conduction- and valence-band tails has been determined by total-photoelectron-yield spectroscopy for doped and undoped *a*-Si:H and *a*-SiGe:H alloys. We find that all films possess purely exponential conduction- and valence-band-tail densities of states; however, the characteristic energy of the conduction-band tail increases much more rapidly with temperature than that of the valence-band tail. This indicates that the conduction-band tail is considerably more susceptible to thermal disorder than to structural disorder, whereas the reverse holds for the valence-band tail.

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The origin of exponential absorption (Urbach) edges, observed in a large host of crystalline and amorphous semiconductors, is one of the more intriguing problems in basic semiconductor physics. It is generally accepted that its shape largely derives from the exponential falloff into the gap of the conduction- and valence-band densities of states (DOS) which result from static and dynamic site disorder in the material.<sup>1-3</sup> In the (hydrogenated) amorphous elemental semiconductors the existence of exponential band tails has been well demonstrated;<sup>4,5</sup> however, most of what is known about their energy distributions over a range of temperatures has been taken from the analysis of subgap optical-absorption measurements<sup>1,6</sup> which really represent a convolution of both band tails together.

Recently, Winer and co-workers<sup>5,7</sup> showed that total-yield-photoelectron spectroscopy can be used to measure separately the energy distribution of valence- and conduction-band-tail states in *n*-type amorphous silicon. In this Letter, we examine the temperature (*T*) dependence of such total-yield spectra in a wide range of doped and undoped *a*-Si:H and *a*-SiGe:H alloys to directly obtain the *energy and temperature* dependence of both the conduction- and valence-band tails in these semiconductors. Thus, for the first time, we may accurately deduce the role of *thermal* and *structural* disorder on the shallow localized gap state distributions for each band-tail region separately and obtain results which contrast markedly with earlier conclusions.

Hydrogenated amorphous silicon (*a*-Si:H) and silicon-germanium alloys (*a*-SiGe:H) were deposited by standard rf (13.56 MHz) glow-discharge decomposition of silane, germane, and hydrogen gas mixtures in an ultrahigh-vacuum reactor. Standard deposition parameters were employed.<sup>8</sup> Within one minute of the termination of growth, the films were transferred under  $2 \times 10^{-10}$  Torr UHV to the analysis chamber for Kelvin-probe and total-yield measurements. Prior to such measurements all films were annealed at 250°C and then cooled slowly to room temperature.

The Kelvin-probe technique allows the determination of the surface Fermi-level position  $E_F$  to within  $\pm 2$  meV by measuring the contact potential difference with respect to a vibrating metal reed of known work function.<sup>5,7</sup> In total-yield spectroscopy, incident uv illumination ( $3.5 \text{ eV} < \hbar\omega < 6.4 \text{ eV}$ ) excites electrons from occupied states in the mobility gap to energies lying just above the vacuum level  $E_{\text{vac}}$ . As the optical excitation energy  $\hbar\omega$  is scanned the total number of photoemitted electrons is counted. The ratio of the number of emitted electrons to the incident photon flux defines the photoelectric yield  $Y(\hbar\omega)$ . In amorphous solids,  $Y(\hbar\omega)$  is simply proportional to a convolution between the occupied DOS,  $g_{\text{occ}}$ , and a final (unoccupied) DOS above  $E_{\text{vac}}$ ,  $g_{\text{vac}}$ , weighted by the square of the average dipole matrix element. Because both the transition matrix elements and  $g_{\text{vac}}$  are well known, we may quite accurately determine the occupied DOS distributions by differentiating the yield data with respect to  $\hbar\omega$ . To agree with conventional photoemission data, we normalize the occupied DOS to a value of  $10^{22}$  states/eV cm<sup>2</sup> at a photon energy of 6.2 eV.<sup>5</sup>

