

Conduction-Band Density of States in Hydrogenated Amorphous Silicon Determined by Inverse Photoemission

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The first direct determination of the conduction band of hydrogenated amorphous silicon has been performed by means of x-ray inverse photoemission. We found a feature 1.2–4 eV above the Fermi level which may be associated, on the basis of its annealing behavior and energy position, with the Si-H antibonding orbital. Comparison with data on crystalline silicon clearly shows that the amorphous-silicon conduction-band density of states does not exhibit critical-point structures.

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Hydrogenated amorphous silicon (α -Si:H) has been studied extensively to determine the effects of long-range disorder and hydrogen incorporation on the electronic and optical properties of solids. In understanding these properties, knowledge of the conduction-band (CB) electronic density of states (DOS) is particularly important. For example, there has been speculation that the states near the bottom of the CB are derived from Si-H antibonding orbitals and that the CB consequently may exhibit strong electron-lattice coupling, unusual transport properties, and/or, perhaps, unique recombination channels.¹ Also, the magnitude and nature of the CB DOS determine the electron transport and the location of the mobility edge, an energy separating localized states from extended states. Finally, since optical measurements depend on a convolution of the valence- and conduction-band DOS, a detailed understanding of the optical properties requires a knowledge of the CB DOS. In fact, the optical band gap is often determined by the assumption of a DOS with a square-root dependence on energy near the band edges.²

Although significant progress has been made in measuring the valence band DOS by means of photoemission,³ no comparable measurements of the conduction band have been performed. Some indication of the CB DOS has been obtained by utilization of partial yield or core-level absorption measurements which attempt to determine the CB DOS by transitions from the Si core levels to the CB.^{4–6} Unfortunately, as discussed in Refs. 4–6, such measurements are significantly distorted by the Coulomb attraction between the core hole and the excited electron. Near critical points of the CB, this interaction produces peaks in the absorption and shifts spectral weight of other peaks.^{7,8} Furthermore, the spectra are broadened as much as 1 eV by the core-hole lifetime broadening, and matrix element effects also distort the observed spectra. The

result is that absorption spectra do not represent one-electron CB DOS, and a large exciton peak near the CB edge is observed.⁶ Because of these problems, no evidence for Si-H antibonding orbitals has been found.⁹

In order to overcome the limitations of core-level absorption, the CB DOS has been determined by bremsstrahlung isochromat spectroscopy (BIS), which yields information similar to a recent inverse photoemission study of α -Si surface states.¹⁰ An electron beam of variable energy is directed onto a sample. The electrons deexcite within the solid, emitting x rays which are detected by a fixed energy monochromator. The CB DOS is obtained by measuring the x-ray intensity as the electron beam energy is varied.

Both x-ray photoemission spectra, useful for sample characterization, and BIS spectra were obtained with a Vacuum Generators Escalab, factory modified for BIS measurements. The pressure during a measurement was lower than 3×10^{-10} Torr. The 100-nm-thick, undoped samples were deposited in an rf-discharge system at low deposition rates onto Mo substrates held at a temperature of 25 °C.¹¹ The Mo substrates do not induce crystallization of the amorphous films even at high temperatures.¹² All annealing was performed *in situ*. The H content was estimated by means of evolution studies.

The samples were transferred to the UHV chamber after less than 3 min exposure to the atmosphere. Any effects due to oxidation could be ruled out. First, the ratio of the O 1s to Si 2p core-level intensity ratio was 0.03, indicating that the oxidation was negligible (< 0.05 monolayer) and confirming previous results which indicate that hydrogenation passivates the surface and reduces oxidation rates by a factor of 10^7 compared with crystalline surfaces.⁹ Second, the measurement is not very surface sensitive since the penetration depth is ~ 4 nm for the ~ 1490 -eV electrons used in BIS.

Third, measurement of lightly sputtered samples or films with small increased oxidation did not exhibit any differences. No evidence for Mo core levels was found indicating complete sample coverage even after annealing.

The Fermi level, E_F , and instrumental broadening, full width at half maximum of 0.72 eV, were determined by measurement of the CB DOS of Ag near E_F . The Fermi level to Si $2p$ core-level energy difference changed less than 0.2 eV between all the undoped samples and a c -Si sample cleaved along [111] direction *in situ*. No evidence of charging was found since the sharp core levels occurred at the same energy in the 100-nm films as for a thinner sample consisting of a -Si:H islands on a Mo substrate.

