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Surface states and the exponential valence-band tail in a-Si:H

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We use total-yield photoelectron spectroscopy to measure the density of occupied states in undoped and lightly boron-doped a-Si:H. We observe a large density of states in the gap of undoped a-Si:H, which we ascribe to near-surface defect states. Incorporation of boron removes these states and allows an unobstructed view of the valence-band tail. This is shown to be exponential over more than 3 orders of magnitude in the density of states with an inverse logarithmic slope of 45 meV, in good agreement with the results of dispersive transport measurements.

I. INTRODUCTION

Optical-absorption spectra of amorphous hydrogenated silicon (a-Si:H) prepared under a variety of conditions invariably show an exponential absorption edge, also known as the Urbach edge.[1] This behavior has been interpreted as arising from optical transitions between exponential valence- and conduction-band tails.[2] This interpretation requires the valence-band tail to be broader than the tail of the conduction band; the slope of the Urbach edge would then be characteristic of the valence-band tail. Evidence for the exponential nature of band tails in a-Si:H is provided by the results of dispersive transport measurements,[3] which are consistent with exponential conduction- and valence-band tails with inverse slopes of 27 and 43 meV, respectively. Further support for this view derives from the results of electron paramagnetic spin resonance (ESR) measurements.[4] Several other mechanisms have been proposed to account for the Urbach edge in disordered semiconductors. These include electric-field-broadened excitonic transitions,[5] strong electron-phonon coupling,[6] and broadening of the normally sharp absorption edge due to random internal electric fields.[7]

Although the prevailing view is that some portions of the valence- and conduction-band tails in a-Si:H decrease exponentially into the band gap, the experimental evidence for this behavior is only indirect. Optical-absorption measurements of the joint density of states in the gap of a-Si:H and transport measurements of carrier lifetimes are consistent with, but not proof of, an exponential distribution of band tail states. The precise determination of the behavior of these states is important for the interpretation of optical absorption data. At the same time, this information would be useful for discriminating between various theoretical models of the distribution of band tail states in disordered systems.[8–13] Here we apply total-yield photoelectron spectroscopy[14,15] to obtain a direct, spectroscopic determination of the density of occupied band tail and defect states in the gap of a-Si:H. We compare our results with optical-absorption spectra measured by photothermal deflection spectroscopy (PDS).

II. TOTAL-YIELD PHOTOELECTRON SPECTROSCOPY

Total-yield photoelectron spectroscopy is a simple variant of conventional photoemission spectroscopies. Instead of measuring the energy distribution of electrons excited from the sample by monochromatic light as in ultra violet (UPS) and x-ray (XPS) photoelectron spectroscopies,[16] we collect *all* of the emitted electrons regardless of their kinetic energy and vary the energy of the incident light ($4.0 \leq \hbar\omega \leq 6.4$ eV). The resulting total-yield spectrum $Y(\hbar\omega)$ of amorphous materials, defined as the number of emitted electrons per incident photon, bears a close relationship to the absorption coefficient $\alpha(\hbar\omega)$. Both are proportional to the convolution of initial and final densities of states weighted with an average dipole transition matrix element $R(\hbar\omega)$:[16]

$$Y(\hbar\omega) \propto \hbar\omega R^2(\hbar\omega) \int_{E_{\mathrm{vac}}}^{\infty} g_v(E-\hbar\omega) g_c(E) dE \ , \qquad (1)$$

and

$$\alpha(\hbar\omega) \propto \hbar\omega R^2(\hbar\omega) \int_{E_{\mathrm{F}}}^{\infty} g_v(E-\hbar\omega) g_c(E) dE \ , \qquad (2)$$

where E_F is the Fermi energy, E_{vac} is the vacuum level, and g_v and g_c are the densities of occupied valence-band states and empty conduction-band states, respectively.