In an earlier study we demonstrated that for a fixed optical energy  $E$  the occupied DOS a few tenths of an eV above  $E_F$  varies with temperature as  $\exp[-(E - E_F)/k_B T]$ ; that is, precisely as expected from thermal occupation statistics.<sup>9</sup> Hence, it is justified to divide  $g_{\text{occ}}$  by the Fermi-Dirac occupation function to obtain the *total* DOS,  $g(E)$ , extending several tenths of an eV above  $E_F$ . This offers the unique opportunity to observe *both* the valence- and conduction-band tails in the same sample provided (1)  $E_F$  is sufficiently close to the conduction-band edge to provide a measurable occupation of these states, and (2) the photoemission spectra are not appreciably broadened by extraneous sources such as surface-potential variations, inelastic scattering of the photoelectrons, etc. Because of the very large dynamic range of our yield measurements the first condition is easily satisfied in all of our *n*-type doped samples and even some intrinsic films.<sup>5,9</sup> Regarding the second condition,

we observe that below 190 K our spectra fall off exponentially (above  $E_F$ ) with a slope of 0.015 eV. This, we believe, establishes a lower limit for resolving the actual energy variations of  $g(E)$ . Further, because the dominant mechanisms for inelastic scattering (primarily the emission of optical phonons at 57 meV) are nearly independent of temperature, these could not account for the  $T$ -dependence effects we observe.

The occupied DOS distributions for several temperatures are shown for a 1000-ppm  $\text{PH}_3$ -doped  $a\text{-Si:H}$  film in Fig. 1. The spectra display several notable features including a clear shift in the valence-band edge towards  $E_{\text{vac}}$  with increasing temperature (reflecting the well-known decrease of the optical gap with  $T$ ), a *temperature-independent* deep-defect band located roughly 5.1 eV below  $E_{\text{vac}}$ , and an electron density which *decreases continuously* from the valence-band edge (located near 5.7 eV) with decreasing optical energy. In particular, these data indicate that  $g_{\text{occ}}$  decreases continuously above  $E_F$  even for  $T > 500$  K. Because the gap-state density is believed to increase exponentially toward the conduction-band mobility edge  $E_C$  with a characteristic energy of 35 meV or less, it has been assumed that the occupied DOS would exhibit a peak above  $E_F$  at moderate temperatures ( $T > 400$  K).<sup>10</sup> Indeed the assumed presence of such a peak has been incorporated into recent attempts to model the dc conductivity and to account for the observed variation in the activation energies of conduction for  $T > 450$  K.<sup>10,11</sup>

The reason that no such peaks appear in our deduced

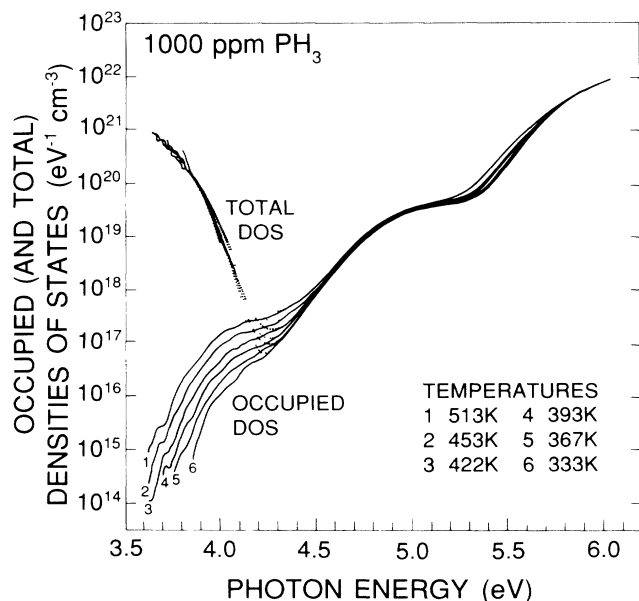


FIG. 1. Occupied (solid curves) and total densities of states (dotted curves) determined from photoelectric-yield spectra for a 1000-ppm  $\text{PH}_3$ -doped  $a\text{-Si:H}$  sample at six different temperatures. The Fermi-level positions determined by the Kelvin-probe measurements all lie near 4.2 eV.