BIS spectra over a wide energy range with coarse energy spacing are shown in Fig. 1 for c -Si and a -Si:H. The large rise at ~ 16 eV is probably not a DOS feature but due to plasmon losses, which create a broadened replica of the bottom of the CB at the plasmon energy. When the core-level spectra are used to estimate the plasmon energy and scattering efficiency, the plasmon losses account for most of the rise at 16 eV. In the a -Si:H spectra, there are no significant features in the CB within 6–15 eV of E_F . The lack of structure is expected since the CB states are more delocalized and conse-

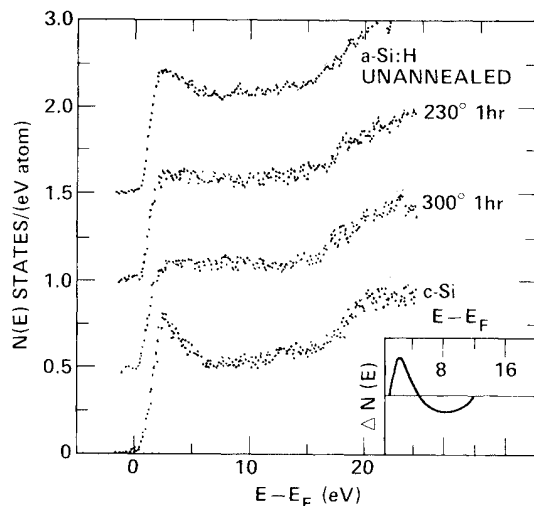


FIG. 1. BIS spectra for c -Si and a -Si:H after different annealing periods. The vertical scale was obtained by normalizing the a -Si:H and c -Si to each other at energies ~ 200 eV above the CB edge. The absolute value for the c -Si DOS was estimated with use of the theoretical calculations of Ref. 17. The inset shows the difference between the as-deposited and the 310°C-annealed sample.

quently are more sensitive to the presence of disorder.

For the as-deposited film (30 at.% H), the CB DOS exhibits a peak in the 1.2–4 eV region above E_F (inset, Fig. 1), which partially disappears upon annealing at 230°C for 1 h (25 at.% H) and completely disappears upon further annealing at 300°C for 1 h (19 at.% H). Anneals of 1 h at temperatures as high as ~ 650 °C do not result in a reappearance of the peak. This indicates that the peak is not the result of crystallization of the sample. The peak does not occur in samples deposited at 230°C containing 8% H in the bulk and is not observed in partial yield measurements since it is obscured by the exciton formation pulling spectral weight higher in the CB.

On the basis of the magnitude, annealing behavior, and energy position, the peak at the CB edge can be assigned to the Si-H antibonding orbital in an undetermined hydride configuration. We cannot conclusively determine whether the Si-H antibonding peak is due to the monohydride (the isolated Si-H bond), or to the polyhydride (Si-H₂, Si-H₃, etc.) since the H configurations within the 4-nm sampling region are not known exactly after annealing.

The energy of the peak is consistent with the measured energy of the Si-H antibonding states on c -Si (111) surface (1–3 eV above E_F)¹⁰ and estimates of the energy of the Si-H antibonding energy from tight-binding calculations on large clusters.¹³ These calculations which accurately predict the correct valence-band Si-H energies show that Si-H bonds, polyhydrides in particular, pull spectral weight from Si states above 4 eV to energies near the CB edge as is observed. Because the Si-H₂ and Si-H₃ configurations are less strongly coupled to the lattice, the calculated CB DOS of the polyhydrides exhibits a significantly sharper peak than the isolated Si-H bond.¹³ Consequently, the polyhydride DOS features are expected to be more readily observed. Furthermore, the calculations predict that the centroid of the CB states shifts to lower energy as the H content is increased. In the BIS spectra, the peak at the CB edge recedes from the gap as H is removed. Consequently, the calculations are consistent with the hypothesis that the peak arises from Si-H antibonding orbitals.

The magnitude of the peak is consistent with the H content of the film. When the hydrogen content, X , of a film is decreased from 30% to 19%, the number of Si-H bonds per Si atom, $X/(1-X)$, is reduced by 0.2 state per Si atom compared with a change of ~ 0.15 state per atom determined from

Fig. 1.

Finally, the dependence of the peak upon annealing indicates that it is caused by Si-H bonds most likely in the polyhydride phase. Samples deposited at 25 °C contain a large concentration of H bonded in the polyhydride configuration causing a pronounced peak in the BIS spectra. Annealed films and as-deposited 230 °C films have little polyhydride within 4 nm of the surface resulting in a reduced peak.¹⁴ Raman¹⁵ and uv photoemission¹⁴ studies of annealed and 230 °C samples show that the monohydride is still present in these samples. The antibonding features due to the remaining ~8% estimated H concentration within 4 nm of the surface would be ~0.01 of the background. Because the antibonding monohydride feature is expected to be broad, this small feature is not observable. Thus, the energy, the magnitude, and the annealing behavior indicate that the feature is due to the Si-H antibonding orbital probably in a polyhydride configuration.