The two expressions differ only in the lower limit for the final-state energy. However, this has important consequences. The lower limit for the absorption coefficient $\alpha(\hbar\omega)$ is the Fermi energy E_F, which separates (at $T=0$) occupied from unoccupied states. As a consequence, characteristic features in $\alpha(\hbar\omega)$ cannot be unambiguously attributed to either g_v or g_c, a problem which hampers the interpretation of a-Si:H absorption spectra. On the other hand, the requirement that the electrons leave the sample in total-yield spectroscopy places a sharp lower limit on the integral in Eq. (1) at the vacuum level E_{vac}, which lies typically ~ 4 eV above E_F in a-Si:H. The density of final states g_c, located between 0 and ~ 2 eV above E_{vac}, is directly accessible to spectroscopic investigation and is known to be essentially flat and featureless.[16] Assuming that the final-state density is *exactly* constant, we can take g_c out of the integral in Eq. (1). Therefore the measured yield depends only on the density of initial states g_v and the square of the average dipole transition matrix element $R(\hbar\omega)$.

Following Jackson *et al.*,[17] we take $R^2(\hbar\omega) \propto (\hbar\omega)^{-5}$ for photon energies above 3.4 eV, so that the initial density of states is given in terms of the measured yield as follows:

$$g_v(\hbar\omega) \propto (\hbar\omega)^4[4Y(\hbar\omega)/\hbar\omega + dY(\hbar\omega)/d(\hbar\omega)] \ . \quad (3)$$

Von Roedern *et al.*[18] studied the gap-state density of phosphorous-doped *a*-Si:H with UPS and normalized their spectra to 2.5×10^{22} states/(eV cm^3) at the maximum of the Si 3*p* valence-band peak (5×10^{22} atoms/cm$^3\times2$ states/atom divided by a bandwidth of 4 eV). We therefore normalize $g_v(\hbar\omega)$ to 1×10^{22} states/(eV cm^3) at a photon energy of 6.2 eV, which corresponds to a point in the valence band about halfway down from the Si 3*p* maximum. We estimate that the densities of states we extract from the measured yield spectra are accurate to within a factor of 2 using this procedure.

III. EXPERIMENTAL CONSIDERATIONS

A. Sample preparation

Thin (1.0 μm) films of undoped and lightly boron-doped *a*-Si:H were produced in an ultrahigh-vacuum (UHV) deposition system (base pressure $\leq 10^{-8}$ mbar) by standard rf (13.56 MHz) glow-discharge decomposition of either pure, undiluted silane or diborane diluted in pure silane for the doped films. The films were either deposited onto clean, polished stainless-steel substrates or onto freshly sputtered molybdenum surfaces. Other deposition parameters were substrate temperature 230 °C, gas pressure 0.3 mbar, flow rate 5 sccm (sccm denotes cubic centimeters per minute at STP) and rf power density 50 mW/cm^2. Samples for measurement by PDS were prepared on quartz substrates at the same time those used for the total-yield measurements were prepared, and were stored in UHV until removed for the PDS measurements. The film thicknesses were determined from the deposition time and the deposition rate, which was calibrated by direct profilometric measurement of thick films prepared under identical deposition conditions. We estimate that determinations of film thickness using this method are accurate to within $\sim$10%. The freshly prepared *a*-Si:H films were transferred to the analysis system (base pressure $\leq 5\times10^{-10}$ mbar) under UHV directly after the deposition for the yield measurements. Some samples were exposed to activated oxygen in the UHV analysis system after deposition to determine the effect of adsorbates on the density of states.

B. Determination of the Fermi energy

The Fermi energy of each film was determined by measuring the contact potential difference (CPD) between the film and a reference electrode (Kelvin's method). The operation of the Kelvin probe and its use for work-function determinations is described in detail elsewhere.[19–21] We use an aged molybdenum vibrating reed to measure the CPD of the *a*-Si:H films *in situ* both before and after the total-yield measurements. The work function of the molybdenum reed, the knowledge of which is required for accurate determination of the Fermi energies of the *a*-Si:H films, was regularly measured between successive yield experiments by comparing the CPD of a freshly evaporated gold film, measured with the Kelvin probe, with the Fermi energy of the film determined by fitting its photoelectric yield spectrum to the Fowler function.[22] This function provides an excellent description of the yield spectra of clean metals and only depends on the temperature and the Fermi energy of the metal of interest. The value obtained for the work function of the Kelvin probe (4.45±0.01 eV) was always reproducible within the stated error and was stable over several months of measurement.

