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Lack of Photoemission Evidence for Tailing of Density of States into Energy Gap of Amorphous Si

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A photoemission study of amorphous Si for $5.5 \leq \hbar\omega \leq 11.7$ eV has been made with emphasis placed on checking an earlier report of photoemission evidence for a tailing of the density of states into the energy gap. A comparison of photoelectron energy distribution curves from amorphous Si with those of Au and crystallized Si yielded no evidence for tailing of the density of states. It is concluded that the large tailing of the density of states previously reported is not an intrinsic property of amorphous Si but probably a result of the different sample preparation. In both our amorphous and crystallized Si films the Fermi level is located 0.28 ± 0.05 eV above the valence band maximum at the surface.

Much of the experimental and theoretical work on amorphous materials has been centered around the postulate that the lack of long-range order results in the loss of sharp band edges because the density of states has a tail of localized states into the energy gap.[1,2] In a previous Letter,[3] Peterson, Dinan, and Fischer (PDF) interpreted their photoemission data from amorphous Si in terms of an exponential tailing of the density of states into the energy gap. Our photoemission data provide no evidence for such tailing and in fact allow us to place an upper limit of 3×10^{19} states/cm^3 eV on the number of states in the energy gap. Previous studies of Ge combining both optical absorption and photoemission measurements similarly found no evidence for a tail of localized states in the gap.[4] Optical-absorption and photoconductivity measurements[5] are more sensitive to states in the gap; the importance of this work is not just in setting an upper bound but in showing that it is possible to prepare samples which do not show the large tailing effects previously observed by photoemission.

The essence of the present work is a comparison of photoelectron energy distribution curves (EDC's) from amorphous Si with those of Au and crystallized Si films keeping factors which affect experimental resolution, such as the analyzer geometry and collector surface, as nearly identical as possible. To this end, all films were formed and measured in the same apparatus and ultrahigh vacuum was maintained without interruption throughout a series of experiments, such as comparison of EDC's from amorphous and annealed films or EDC's from Au and amorphous Si films.

The amorphous Si films, about 1000 Å thick, were electron-gun evaporated from both 100-Ω-cm n-type and 1000-Ω-cm p-type crystals onto polished Si single crystals [1000-Ω-cm (111) n type], and subsequently onto annealed polycrystalline Si films, and polycrystalline Au films. The source-to-substrate distance was 48 cm. The base pressure was less than 1×10^{-11} Torr and the pressure during evaporation less than 5×10^{-9} Torr at the typical evaporation rate of 2 Å/sec.[6] Similar results were obtained from samples prepared and measured on the different substrates at room temperature and on substrates maintained at temperatures as low as 100°K.

The EDC's were measured over a photon energy range $5.5 \leq \hbar\omega \leq 11.7$ eV using a spherical retarding field energy analyzer.[7,8] The EDC's were obtained by taking the derivative of the current-voltage curve using a previously described ac technique.[9,10]

Evidence for disorder-induced tailing of the density of states of amorphous Si into the gap might be first sought by comparing the high-en-

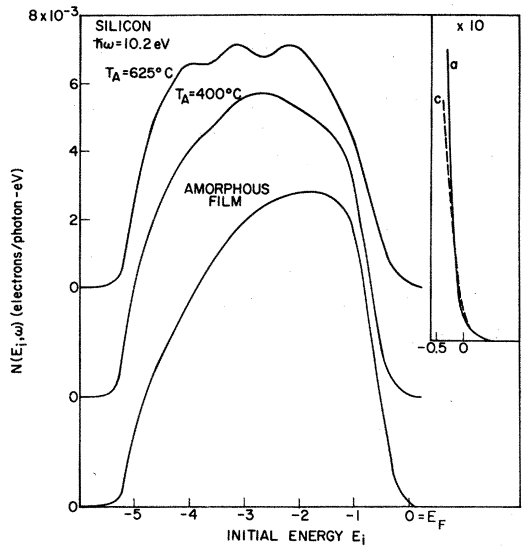

FIG. 1. EDC's from amorphous and annealed Si films. The insert, a 10× vertical magnification of the high-energy tails, shows the absence of any extra tailing in the amorphous (*a*) film as compared to the crystalline (*c*) film ($T_A = 625$°C).

