Thermal Equilibration of Surface Defects in Hydrogenated Amorphous Silicon-Germanium Alloys

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We measured the energy and density of near-surface defects in hydrogenated amorphous silicon, germanium, and their alloys by total-yield photoemission spectroscopy. The defects lie 0.56 eV above the valence-band edge, independent of alloy composition. The defect density at the clean surface is constant at $\sim 2\times10^{11}$ cm^{-2}. These values agree exactly with the equilibrium theory of dangling bonds, so that our experiments furnish the first evidence for thermal equilibration of semiconductor surface defects.

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Thermodynamic equilibration in hydrogenated amorphous silicon (*a*-Si:H) was first invoked by Street to explain the relation between dopant concentration in the gas phase and the incorporation of electrically active dopants at the growing film surface.[1] At the time, one of the outstanding questions in the defect physics of *a*-Si:H was the mechanism by which the density of dangling-bond defects in the bulk is controlled and limited. This question was answered by showing that at sufficiently high temperature the strained bonds in the film (which form the valence-band tail states) are in thermal equilibrium with the dangling bonds.[2-4] In this Letter we address the density of *surface* defects in *a*-Si:H and its alloys with germanium. It has been observed that although this density can be varied over a wide range, it cannot be brought below a level of 10^{11} to 10^{12} cm^{-2}.[5-7] In this work we demonstrate that in an ~4-nm-deep layer at the surface, the (near-surface) defects are in equilibrium with the valence-band tail. We verify the equilibration experimentally by total-yield photoelectron spectroscopy on *a*-Si:H, *a*-Si_x,Ge_{1-x}:H alloys, and *a*-Ge:H with optical gaps E_{04} (defined as the photon energy at which the optical absorption coefficient is equal to 10^4 cm^{-1}) ranging from 1.9 to 1.2 eV. Our experiments furnish the first proof for the establishment of thermodynamic equilibrium for a defect at a semiconductor surface.

The *a*-$\mathrm{Si}_x\mathrm{Ge}_{1-x}$:H alloys were deposited by conventional rf glow discharge from mixtures of silane, germane, and hydrogen. The $\mathrm{GeH_4/SiH_4}$ ratio was varied continuously to obtain material spanning the full composition range from nonalloyed *a*-Si:H to *a*-Ge:H. The hydrogen-dilution ratio (flow rate of $\mathrm{H_2}$ to flow rate of $\mathrm{SiH_4+GeH_4}$) was kept constant at 5. The films were grown to a thickness of typically 500 nm. Within a minute after termination of growth the films were transferred, under ultrahigh vacuum, from the growth chamber to the analysis chamber (base pressure $<2\times10^{-10}$ Torr) for the Kelvin-probe and photoemission measurements.

In total-yield photoemission spectroscopy, spectrally resolved ultraviolet light (with photon energy from 3.5 to 6.4 eV) is applied to excite electrons from occupied states to the vacuum level. As the photon energy is scanned, the total number of photoemitted electrons is counted. The ratio of the number of collected photoelectrons to the incident photon flux defines the photoelectric yield $Y(h\omega)$ which in amorphous semiconductors is proportional to a convolution between the initial (occupied) density of states $g_v(E)$ and the final density of states just above the vacuum level $g_{\mathrm{vac}}(E)$.[8] The latter is known from earlier measurements to be constant between 0 to 2 eV above the vacuum level.[9] The energy dependence of the dipole matrix element for the transition is also well established.[9] Thus, the occupied density of states $g_v(E)$ can be handily obtained from a photoyield spectrum by simple differentiation:

$$g_v(h\omega)\propto(h\omega)^4[4Y(h\omega)/h\omega+dY(h\omega)/d(h\omega)]\,. \quad (1)$$

Winer, Hirabayashi, and Ley normalized $g_v(E)$ in *a*-Si:H to a value of 1×10^{22} states/eV cm^3 at 6.2-eV photon energy.[8] We employed the same normalization factor for the *a*-$\mathrm{Si}_x\mathrm{Ge}_{1-x}$:H spectra.[10] The resultant densities of states are estimated to be accurate within a factor of 2. The valence-band edge is defined[9] at $g_v(E)=3\times10^{21}$ cm^{-3}eV^{-1}. The Fermi-level position E_F was determined by measuring the contact potential difference with respect to a vibrating molybdenum reed of known work function (a Kelvin probe).