C. Total-yield measurements

Light from a 1000-W xenon arc lamp was passed through a double-grating monochromator ($4.0 \leq \hbar\omega \leq 6.4$ eV) and focused onto the sample surface through a MgF$_2$ window mounted on one of the ports of the analysis chamber. A part of the light was deflected by a small quartz sliver to a photomultiplier in order to measure the incident photon flux for the normalization of the electron count rate. Photoelectrons were collected with a channeltron placed directly in front of the sample surface below the focused light. A ceramic cap with a small (1 mm^2) hole in the top was fitted over the channeltron entrance to reduce the background signal due to stray or scattered light hitting the metalized collar of the channeltron. The yield spectra were corrected for the response characteristics of the photomultiplier tube; because the reflectivity of *a*-Si:H is essentially constant over the measured photon energy range, no correction for reflection losses was applied. Yield spectra were taken at 1-nm intervals between 195 (6.4) and 310 (4.0) nm (eV), and the output of the channeltron and photomultiplier were recorded by digital photon-counting electronics and transferred to a PDP minicomputer for storage and subsequent analysis.

Typical channeltron and photomultiplier spectra for undoped *a* –Si:H are shown in Fig. 1. The channeltron count rate is essentially constant and close to the dark count rate (0.1 counts/s) from the start of the spectrum at 4 eV until just before the Fermi energy, where the rate begins to increase rapidly. The fact that the maxima of the photon and electron count rates occur at opposite extremes of the energy scale provides the total-yield method with a dynamic range of over 7 orders of magnitude. The yield spectrum $Y(\hbar\omega)$ consists of the ratio of the channeltron and photomultiplier count rates properly corrected for the response of the phototube, and with the dark count rates removed.

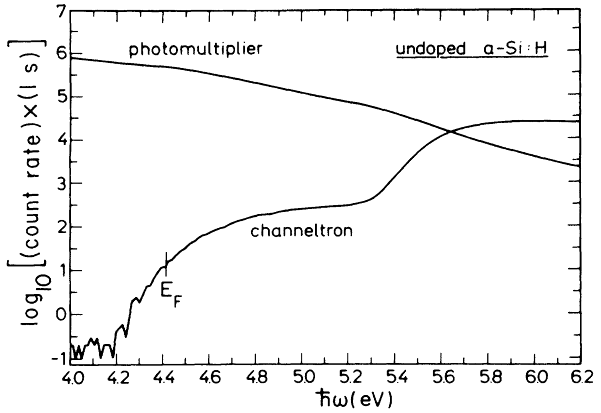

FIG. 1. Typical photomultiplier and channeltron count rates measured for undoped a-Si:H. The ratio of the channeltron and photomultiplier count rates results in a total-(relative-) yield spectrum, which can be used to extract the occupied density of states. Note the large dynamic range afforded by the total-yield method.

IV. RESULTS AND DISCUSSION

The measured yield spectra from a-Si:H films prepared with various gas-phase diborane concentrations C_B ($\equiv[B_2H_6]/[SiH_4]$) are shown in Fig. 2 together with corresponding absorption spectra measured by PDS. The (relative) photoelectron yield varies slightly from sample to sample. Because the addition of small concentrations of boron can have only a negligible effect on the total integrated density of states, we have normalized the total-yield spectra at 6.36 eV to allow a direct comparison of the spectra as a function of boron doping. The most striking aspect of this comparison is the dramatic reduction in the yield near 5 eV with increasing boron incorporation.