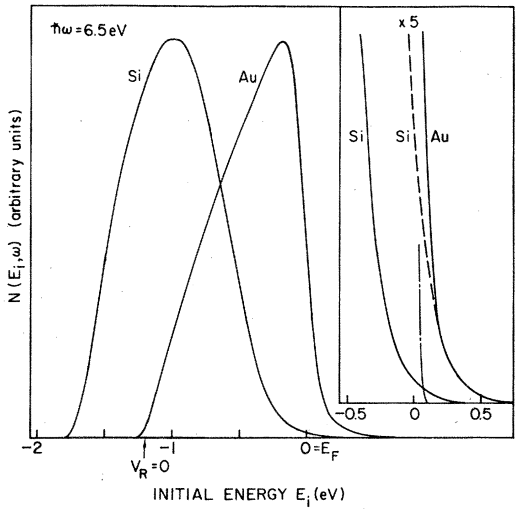

FIG. 2. The effect of instrumental resolution on the high-energy edge is shown by the comparison of EDC's from Au and amorphous Si at $\hbar\omega = 6.5$ eV. The insert shows the high-energy tails with a 5× magnification of the vertical scale; the dashed curve is the Si tail shifted 0.35 eV higher in energy to overlap the Au tail, and the broken curve is the true Fermi function cutoff of the Au. No extra tailing is apparent in the Si compared to the Au, but both are resolution broadened compared to the Fermi function cutoff. $V_R = 0$ is the point of zero retarding voltage.

ergy cutoffs of an EDC from an amorphous film with an EDC from the same film after it had been annealed to form a polycrystalline film. The three EDC's in Fig. 1 represent the film at three stages of the annealing process. The film was annealed for 30 min at temperatures of 250, 400, and 550°C, and for 90 min at 625°C. As seen in Fig. 1, some overall change in the EDC is observed at $T_A = 450$°C, and at $T_A = 625$°C the EDC has structure characteristic of the crystalline material.

The high-energy cutoffs of EDC's from the amorphous (*a*) and polycrystalline (*c*) films are shown in more detail in the insert of Fig. 1 which has a 10× enlargement of the vertical scale. The two striking features of the high-energy cutoffs are that (1) the amorphous and crystalline cutoffs are so similar and (2) they both appear to have tails extending above the Fermi level. Clearly no extra tailing is observed in the EDC of amorphous Si that could be attributed to the lack of long-range order. The high-energy tails observed in both the amorphous and crystalline EDC's result from the imperfect resolution found in any photoemission measurement system.

To get a measure of the effect of the imperfect instrumental resolution on the high-energy edge of an amorphous Si EDC we compare, as in Fig. 2, to an EDC from Au where the true high-energy edge is determined by the Fermi distribution. The relative position of the two EDC's is established by the retarding-voltage scale V_R which is the same in each case since the collector work function is the same. The energy scale drawn on Fig. 2 shows the initial state energy of the electrons, $E_i = E - \hbar\omega + \varphi$, where E is the measured electron kinetic energy, φ is the work function, and $E_i = 0$ corresponds to the Fermi level E_F. The 1.2-eV measured width of the Au EDC from the low-energy edge to E_F is consistent with $\hbar\omega - \varphi$, where φ is independently determined to be 5.3 eV from a Fowler plot of the photoelectric yield.

The shape of the true high-energy edge and the location of valence-band maximum in a semiconductor is ordinarily more difficult to determine than in a metal. Measurements over a wide range of photon energy show that the EDC's of amorphous Si can be described by the nondirect transition model[11] (as expected since in the absence of long-range order the wave vector k is not well defined). Thus the true high-energy cutoff of an EDC from amorphous Si is at the valence band edge. Ideally we would like to determine the exact resolution function which convolved with the Fermi function gives the measured Au

high-energy edge and then deconvolve this resolution function and the measured Si edge to determine the true Si edge. Actually we must be satisfied with a model rectangular resolution function 0.25 eV wide which convolved with the Fermi function produces the slope of the Au EDC edge.[12] When the model resolution function and the Si edge are approximately deconvolved we find the valence-band edge 0.28 ± 0.05 eV below E_F in agreement with a linear extension of the edge. The insert of Fig. 2 shows a 5× vertical magnification of the Si and Au tail and of the Fermi tail which would give the undistorted EDC. The measured Au tail extends well beyond the small Fermi tail calculated for the measurement temperature of 130°K.[13] The similar shapes of the Si and Au tails indicate that when resolution effects are accounted for, Si will have a cutoff as sharp as the Au and the valence-band maximum will correspond to the linear extension of the high-energy edge. The work function and threshold of amorphous Si are found to be 4.8 ± 0.05 and 5.08 ± 0.05 eV, respectively.

The experimental noise determines the minimum difference which can be detected between the Au tail (no tailing of localized states) and the Si tail (possible tailing). An EDC at 10.2 eV is a good approximation to the optical density of states within 5.1 eV of the valence-band maximum[14] and is expected by analogy to the crystalline density of states[15] to contain about 2.3 electrons. Knowing the yield at $\hbar\omega = 6.5$ and 10.2 eV we find that our noise level allows an upper bound of 3×10^{19} states/cm^3 eV to be placed on the tailing of the density of states in amorphous Si. If states are taken to be concentrated in a 0.1-eV-wide peak in the gap the number must be less than 3×10^{18} states/cm^3.

