

Invited

Electronic Structure of Crystalline and Amorphous Semiconductors and Heterojunctions Using Bremsstrahlung Isochromat Spectroscopy

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The conduction band (CB) density-of-states (DOS) in crystalline and amorphous semiconductors as well as CB band offsets in semiconductor heterojunctions may be obtained using bremsstrahlung isochromat spectroscopy (BIS). Spectra of crystalline semiconductors reveal a wealth of structure which can be identified with critical points in the band structure. The CB DOS for hydrogenated amorphous silicon (a-Si:H) on the other hand is virtually featureless. The CB offset for a-Si:H/silicon nitride conduction band offset was found to be ~ 2.2 eV.

§1. Introduction

The conduction band (CB) density-of-states (DOS) is of fundamental importance for the understanding of semiconductors and heterojunctions. In particular, the transport properties are determined by the density and capture cross section of the CB states while the optical properties depend on both the valence and CB DOS in addition to the optic matrix element. Recently, a method known as bremsstrahlung isochromat spectroscopy (BIS) or inverse photoemission has been used to measure the CB DOS of semiconductors directly without exciton or core hole broadening effects which plague alternative methods.¹⁻⁴ A brief overview of some of the results and types of information that can be obtained from BIS for semiconductors, both crystalline and amorphous, as well as heterojunctions is presented in this paper.

§2. Experiment

The BIS spectra are obtained by mounting a sample in an ultrahigh vacuum chamber of a VG ESCLAB facory modified for BIS. A monoenergetic beam (1486.6 eV) of electrons impinges on the sample. X-rays are emitted when the electrons make transitions from this highly excited state into the conduction band. Because the rate of x-ray emission at a fixed photon energy is proportional to the density of final CB states, the CB DOS is determined by measuring the rate of x-ray emission for a fixed photon energy as the electron energy is varied. Further details may be found in Refs. 1,3,4.

The experiment is equivalent to a time reversed x-ray photoemission experiment—hence, the term inverse photoemission.

§3. Crystalline Semiconductors

The sensitivity and accuracy of BIS spectra for determining CB DOS is demonstrated by examining the spectra of c-Si, c-Ge, and c-GaAs presented in Fig. 1. Six

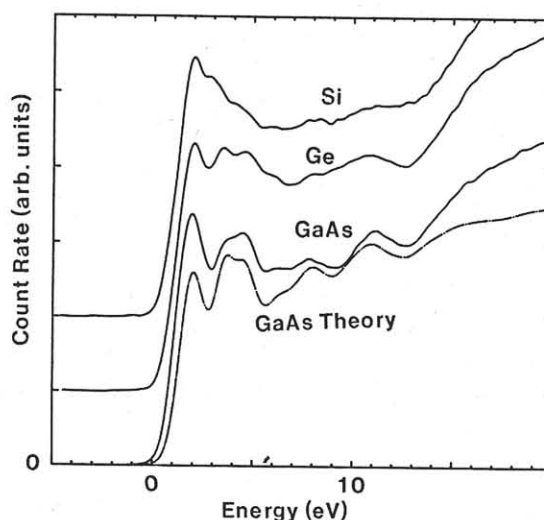


Fig. 1. BIS spectra for crystalline Si, Ge, and GaAs versus energy (solid) and the calculated density of states for GaAs using a local density functional calculation. The experimental spectra were smoothed by a 0.3 eV Gaussian while the theoretical spectra were broadened by the experimental resolution and by lifetime broadening as in Ref. 6.

peaks in the DOS can readily be identified in all 3 semiconductors and correspond in magnitude and relative energy with DOS features found in calculations⁵ (e.g., dot-dashed line Fig. 1). The deviations between theory and experiment at energies greater than ~ 16 eV are due to intrinsic and extrinsic plasmon effects. Note that unlike the case of x-ray photoemission, there is no significant elastic background which must be subtracted. Furthermore, since the atomic character of the states within the CB are more mixed than in the valence band, there is less distortion due to variations in the photoemission cross section. The energy shift of the BIS features compared to local density functional theoretical calculations yield a measure of the real part of the self energy corrections while the loss of structure at higher energies above the CB edge are related to the imaginary part.⁶ The close correspondence between theory and experiment indicates that the BIS spectra represent an accurate determination of the CB DOS.

§4. Hydrogenated Amorphous Silicon

Having established that BIS spectra are accurate representations of the CB DOS, consider next the spectra of hydrogenated amorphous silicon (a-Si:H) presented in Fig. 2 for a heavily hydrogenated a-Si:H (30 atomic % H) as-deposited film and following various annealing periods which reduced the hydrogen concentration to 19 at. % H. This feature is not due to crystallization of the film since the feature does not reappear even after a 550 °C anneal. On the basis of the energy and number of the states which are removed, the peak near the CB edge can be attributed to the Si-H antibonding orbital in the polyhydride configurations (SiH₂ and SiH₃).⁶ Other than the feature due to the silicon hydrogen antibond states, the CB DOS a-Si:H is essentially featureless in contrast to the crystalline semiconductors. The rise ~ 16 eV above the CB edge is due to plasmon effects.