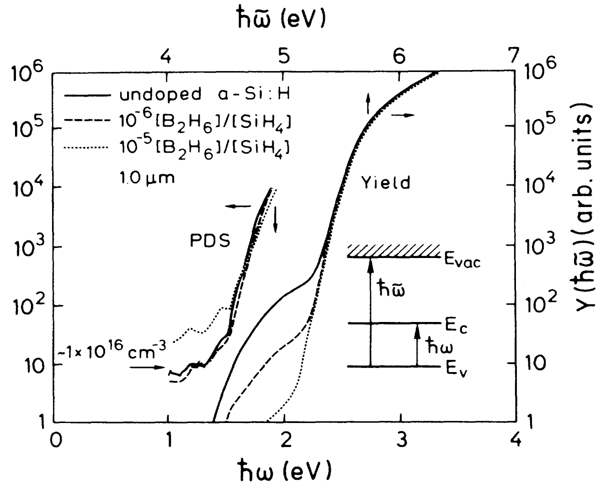

FIG. 2. Total-yield and PDS absorption spectra of simultaneously prepared undoped and lightly boron-doped a-Si:H thin films. The diagram in the inset shows schematically the difference between the transitions that contribute to the total-yield and optical-absorption spectra. E_v and E_c represent the energies of valence- and conduction-band states, respectively.

Because the formal description [Eqs. (1) and (2)] of optical absorption and total yield in a-Si:H is identical, the essential difference between the two lies in the different photon energy regimes employed in each experiment. Neglecting the conduction-band-edge contribution to the absorption, this difference manifests itself primarily through the effect of the photon-energy-dependent matrix element $R(\hbar\omega)$. However, this effect can only produce small differences in the relative spectral distributions over the small (~ 1 eV) energy range probed by the two experiments. Therefore, we should expect the shapes of the total-yield and the absorption spectra to be similar. Indeed, the total-yield spectra exhibit many of the same features that are characteristic of optical-absorption spectra: a power-law region above $\alpha \approx 10^4$ cm^{-1} ($Y \approx 10^4$ a.u.), followed by an exponential edge towards lower energy, and a shoulder due to electronic transitions from defect states deep in the gap. The similarity is particularly apparent in the exponential edges of the two groups of spectra in Fig. 2, whose inverse logarithmic slopes E_0, defined by

$$E_0 \equiv (-\delta \ln X / \delta\hbar\omega)^{-1} , \tag{4}$$

where X is $\alpha(\hbar\omega)$ or $Y(\hbar\omega)$, are in good agreement ($E_0 = 50$ meV). This agreement is, without further analysis, direct spectroscopic proof that the valence-band tail dominates the Urbach edge in a-Si:H because only electrons excited from occupied (valence-band) states are detected by total yield. That the valence-band tail in the density of states of a-Si:H must also decrease exponentially into the gap follows from the exponential shape of the edges in the absorption and yield spectra. We will show this in a direct manner presently.

The defect densities of the a-Si:H films whose PDS and total-yield spectra are shown in Fig. 2 can be estimated by comparison with PDS spectra from samples with known defect densities.[23] Employing this method, we find the defect density to be 1×10^{16} cm^{-3} for the undoped film and that produced with $C_B = 10^{-6}$. The defect density increases to 4×10^{16} cm^{-3} for the film produced with $C_B = 10^{-5}$, in agreement with earlier studies of boron doping with PDS.[24] However, the increase of the density of defect states measured by PDS with increasing boron concentration is in apparent contradiction to the results of the total-yield measurements.

The occupied densities of states derived from the measured yield spectra [according to Eq. (3)] of a-Si:H with various dopant concentrations are shown in Fig. 3. The spectra have several features in common including a linear valence-band edge decreasing into the gap, an exponential tail, and a defect band centered near 5.0 eV. Photoemission beyond the Fermi energy (denoted by vertical bars in Fig. 3) is observed at finite temperatures due to the tail of the Fermi distribution function. The effect of the boron in decreasing the density of states in the defect band can clearly be seen. Because the occupation of states depends on the Fermi energy through the Fermi distribution function, one expects a reduction in the defect-band contribution to the yield as the Fermi