$g_{\text{occ}}$  is made apparent when these distributions are divided by the Fermi occupation function to obtain the total DOS distributions. These are plotted as the dotted lines in Fig. 1. We find, indeed, that for all temperatures, the conduction-band-tail DOS is exponential in energy from slightly above  $E_F$  up to approximately 0.3 eV above  $E_F$ . However, the total DOS spectra also exhibit a previously unexpected and significant *broadening* with temperature. We define the characteristic energy  $E_{0C}$  of the conduction-band tail (CBT) as

$$E_{0C} \equiv [\partial \ln g(\hbar\omega) / \partial (-\hbar\omega)]^{-1}. \quad (1)$$

The condition that a peak appear above  $E_F$  in the occupied DOS at temperature  $T$  is that  $k_B T > E_{0C}$ . As a result of the significant broadening of  $E_{0C}$  as  $T$  is increased, however, this condition is never achieved for this or any other sample studied.

Figure 2(a) displays the full variation of  $E_{0C}$  with  $T$  for our 1000-ppm P-doped sample as well as for a 50-ppm P-doped sample and an undoped  $a\text{-Si:H}$  film. We similarly define and display the  $T$  dependence of the valence-band-tail (VBT) characteristic energy  $E_{0V}$  in Fig. 2(b) for several undoped and B-doped  $a\text{-Si:H}$  films. Figure 2 thus reveals a sharply contrasting behavior between the two band tails; namely, *while  $E_{0C}$  increases rapidly with temperature,  $E_{0V}$  remains comparatively constant.*

The characteristics of  $E_{0C}$  vs  $T$  fall into two regimes.

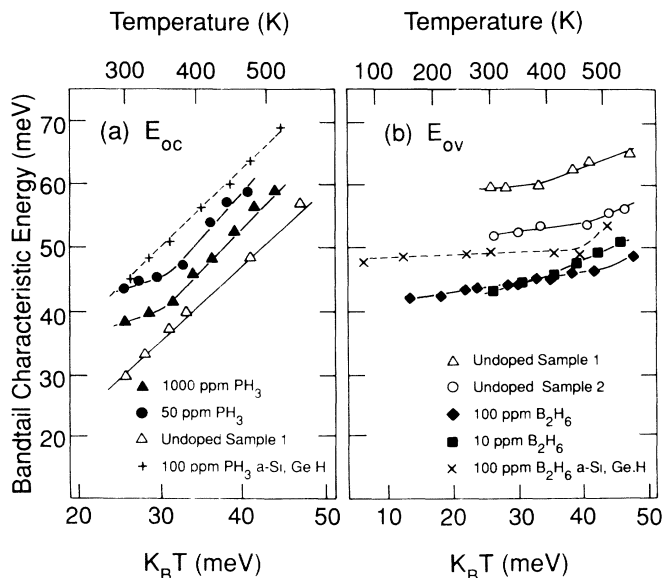


FIG. 2. (a) Characteristic energy  $E_{0C}$  vs temperature for the exponential region of the conduction-band tail determined from the total DOS curves such as those displayed in Fig. 1. Results are given for several  $a\text{-Si:H}$  samples (solid curves) plus one  $a\text{-SiGe:H}$  sample (dashed curve) with  $E_{04} = 1.6$  eV. (b) Characteristic energy  $E_{0V}$  vs temperature for the valence-band tail for several  $a\text{-Si:H}$  samples (solid curves) plus one  $a\text{-SiGe:H}$  sample (dashed curve) again with  $E_{04} = 1.6$  eV.

Below a temperature  $T_C^*$ ,  $E_{0C}$  is approximately constant ( $E_{0C}^*$ ) while above  $T_C^*$ ,  $E_{0C}$  increases *linearly* with thermal energy  $k_B T$  with a slope that lies in a range between 1 and 2 for different samples. In addition, the extrapolation of the linear portion of  $E_{0C}(T)$  intersects the origin ( $E_{0C}=0$  at  $T=0$ ). Thus, the functional form of  $E_{0C}$  is

$$E_{0C} = \begin{cases} E_{0C}^*, & T < T_C^*, \\ E_{0C}^* T / T_C^*, & T > T_C^*. \end{cases} \quad (2)$$

For the *n*-type films,  $T_C^*$  lies in the range 300–360 K. For the undoped sample we could not determine  $E_{0C}^*$  and  $T_C^*$  due to the much lower thermal occupation of CBT states for  $T \leq 300$  K.