Significant progress may be made in understanding the transport properties of amorphous silicon using this CB DOS information. For example, from the fact that the BIS spectra are referenced to the Fermi level and that the conductivity activation energy is the difference between the Fermi energy and the conduction band mobility edge, the DOS at the mobility edge, $N_c(E_c)$, was determined to be 3.6×10^{21} states eV⁻¹ cm⁻³ for low defect a-Si:H deposited at 230 °C.³ This value of $N_c(E_c)$ is remarkably consistent with the minimum metallic conductivity^{7,8} and the random phase approximation for the mobility. Using the expression⁸

$$\mu = 2\pi e \hbar^3 a N_c(E_c) / (3m^2 kT) \quad (1)$$

for the microscopic mobility, μ , where m is the electron mass, a is the phase coherence of the electron wave function ($\simeq 1$ lattice spacing), and T is the temperature, yields a value of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ which is in excellent agreement with measured values from time-of-flight experiments.⁹ Hence, the phase coherence is on the order of 1–2 lattice spacings.

The attempt-to-escape frequency for emission from dangling bond defects can also be determined with the aid of the relation

$$\gamma = kT N_c(E_c) \nu_{th} \sigma \quad (2)$$

where ν_{th} is the thermal velocity and σ is the capture cross section. Deep trapping time-of-flight measurements¹⁰ give a value of 4×10^{-8} for $\sigma \nu_{th}$ and hence, 4×10^{12} Hz for the attempt-to-escape frequency—a value consistent with previous measurements.¹¹

Further progress in understanding transport in amorphous silicon may be made by incorporating DOS information obtained from other measurements to obtain a nearly complete DOS (Fig. 3). Such a DOS was obtained by utilizing x-ray photoemission spectra for the valence band density of states, band tail densities were obtained from dispersive transport measurements, and mid-gap densities were determined by isothermal capacitance spectroscopy.^{11,12} This DOS has been used to explain the temperature and doping dependence of the

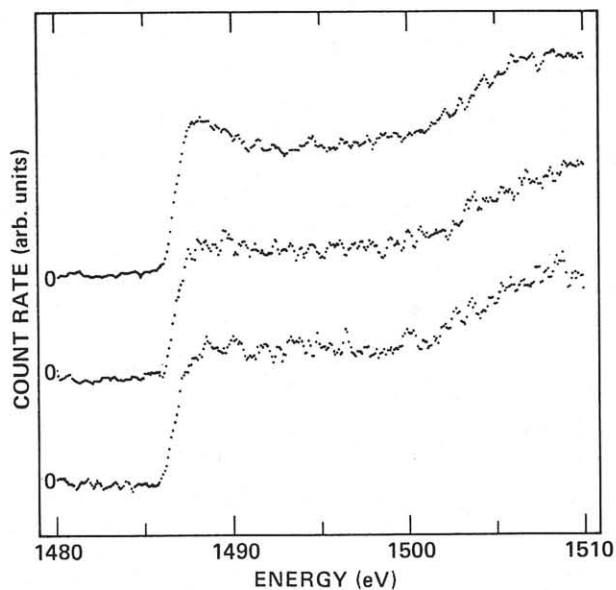


Fig. 2. BIS spectra for an a-Si:H sample deposited at 25 °C (top) and following an anneal at 250 °C for 1 hr. and at 310 °C for an additional hr. (bottom) from Ref. 4.

conductivity for phosphorus doped samples. The observed conductivity activation energy of ~ 0.19 eV for a 10^{-4} P doped sample, for example, is consistent with this DOS.⁷ The above examples demonstrate that the DOS is extremely useful for understanding transport.

The complete DOS indicated in Fig. 3 can also be used to understand the optical properties of hydrogenated amorphous silicon. The imaginary part of the dielectric function, $\epsilon_2(E)$, is given by the expression³

$$\epsilon_2(E) \sim R^2(E) \int N_v(x) N_c(x+E) dx \quad (3)$$

where $R^2(E)$ is the dipole matrix element squared averaged over all transition separated by energy E , N_v is the density of occupied valence band states, and N_c is the density of occupied conduction band states. The imaginary part of the dielectric can be measured using ellipsometry and photothermal deflection spectroscopy and N_v and N_c are obtained from Fig. 3. Hence, the averaged dipole matrix element may be determined as a function of energy. It has been found to be independent of energy from 1.0 to 3.4 eV with a value of $10 \text{ \AA}^2$ above 3.4 eV, it drops as E^{-5} —a dependence similar to the

energy dependence for the absorption of a classical dipole. The fact that the dipole matrix element does not change significantly for localized-to-extended state transitions at low energies (< 1.7 eV) and for extended-to-extended transitions at energies above (2.0 eV) indicates that the phase of the conduction band wavefunction is essentially random from site to site.¹³ This result is consistent with the similar finding presented above from the transport measurements.