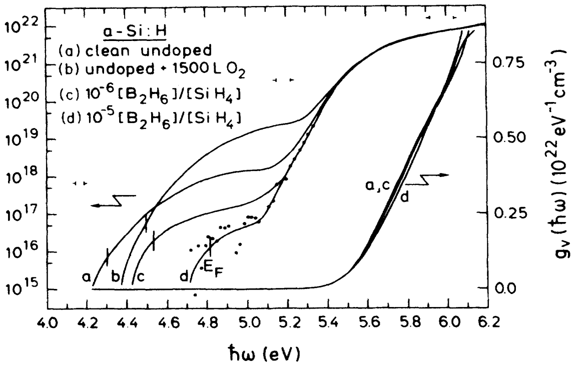

FIG. 3. Occupied density of states extracted from the measured yield spectra of undoped and lightly boron-doped a-Si:H thin films. The Fermi energy for each curve is marked by a vertical bar. The large scatter at low densities is due to statistical noise in the yield at low count rates that is exaggerated by taking the derivative according to Eq. (3). Horizontal bars mark the bandwidth of the incident light that imposes an upper limit to the spectral energy resolution.

energy shifts towards the valence-band edge with increasing boron doping. However, changes in the occupation cannot account for the large decrease in the density of states with boron doping far from (to the high photon energy side of) the Fermi energy, where the effect of the Fermi distribution cutoff is negligible.

PDS is a sensitive measure of the bulk state absorption. Contributions from the surface or sample-substrate interface should be negligible for thick (> 1 μm) films. Total-yield spectroscopy on the other hand, as a variant of photoemission, is expected to be sensitive to the state of the surface in a-Si:H. The relatively high absorption coefficient between 4 and 6 eV photon energy in a-Si:H [$\alpha(\hbar\omega) = 1-2 \times 10^6$ cm^{-1}] means that the incident light can only excite electrons from the first few hundred angstroms of the surface; the flux of photons of energy 4 (6) eV penetrating into the sample decreases by $1/e$, a distance $\lambda_{\hbar\omega} = 100$ (50) Å from the surface. The inelastic mean free path of electrons λ_e in c-Si at an energy of 5 eV above the Fermi energy is 25 Å, and increases rapidly as the energy approaches the Fermi energy.[25] Assuming that λ_e in a-Si:H is similar, we can expect the electron escape depth to be 25 Å or less for photon energies above 5 eV and to increase rapidly near the Fermi energy.

Measurements of the attenuation of the stainless-steel substrate contribution to the yield with increasing a-Si:H film thickness (Fig. 4) are consistent with a probe depth in total yield of less than 40 Å above 5.0 eV photon energy and therefore are in reasonable agreement with the electron escape depths measured in c-Si. As such, contributions to the yield from surface states should be easily observable. Because of the thickness of our a-Si:H samples (1 μm), contributions to the yield from the sample-substrate interface can be neglected. Therefore, the simplest explanation for the apparent decrease in the defect density with increasing boron doping observed by total yield would be the presence of a large density of surface states on clean, undoped a-Si:H and their elimination with boron incorporation.

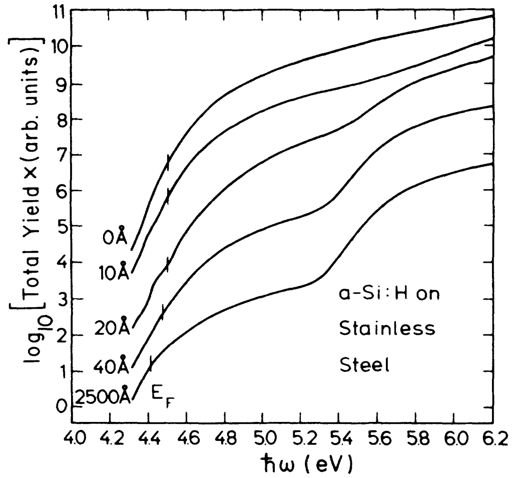

FIG. 4. Attenuation of the stainless-steel substrate contribution to the total-yield spectrum as a function of undoped a-Si:H film thickness. A vertical bar marks the Fermi energy E_F for each spectrum. The clean stainless-steel substrate spectrum has been shifted uniformly to higher photon energy by 0.55 eV for comparison with the spectra of the a-Si:H covered substrate. Note the shift of E_F to lower photon energies as the a-Si:H film thickness increases.