The spatial resolution of the yield technique is set by the depths for photon absorption and for photoelectron escape. Both vary from 2.5 to 10 nm over the energy range encompassed by our measurements. We take 4 nm as the average probing depth. Thus, the spectra describe the near-surface layer of the measured films. We took advantage of this feature to study the near-surface density of states.

Figure 1 shows two near-surface distributions of occu-

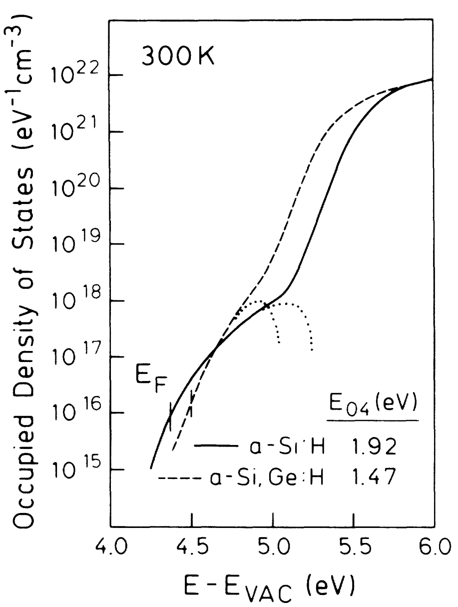

FIG. 1. Typical occupied density-of-states spectra for a-Si:H and an a-Si$_x$Ge$_{1-x}$:H alloy. The exponential region spanning about 2 orders of magnitude in the density of states defines the valence-band tail. The defect subband is uncovered by subtracting the valence-band tail from the total DOS. The FWHM of the defect distribution narrows abruptly as the Ge concentration is increased to approximately 20% (E_{04}=1.7 eV).

pied states, one for a-Si:H and the other for a typical alloy. The distributions show clearly exponential valence-band tails from which the characteristic energy E_{0v}, defined by $E_{0v} \equiv -1/[d\ln g_v(E)/dE]$, can be obtained. Subtracting the valence-band tail from the total density of states reveals the near-surface defect states from which the defect energy E_{sd} and defect density N_{sd} are readily evaluated. In an analogous manner, E_{0v}, E_{sd}, and N_{sd} were obtained for several other samples. Figures 2 and 3 show the data for eleven samples whose E_{04} range from 1.2 to 1.9 eV. The lines shown for E_{0v} and E_{sd} represent fits to the data. The solid line for N_{sd} is the theoretically calculated result, obtained from equilibrium theory as discussed below.

In the thermodynamic equilibrium theory proposed for a-Si:H, the density of dangling bonds is governed by a balance between the breaking of strained bonds and the joining of pairs of dangling bonds. Developed for bulk material, the theory predicts that the defect density N_s varies with the defect energy E_d (counted from the valence-band edge), the density of valence-band tail states expressed in terms of the density at the valence-band edge N_v, and the characteristic tail energy E_{0v} as

$$N_s = [4N_A \exp(-2E_d/kT)]^{kT/(2E_{0v}+kT)} \times (N_v E_{0v})^{2E_{0v}/(2E_{0v}+kT)}, \qquad (2)$$

where $N_A = 4.7\times10^{22}$ cm^{-3}, the average of the atomic densities of Si (5.0×10^{22}) and Ge (4.4×10^{22}), and N_v is 3×10^{21} cm^{-3}eV^{-1}, as described earlier. With N_{sd}, E_{sd}, and E_{0v} extracted from the total-yield photoemission spectra, we have all the tools needed to test the thermal equilibrium theory for the surface.

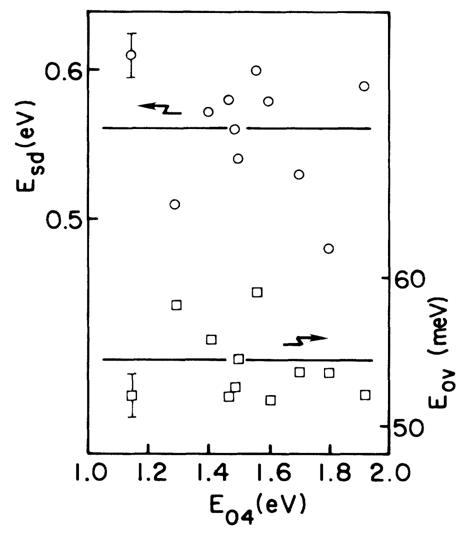

FIG. 2. Experimental results for the valence-band-tail characteristic energy E_{0v} and the energy of the near-surface defect subband E_{sd} referenced to the valence-band edge (defined at a density of states of 3×10^{21} cm^{-3}eV^{-1}). The solid lines are the averages of the measured values (note that although E_{0v} has an average at about 54 meV, the best films have an E_{0v} of 52 meV across the full alloy range).