In determining this upper bound on the density of states in the gap we have assumed that the optical matrix elements between localized gap states and the extended conduction states (5–6 eV above the conduction band edge) are the same as the matrix elements between extended valence states and the conduction states. A variation of matrix elements would change the upper bound on the states in the gap but not the conclusion that no states are observed in our photoemission measurement.

Our conclusion that no localized states are observed differs from the result of PDF[3] that there is a clearly observable tailing of localized states up to the Fermi level. In Fig. 3 we compare our EDC at $\hbar\omega = 6.5$ eV with an EDC of PDF at $\hbar\omega$ = 6.53 eV. The EDC of PDF is 0.4 eV wider than ours as a result of a lower photoelectric threshold. Both the difference in the photoelectric threshold and the different position of the high-energy edge are presumably caused by the different sample preparation. PDF suggest that the cross-hatched area between −0.6 eV and the Fermi level is due to an exponential tail in the density of states. This cross-hatched area is approximately 10 times larger than the area corresponding to our upper limit of 3×10^{19} states/cm^3 eV. The conclusion which we draw from this comparison is that while a tailing of the density of states may be caused by a given sample preparation, such a large tailing as previously reported is not an intrinsic property of amorphous Si. We suggest that the previously reported tailing[3] is probably due to imperfections such as impurities and voids in the sample films.

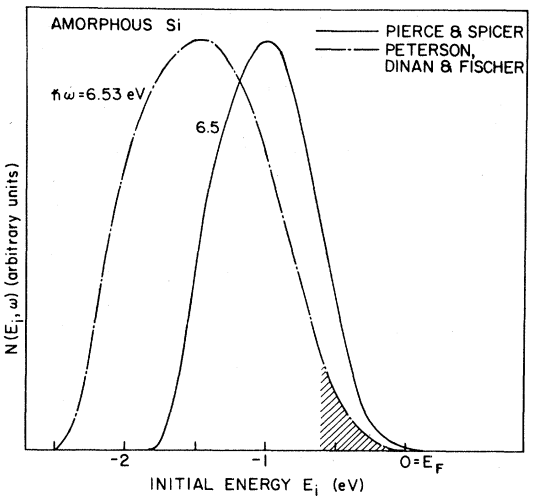

FIG. 3. A comparison of EDC's of amorphous Si obtained in the present work and in the work of Ref. 3. The cross-hatched area shows the area attributed to an exponential tailing of the density of states. This area is about 10× larger than the area corresponding to the upper bound 3×10^{19} states/cm^3 eV established in this work.

Interestingly, the position of the Fermi level 0.28 ± 0.05 eV above the valence band maximum at the surface of amorphous and crystallized Si films is the same as the position found for cleaved Si crystals.[16] It is likely that the Fermi level at the surface is pinned by surface states associated with unsatisifed covalent bonds which are little affected by long-range order.

It is interesting to speculate that since (1) there is considerable evidence for the presence of

microvoids in the interior of many amorphous Si samples,[17,18] (2) Fermi-level pinning is likely on the surfaces of the microvoids, and (3) the bulk Fermi level away from the microvoids may differ from the Fermi level at the surface of the microvoids, band bending in the volume of amorphous samples is likely. This could lead to microbarriers and produce activated mobility and other transport characteristics usually associated with "tailing states." The probable relation of internal surfaces in amorphous Si to the optical properties has been previously noted.[19] The microvoid density can be reduced by careful sample preparation (exclusion of oxygen impurities appears important) and annealing.[17] In interpreting transport data, it is important to distinguish between effects due to microvoids which decrease as the microvoid density is reduced and effects due to "true tailing states" which should not be affected as long as long-range order is not produced.

The microbarriers discussed above could produce the undulating bands which have been suggested by Cohen,[20] Fritzsche,[21] and Tauc.[22] However, any such effects in the present samples would have to be small since appreciable "undulation" would produce spatial variation in the absolute energy of the valence-band maximum which in turn would lead to a measurable smearing of the high-energy edges of the EDC's.

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Tailing in the Density of States in Amorphous Silicon

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The appropriate measurements and interpretation for deciding on the existence of a tail in the density of states at the top of the valence band of amorphous semiconductors are described. The data presented clearly show the existence of such a tail. The magnitude of the latter depends on method of preparation and annealing. The tail is therefore attributed to short-range defects.

In a previous publication, Peterson, Dinan, and Fischer[1] presented yield spectra and energy distributions of electrons obtained in photoelectric emission from amorphous silicon. The results were interpreted in terms of a tail in the density of states near the top of the valence band, supporting the models of Mott[2] and of Cohen, Fritzsche, and Ovshinsky.[3] Pierce, Ribbing, and Spicer[4] have performed similar measurements, found no evidence for the high-energy tail, and reinterpreted the previous results[1] in terms of an error in interpretation,