In order to test for the presence of surface states we exposed a clean, undoped a-Si:H film whose yield spectrum had been measured to a boron-containing ($C_B = 10^{-5}$) plasma for 3–5 s. We observed a decrease in the measured yield by nearly 2 orders of magnitude at 5.0 eV just as we observed in the bulk doped films, corresponding again to nearly a 100-fold decrease in the occupied defect density of states. Absorption of 1500 L (1 L $\equiv 1 \times 10^{-6}$ Torr s) activated O_2 onto the clean, undoped a-Si:H surface increases the defect density of states by more than an order of magnitude and changes the shape of the defect band (see Fig. 5). In undoped a-Si:H, the asymmetric defect band has a full width at half maximum (FWHM) of 0.43 eV and the band maximum is at 5.0 eV, where the density of states is 1.5×10^{18} states/(eV cm^3). The defect band narrows to 0.35 eV FWHM after absorption of 1500 L O_2 and the band maximum shifts by 0.15 eV towards the valence-band edge (to higher photon energy). These experiments demonstrate the surface sensitivity of the total-yield method, and leave little doubt that the large density of defect states observed in undoped a-Si:H is indeed due to surface or near-surface states. It also argues against the possibility that these states might be due solely to residual gas contamination. The effects of residual gas contamination do appear after several hours in UHV for all dopant levels in the form of an increased defect density of states. Because the defect density of boron-doped films increases with oxidation (or residual gas contamination) in the same manner as in undoped films, any preferential adsorption of oxygen that would lead to a large density of gap states in undoped a-Si:H and not in

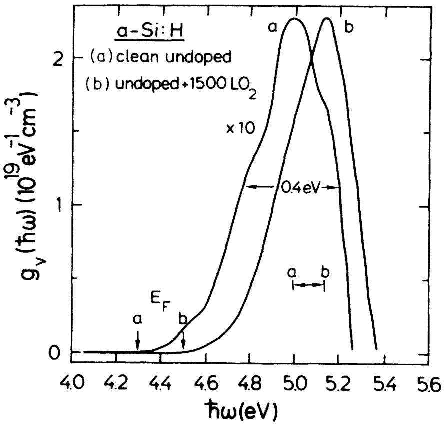

FIG. 5. Defect density of states of clean, undoped *a*-Si:H before and after oxidation. The spectra are obtained by subtracting the exponential part from the density of states in Figs. 3(a) and 3(b). Note the linear scale.

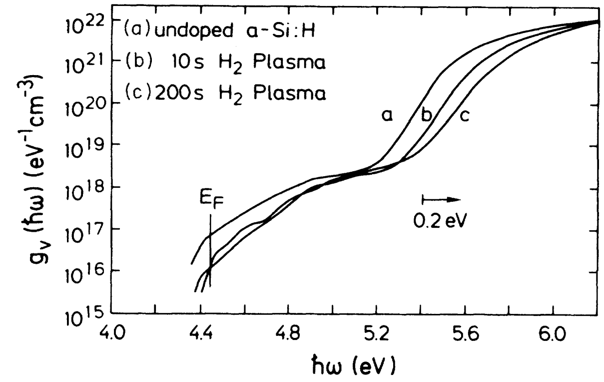

FIG. 6. Effect of posthydrogenation on the occupied density of states in undoped *a*-Si:H. The 0.2 eV shift of the valence-band edge to higher photon energies corresponds to a widening of the band gap.

boron-doped films can be ruled out. Furthermore, the fact that the shape of the defect band in undoped *a*-Si:H changes after exposure to oxygen suggests that the origin of the defect bands is different in the two cases. Therefore, adsorbate-induced gap states cannot account for the large density of defect states observed on the freshly prepared undoped *a*-Si:H films. We conclude that these states must be intrinsic to the clean, undoped *a*-Si:H surface.

The increase in the defect density with oxidation observed by total yield correlates well with the increase of the 1.1 eV luminescence observed in *a*-Si:H with increasing oxygen content,[26] and with the increase in the defect density in *a*-Si:H after oxygen ion implantation observed by deep-level transient spectroscopy.[27] However, this is opposite to the effect of oxygen on cleaved crystalline silicon (*c*-Si) surfaces where it removes surface states.[28] This suggests that the surface defects observed in undoped *a*-Si:H are not of the same type as those present on *c*-Si surfaces, and are most probably due to the presence of large structural distortions near the surface.