Figures 2 and 3 show that E_{0v}, E_{sd}, and N_{sd} remain essentially constant, independent of alloy composition. Since the characteristic tail energy and the defect energy

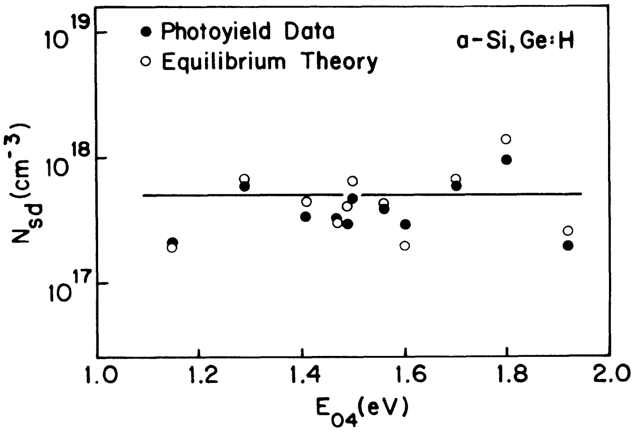

FIG. 3. Point-by-point comparison between experimental results for the near-surface defect density N_{sd} and the values predicted by equilibrium theory, with the experimentally determined values of E_{0v} and E_{sd} as inputs. The solid line represents the average of the experimentally determined N_{sd} (which also coincides with the average of the theoretically calculated values).

enter together in determining $N_{\rm sd}$ within the framework of the equilibrium model, this invariance of all three parameters is a first intimation that thermodynamic equilibrium determines the near-surface defect density $N_{\rm sd}$. E_{0v} scatters between 50 and 58 meV with a mean at approximately 54 meV (Fig. 2) which is comparable to values for bulk a-Si$_x$Ge$_{1-x}$:H alloys.[11-13] Our measurements show that the near-surface defects lie at $E_{\rm sd}$ approximately 0.56 eV above the valence-band edge (Fig. 2). Photoyield measurements of E_{0v} show that it begins to rise more rapidly with increasing temperature between 150 and 200 °C.[14] Therefore, we take the freeze-in temperature of the valence-band tail, and thus of the surface defects, as 170 °C. Substituting these values for E_d, E_{0v}, and T in Eq. (2) yields an $N_{\rm sd}$ of $\sim 5\times 10^{17}$ cm^{-3}. This value is between 1 and 2 orders of magnitude higher than bulk defect densities measured in the same energy region of the band gap for the same films via the constant-photocurrent method and photothermal deflection spectroscopy, which are spectroscopic techniques sensitive to the bulk.

As shown in Fig. 3, a point-by-point comparison between experimentally determined and theoretically calculated values of $N_{\rm sd}$ reveals almost perfect agreement despite the scatter of the individual values. Small discrepancies are accounted for by experimental uncertainty in the determination of E_{0v} (± 1.5 meV) which produces an approximately 40% uncertainty in the value of $N_{\rm sd}$. The solid agreement between theory and experiment is a strong affirmation of thermal equilibrium between the strained and the dangling bonds in the near-surface layer of the a-Si:H–a-Ge:H alloy system.

The defect density of 5×10^{17} cm^{-3}, when multiplied by the 4-nm probe depth of the yield measurement, translates into a surface-state density of 2×10^{11} cm^{-2}, a value which is typical of optimized a-Si:H film surfaces.[8]

We have shown that the surface defect density is described accurately by equilibrium between strained and broken bonds. This description implies that the surface defects are associated with dangling bonds. Yet, several issues relating to these surface states remain to be clarified. For instance, they lie 0.56 eV above E_v, deeper than the bulk defects which roughly track midgap.[15,16] The lower energy of the surface defects may result from a surface reconstruction, perhaps associated with the extensive surface coverage by SiH$_2$ groups.[17] In a defect pool mechanism[2,18-20] the shallow distribution is a consequence of the presence of an electron accumulation layer at the growing surface (E_F lies approximately 0.5 eV below E_c at the clean surface of a-Si:H[8]). Why this layer forms is not understood at present. Another puzzle is the narrowing of the surface defect distribution with Ge alloying (see Fig. 1). We observe that the full width at half maximum (FWHM) decreases from 0.4 eV in nonalloyed a-Si:H ($E_{04}=1.9$ eV) to 0.27 eV for a-Si$_x$Ge$_{1-x}$:H alloys with E_{04} of 1.7 eV ($x=0.8$) or less. This rather abrupt decrease in the FWHM with initial Ge alloying signals a transition in the character of near-surface defects which reflects either a change in the nature of the defects (Ge vs Si dangling bonds) or, alternatively, a change in the charge state of the dangling bonds. These are intriguing questions that deserve further study.