By contrast, the valence-band-tail DOS in these samples appears to be little affected by temperature [Fig. 2(b)]. The value of  $E_{0V}$  increases by about only 6 meV between 80 and 550 K, which agrees generally with the increase exhibited by the Urbach absorption edge (with characteristic energy  $E_U$ ) over this same range of temperatures.<sup>1,12</sup> Indeed, one expects  $E_U$  to closely agree with the value of  $E_0$  of the *broader* band tail. Previous studies have demonstrated that one can fit such a temperature variation by the expression

$$E_U = \frac{\hbar \omega_0}{2L} \coth \left[ \frac{\hbar \omega_0}{2k_B T} + \frac{1+X}{2} \right], \quad (3)$$

where  $L$  is a dimensionless coupling parameter, and  $\hbar \omega_0$  is a vibrational energy on the order of the Debye temperature ( $\hbar \omega_0 \sim k_B \Theta_D$ ). Thus, the first term in the square brackets gives the average thermal disorder energy due to the excitation of phonon modes, while  $X$  expresses the contribution from *structural* disorder. This equation can be obtained from elementary considerations of the influence of disorder on localized-state energies<sup>1,2,13</sup> and has also recently been established as part of a more detailed theory by Grein and John.<sup>3</sup>

Because of the well documented large susceptibility of the valence-band tail to bond-angle deviations, bonded hydrogen configurations, etc.,<sup>14</sup> the second term in Eq. (3) plays the dominant role in determining  $E_{0V}$  vs  $T$  as deduced by our data. Moreover, a plausible value of  $\hbar \omega_0$  of 35 meV is obtained from a fit of  $E_{0V}$  vs  $T$  by Eq. (3) for the 100-ppm  $B_2H_6$ -doped and -undoped samples [Fig. 2(b)]. On the other hand, applying such a treatment to the  $E_{0C}$  vs  $T$  data [Fig. 2(a)] seems much less satisfactory. First, we find that the role of structural disorder on the CBT DOS must be nearly zero while the thermal component must be much larger. Given the larger susceptibility of the VBT states to disorder it is somewhat difficult to explain this much stronger coupling to thermal disorder for the conduction-band tail. Second, the rapid linear increase of  $E_{0C}$  with  $T$  over our temperature range implies that  $\hbar \omega_0 \leq 14$  meV for all three films. Finally, such a treatment fails completely to

reproduce the abrupt change in slope at  $T_C^*$  exhibited in the  $E_{0C}$  temperature dependence.

The experimental results for  $E_{0C}$  vs  $T$  actually agree much more closely with calculations by Bar-Yam and co-workers<sup>15,16</sup> which derive the temperature dependence of the exponential band-tail characteristic energies from a thermodynamic ensemble theory of defect dynamics in *a*-Si:H. In that model, the DOS is dictated by thermodynamic equilibrium so that gap states are formed according to the free-energy cost of creating deviations from an ideally bonded network. Such a treatment naturally leads to exponential band tails, a linear dependence of  $E_{0C}$  with  $T$ , and a characteristic temperature  $T^*$  below which the thermal deviations are “frozen in.” This exactly mimics the observed temperature dependence expressed in Eq. (2). The value of  $T^*$  is to a degree proportional to the type and extent of disorder.<sup>15</sup> For the *n*-type films measured, we would thus infer that the conduction-band tail exhibits a freeze-in temperature  $T_C^*$  which falls between 300 and 360 K. In the undoped films, for reasons discussed above, we can only establish that  $T_C^* \lesssim 300$  K. However, our results would be quite consistent with a limiting value of  $E_{0C}^*$  near 25 meV, agreeing with values obtained below 250 K for intrinsic samples by time-of-flight measurements.<sup>4</sup>

Adopting such a picture, however, implies once again a fundamental difference between conduction- and valence-band-tail states. That is, the former appear to equilibrate at relatively low temperatures, but this apparently does *not* occur until much higher temperatures for the valence-band tail. Indeed, equilibrium arguments have been used to establish a direct relation between the distribution of VBT states and that of the midgap coordination defects in *a*-Si:H.<sup>17</sup> This is consistent with our results since the deep-defect band, like the distribution of VBT states, varies only slightly over the temperature range studied. Thus we must infer that distinctly different equilibration kinetics govern states in different regions of the mobility gap.