A prediction following from this result would be that the momentum relaxation or scattering time for carriers above the mobility edge to be given roughly by lattice spacing ($\sim 2.5 \text{ \AA}$) divided by the thermal velocity of roughly 1.1×10^7 cm/sec or 2.4×10^{-15} sec. Excited carriers within the conduction band should exhibit a Drude type free electron absorption with a scattering time on the order of 2.4×10^{-15} . Thus, spectrally resolved photoinduced absorption experiments for excited electrons should yield Drude type energy dependence consistent with this scattering time.

§5. Density-of-States a-Si:H/a-Si₃N₄:H Heterojunctions

Finally, we present some new results demonstrating the information that may be obtained on heterojunctions. In Fig. 4, spectra of thin layers (2.5, 5.0, and 10 nm) of a-Si₃N₄:H on a-Si:H layers is presented. As the a-Si₃N₄:H layer thickness increases, the contribution from the a-Si:H decreases. From the decrease as a function of thickness, one can estimate the penetration depth of 1.486 keV electrons in a-Si₃N₄:H to be ~ 2.5 nm. The offset of ~ 2.2 eV between the a-Si:H and the a-Si₃N₄:H edge is a measure of the band offset between the CB edge of a-Si:H and a-Si₃N₄:H. This value is consistent with 1.2 eV offset found for the valence band offset¹⁴ since the band gap of a-Si:H and a-Si₃N₄:H is 1.8 and 5.2 eV, respectively. The advantage of using BIS for determining the CB offsets is that the conduction band offset may be significantly larger than the valence band offset permitting a more definitive separation of the contributions of the various layers.

The CB for a-Si₃N₄:H, exhibits a peak near the CB edge and decreases towards higher energies. This feature may be due in part to the large concentration of hydrogen (30%) present within the film. If much of this H is bonded to silicon, this DOS feature would be similar to that found in the heavily hydrogenated a-Si:H depicted in Fig. 2.

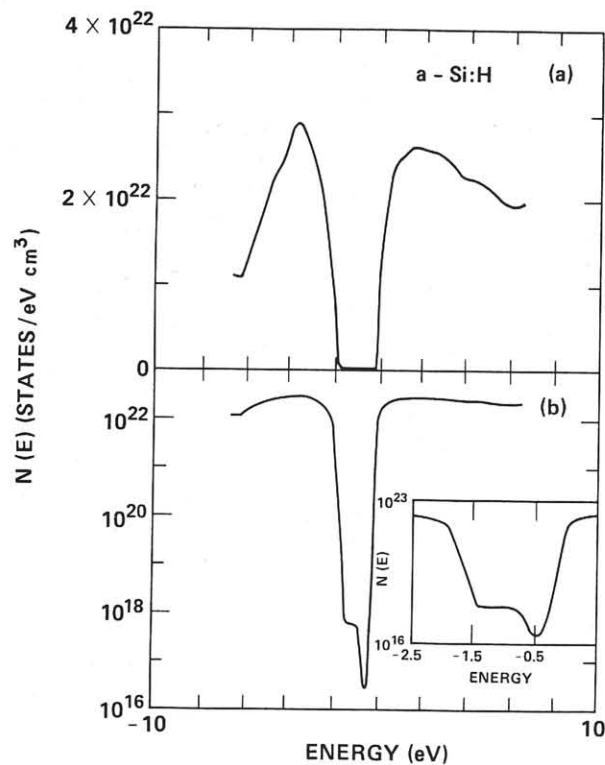


Fig. 3 The complete DOS for a 2×10^{-5} P doped a-Si:H film obtained from various electron spectroscopies, transport, optical, and capacitance measurements discussed within the text (a) linear plot (b) log plot (Ref. 3).

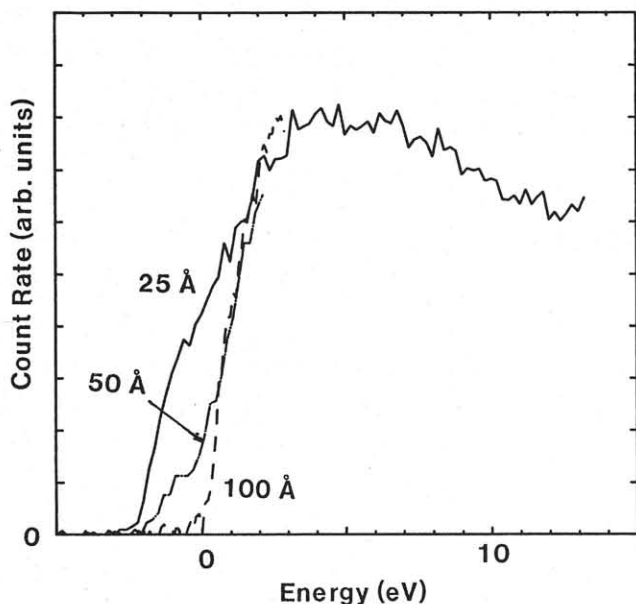


Fig. 4 BIS spectra for a $\text{a-Si}_3\text{N}_4\text{:H}$ overlayer on a-Si:H of various thicknesses.

§6. Acknowledgements

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§7. References

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