One type of structural distortion that might lead to surface states in the gap is the presence of near-surface dangling bonds. One might expect to remove residual near-surface dangling bonds by hydrogen passivation. In an attempt to observe such passivation, we exposed a clean, undoped *a*-Si:H film to a hydrogen plasma for short times. The results are shown in Fig. 6. The spectra are as usual normalized to 1×10^{22} states/(eV cm^3) at 6.2 eV photon energy. We find that posthydrogenation does not cause a shift in the Fermi energy of the film nor does it cause a change in the defect density to any appreciable degree. The main effect of the posthydrogenation is to shift the exponential valence-band tail and the valence-band edge to higher photon energies by as much as 0.2 eV, corresponding to an increase in the band gap.[16] This behavior is in agreement with the results of several calculations and with the results of conventional photoemission measurements,[16] and demonstrates that additional hydrogen is entering the near surface of the film. The fact that the defect density of states is little changed with hydrogen incorporation into the near surface suggests that the structural defects that lead to surface states in the gap of undoped *a*-Si:H are not simply due to a high concentration of dangling bonds in the near surface.

The presence of the smallest amount of boron ($C_B \le 10^{-6}$) either in the bulk or on the surface of *a*-Si:H preferentially removes occupied near-surface defect states from the gap. The 0.5 eV shift in the Fermi energy with boron incorporation is then clearly due to the depinning of the Fermi level as the surface states are removed, similar to the Fermi-level depinning observed in *c*-Si with oxidation.[29] The fact that the activation energies of dark conductivity measured for undoped films and those produced with $C_B = 10^{-5}$ differ by less than 0.1 eV is consistent with this interpretation. Boron may remove these states by promoting a relaxation of the structure near the surface. This would account for the large reduction in defect-state densities observed by total yield when initially undoped films are exposed to boron-containing plasmas for short times (3–5 s).

The reduction of defect states in the gap of *a*-Si:H with boron incorporation has also been observed in field-effect measurements.[30] This reduction was attributed to the removal of divacancy energy levels from the gap by incorporation of three fold-coordinated boron into the amorphous network.[30] Because the field effect has subsequently been shown to be sensitive to surface or interface states,[31] the reduction in defect-state density observed with boron doping is consistent with the results of total yield and the interpretation that boron removes surface states from the gap. Although the divacancy model was originally proposed to account for the boron-induced removal of bulk defect states from the gap, a similar mechanism might be operative at the surface of *a*-Si:H.

Assuming that the 0.4-eV-wide defect band in undoped *a*-Si:H (Fig. 5) is entirely due to near-surface defect states, their density is estimated to be between 2 and 3×10^{11} states/cm^2, the main source of error being the uncertainty in the electron escape depth at 6.2 eV. This is in good agreement with other estimates of *a*-Si:H surface-state densities.[26,32–34] It is more than 3 orders of magnitude less than that observed on cleaved crystalline silicon surfaces,[35,36] which is reasonable considering the presence of hydrogen at the surface of *a*-Si:H films.

We show in Fig. 7 the occupied density of states for *a*-Si:H produced with $C_B = 10^{-5}$. We choose the energy axis for this figure by assuming that the mobility edges E_v and E_c occur at a density of states of 3×10^{21} states/(eV cm^3). Virtually all of the occupied surface defects have been removed at this diborane concentration, yet the doping level is small enough not to increase the bulk defect density to a significantly higher level than that found in undoped films. Therefore the defect density in Fig. 7 serves as an upper limit to the bulk defect density of intrinsic *a*-Si:H. This value, 5×10^{16} states/(eV cm^3), is consistent with defect densities determined from the PDS spectra of Fig. 2 and from a variety of measurements on thick, high-quality undoped *a*-Si:H films.[37]

The removal of occupied near-surface defect states from the gap by boron incorporation provides an unobstructed view of the intrinsic valence-band tail in *a*-Si:H. The valence-band tail is exactly exponential over more than 3 orders of magnitude in the density of states, and extends deep into the gap. The inverse logarithmic slope of the tail, 45 meV, is in excellent agreement with the results of dispersive-transport[3] and ESR measurements.[4]