The conduction band edge was examined in greater detail by obtaining spectra of *c*-Si and *a*-Si:H (Fig. 2) with significantly increased counts and a smaller energy increment between points compared to the spectra in Fig. 1. The *c*-Si spectrum exhibits two peaks near the CB bottom due to critical point structures near the *L* and Γ points in the Brillouin zone. The peaks are a consequence of the long-range order of the crystal. The 0.72 eV resolution of the BIS spectrometer significantly broadens the observed edge. With utilization of measured instrumental broadening, the data can be deconvolved by means of a constrained iterative scheme.¹⁶ Figure 2 shows excellent agreement between the deconvolved data and *c*-Si calculations.¹⁷ Note in particular the square-root region due to the indirect *L* point at the CB edge. This agreement demonstrates that the BIS measurements and subsequent deconvolution provide an accurate determination of the CB edge shape. The discrepancy between the relative peak heights is due to the fact that the Si(3*s*) cross section of the first peak is enhanced over the cross section of Si(3*p*) states of the second peak.¹⁸

When the *a*-Si:H CB edge spectra are examined in similar detail, we find that the as-deposited 25 °C *a*-Si:H sample has a CB edge which lies within ~0.2 eV of the *c*-Si CB edge. This result is consistent with previous absorption threshold measurements.⁹ In addition, the CB decreases more rapidly than *c*-Si from the peak DOS proceeding towards the gap. Annealing apparently broadens the CB edge. The structure in the deconvolved DOS for

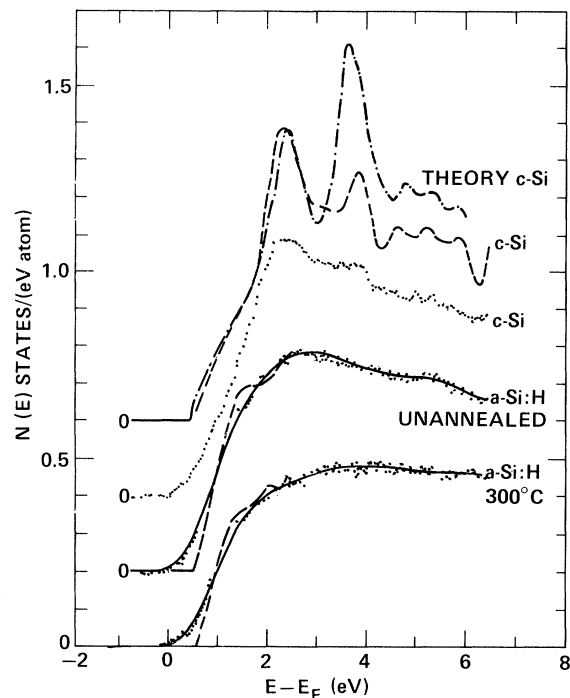


FIG. 2. BIS spectra with improved statistics for *c*-Si and *a*-Si:H near the band edge: dots, data; solid lines, least-squares smoothed; and dashed curves, deconvolved spectra. The dot-dashed line is the calculated DOS (Ref. 17). Because the number of counts for the *a*-Si:H spectra were less than that of *c*-Si, the deconvolved spectra exhibited structure possibly due to noise above ~3 eV.

a-Si:H may be significant and is being investigated in more detail. Unlike the 1-eV-wide square-root region of *c*-Si, the region for *a*-Si:H must be less than ~0.4 eV wide. This result may be caused by disorder broadening of the CB states obscuring the square-root shoulder or by a shift of the CB peak towards the gap sharpening the CB edge. The sharpening of the *a*-Si:H CB edge compared to *c*-Si is similar to the behavior reported for the valence-band edge.⁹ Since the CB DOS is fairly linear over the band edge, and x-ray photoemission spectroscopy measurements suggest that the valence-band DOS is also linear,⁹ the band gap of *a*-Si:H should not be determined by a linear extrapolation of $(\epsilon_2 E^2)^{1/2}$, where ϵ_2 is the imaginary part of the dielectric constant and E is the photon energy, but rather by an extrapolation of $(\epsilon_2 E^2)^{1/3}$.¹⁹

An estimate of the DOS at the mobility edge was obtained by measuring the electric activation energy of the unannealed 25 °C sample with gap electrodes. The distance from the Fermi level to the mobility edge is estimated to be $\sim 0.76 \pm 0.1$ eV. With use of the deconvolved DOS, the maximum state densi-

ty at the mobility edge is estimated to be $\leq 8 \times 10^{21}$ states/(cm³ eV), an estimate quite consistent with electrical estimates.²⁰

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