In conclusion, we have measured the energy and density of states within 4 nm of the surface of a-Si$_x$Ge$_{1-x}$:H alloys. We find that the defects lie 0.56 eV above the valence-band edge and that their density is $\sim 2\times 10^{11}$ cm^{-2}, independent of Ge content. The density agrees with the value calculated from thermodynamic equilibrium theory. This agreement suggests that the surface defects are associated with dangling bonds. Our results represent the first identification of an electronic surface defect in thermal equilibrium.

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[1] R. A. Street, Phys. Rev. Lett. **49**, 1187 (1982).

[2] Y. Bar-Yam, D. Adler, and J. D. Joannopoulos, Phys. Rev. Lett. **57**, 467 (1986).

[3] G. Müller, S. Kalbitzer, and H. Mannsperger, Appl. Phys. A **39**, 243 (1986).

[4] Z E. Smith and S. Wagner, Phys. Rev. Lett. **59**, 688 (1987).

[5] K. Winer and L. Ley, Phys. Rev. B **36**, 6072 (1987).

[6] Z E. Smith, V. Chu, K. Shepard, S. Aljishi, D. Slobodin, J. Kolodzey, T. L. Chu, and S. Wagner, Appl. Phys. Lett. **50**, 1521 (1987).

[7] M. Favre, H. Curtins, and A. Shah, J. Non-Cryst. Solids **97 & 98**, 731 (1987).

[8] K. Winer, I. Hirabayashi, and L. Ley, Phys. Rev. B **38**, 7680 (1988).

[9] W. B. Jackson, S. M. Kelso, C. C. Tsai, J. W. Allen, and S. J. Oh, Phys. Rev. B **31**, 5187 (1985).

[10] S. Aljishi, Shu Jin, and L. Ley, in *Amorphous Silicon Technology,* edited by A. Madan, M. Thompson, P. C. Taylor, Y. Hamakawa, and P. G. LeComber, MRS Symposia Proceedings No. 149 (Materials Research Society, Pittsburgh, 1989), p. 125.

[11] S. Guha, J. S. Payson, S. C. Agarwal, and S. R. Ovshinsky, J. Non-Cryst. Solids **97 & 98**, 1455 (1987).

[12] H. Haku, S. Sayama, Y. Nakashima, T. Takahama, M. Isomura, H. Tarui, Y. Hishikawa, S. Tsuda, S. Nakano, M. Ohnishi, and Y. Kuwano, Jpn. J. Appl. Phys. **26**, 1978 (1987).

[13] V. Chu, J. P. Conde, D. S. Shen, and S. Wagner, Appl. Phys. Lett. **55**, 262 (1989).

[14] Z E. Smith, S. Aljishi, D. Slobodin, V. Chu, S. Wagner, P.

M. Lenahan, R. R. Ayra, and M. S. Bennett, Phys. Rev. Lett. **57**, 2450 (1986).

[15] H. Matsuura, J. Appl. Phys. **64**, 1964 (1988).

[16] H. Matsuura, Z E. Smith, A. Matsuda, S. Yokoyama, M. Tanaka, M. Umeda, and K. Tanaka, Philos. Mag. Lett. **59**, 109 (1989).

[17] Y. Toyoshima, K. Arai, A. Matsuda, and K. Tanaka, Appl. Phys. Lett. **56**, 1540 (1990).

[18] Z E. Smith and S. Wagner, in *Amorphous Silicon and Related Materials, Advances in Amorphous Semiconductors,* edited by H. Fritzsche (World Scientific, Singapore, 1989), Vol. 1, p. 409.

[19] J. D. Cohen and A. Gelatos, in *Amorphous Silicon and Related Materials, Advances in Amorphous Semiconductors* (Ref. 18), p. 475.

[20] K. Winer, Phys. Rev. Lett. **63**, 1487 (1989).