Many recent theoretical treatments of the band tail state distributions in disordered semiconductors predict an exponential dependence of the density of tail states over some range of gap energies.[8–13] This dependence usually results from the assumption of a random (Gaussian) distribution of potential energies. While a discussion of the merits or deficiencies of the various theoretical approaches is not appropriate here, we should point out that any theory of tail state distributions in *a*-Si:H should be able to account for the exponential behavior of the valence-band tail over more than 3 orders of magnitude in the density of states and over a 0.3 eV energy range as observed in this study.

Based solely on the assumption of random potential fluctuations, Zhang and Sheng[11] have recently predicted that the logarithm of the near-edge tail state distribution in disordered systems should exhibit sublinear behavior and that an inflection point should exist in the density of tail states. They argued that the failure to observe this behavior in experimental spectra would mean that some additional mechanism other than random potential fluctuations would be required to describe band tail states. The predicted sublinear behavior of the logarithm of the near-edge density of tail states is in fact observed here above $g_v \approx 8 \times 10^{19}$ states/(eV cm^3) (see Fig. 7). This behavior is, however, necessary considering the smooth transition from the linear valence-band edge to the exponential valence-band tail seen in *a*-Si:H. It thus appears that the simple assumption of random potential fluctuations need not be augmented to account for the observed distribution of localized tail states in disordered systems, at least not in *a*-Si:H.

Finally, we note that the 0.3-eV separation of the mobility edge E_v from the beginning of the exponential part of the valence-band tail [at $g_v \approx 8 \times 10^{19}$ states/(eV cm^3)] is larger by more than a factor of 3 than the value assumed by Jackson *et al.*,[17] although they assumed nearly the same density of states at E_v. This separation plays a crucial role in their estimation of the average dipole transition matrix element $R(\hbar\omega)$ in *a*-Si:H for photon energies between 1.5 and 2.0 eV. Because of the rapidly changing joint density of states at these energies (near the absorption edge in *a*-Si:H), $R^2(\hbar\omega)$ may deviate by up to an order of magnitude from the 10 Å^2 value estimated by Jackson *et al.* within this energy range.

In summary, we have shown that a broad band (0.4 eV wide) of surface states exists on clean, undoped *a*-Si:H films. The band is centered 5.0 eV away from the vacuum level and corresponds to a surface-state density of between 2 and 3×10^{11} cm^{-2}, which agrees with other estimates of surface-state defect densities determined for *a*-Si:H. We have shown that adding boron to the gas phase during film deposition removes occupied surface states from the gap and exposes the intrinsic valence-band tail. This is found to be exactly exponential over more than 3 orders of magnitude in the density of states with an inverse logarithmic slope of 45 meV, in excellent agreement with the results of dispersive transport measurements.

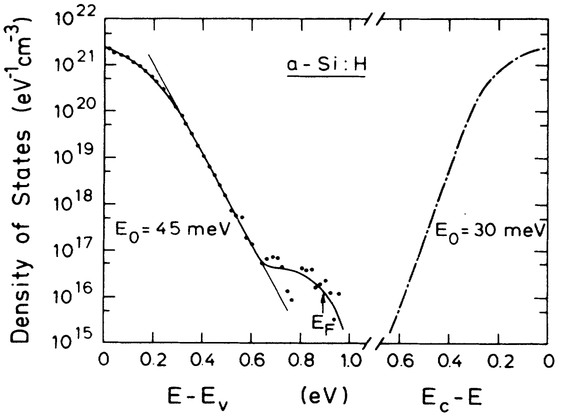

FIG. 7. Density of states in the gap of intrinsic *a*-Si:H. The valence band is represented by the occupied density of states of *a*-Si:H ($C_B = 10^{-5}$) measured by total-yield photoelectron spectroscopy. The conduction band is estimated using the behavior of the tail inferred from dispersive transport measurements (Ref. 3). The sharp decrease in the defect density of states beyond the Fermi energy is due to the effect of the Fermi distribution, which limits the occupation of states near E_F.

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