The DOS in *a*-SiGe:H alloys was also investigated. Figure 3 shows the total DOS distribution across the entire gap at several temperatures for a 100-ppm  $PH_3$ -doped *a*-SiGe:H alloy film with a 1.4-eV optical (Tauc) gap ( $E_{04}=1.6$  eV). As in *a*-Si:H, both the conduction- and valence-band-tails DOS are purely exponential over several orders of magnitude. The temperature dependences of  $E_{0C}$  and  $E_{0V}$  (the dashed lines in Fig. 2) closely parallel those observed in *a*-Si:H. In contrast to our *a*-Si:H data, however, the extrapolation of the linear portion of the alloy  $E_{0C}(T)$  to zero temperature results in a *finite* intercept of approximately 11 meV (rather than a nearly zero intercept). This may be due to compositional inhomogeneities in *a*-SiGe:H alloys (as discussed by MacKenzie *et al.*<sup>18</sup>) which would appear macroscopically as a broadened band tail independent of other structural- or thermal-disorder effects.

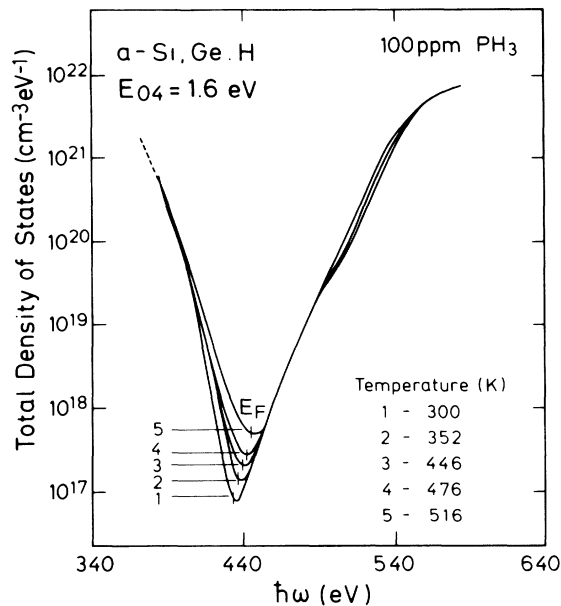


FIG. 3. Total densities of states at five temperatures obtained for a 100-ppm  $\text{PH}_3$ -doped  $a\text{-SiGe:H}$  sample. The Fermi-level positions are indicated.

Finally, we note that the band-tail DOS data presented here considerably alter the interpretation of the Urbach energies  $E_U$  as traditionally measured in these materials. Because it has been assumed that  $E_{0V}$  greatly exceeds  $E_{0C}$  at all temperatures, the behavior of  $E_U$  has been identified exclusively with the valence-band tail. However, we have demonstrated that this is not the case at high temperature where  $E_{0C}$  increases dramatically. Some recent measurements of  $E_U(T)$  in  $a\text{-Si:H}$  have found  $E_U$  to be relatively constant below 300 K, but increasing linearly with  $k_B T$  (with a slope of almost unity) above 350 K.<sup>19</sup> We strongly suggest that these  $E_U(T)$  data actually result from the observed temperature trends of  $E_{0C}$  and  $E_{0V}$  as indicated from our yield measurements in the low- and high-temperature regimes, respectively.

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<sup>(a)</sup>Current address: University of Bahrain, P.O. Box 32038, Bahrain.

<sup>(b)</sup>Permanent address: University of Oregon, Eugene, OR 97403.

<sup>(c)</sup>Current address: Institut für Technische Physik, Universität Erlangen, 852 Erlangen, Federal Republic of Germany.

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<sup>8</sup>SCCM total flow rate, 250 °C substrate temperature, and 40 mW/cm<sup>2</sup> power density. (SCCM denotes cubic centimeter per minute at STP.)

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