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,

namely the neglect of the imperfect resolution of the electron-energy analyzer.

We shall limit ourselves here to the area of disagreement with the Stanford group, i.e., appropriate measurements and their interpretation in view of establishing the existence or absence of a tail in the density of states at the top of the valence band. A more complete report is being published elsewhere.[5] We first discuss the energy resolution of the experiment and show that it cannot account for the tails described in Ref. 1. Then we argue that a comparison of energy distributions from amorphous and crystalline silicon does not show directly the differences in the densities of states because selection rules for optical transitions are different in these two materials. Finally we present energy distributions from films that were prepared in a different way than those of Ref. 1, but confirm the earlier conclusion that a tail in the density of states at the top of the valence band indeed exists in amorphous silicon.

It is clear that an electron excited from a well-defined energy level in the solid will be measured in a photoemission experiment with an uncertainty ΔE_{res}. The latter consists of inhomogeneities of work function of the retarding electrode, of the bandwidth of the monochromator (0.05 eV), of geometric imperfections of the analyzer, and of the magnitude of the modulating voltage in ac differentiation. We shall not go into these details but describe our method for calibrating the analyzer and its resolution. In our experiments, provision is made to replace the sample under investigation *at any time* by a clean metallic emitter. The high-energy end of the distribution from the metal should ideally have the shape of the Fermi-Dirac function. Comparison with the real shape of the distribution for Ta in Fig. 1 allows one to get an immediate measure of the total uncertainty $\Delta E_{expt} = 0.15$ eV.[6] The metallic distribution also serves to locate the energy of the initial states with respect to the Fermi level. (Since the metal and amorphous silicon are electrically connected, their Fermi levels are equal if thermodynamic equilibrium is not significantly disturbed.)

Figure 1 shows energy distributions from an amorphous silicon film, as well as the high-energy end of a distribution (at $h\nu = 6.2$ eV) from the tantalum reference. The energy scale is chosen to represent the energy before excitation with respect to the Fermi level. The silicon film was prepared in ultrahigh vacuum by vapor deposition on clean single-crystal silicon substrates held at room temperature and subsequent annealing at 150°C for 5 min. The source-to-substrate distance was 1 cm in the previous study[1] and 6 cm in the case shown here. This film is thus prepared differently from the ones described by Peterson, Dinan, and Fischer. We shall see below that it leads to the same conclusion, namely the existence of a tail in the density of states at the top of the valence band of amorphous silicon.

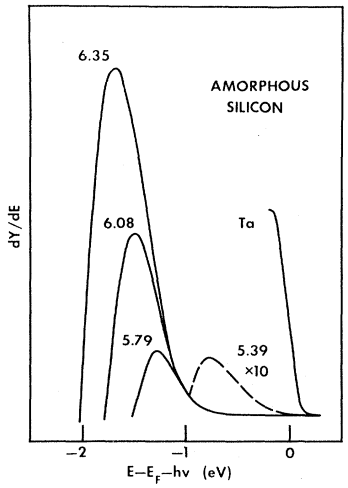

FIG. 1. Energy distributions of photoelectrons from tantalum and amorphous silicon. The abscissa represent the energy of electrons prior to excitation; zero is the Fermi level. The distribution at $h\nu = 5.39$ eV is shown 10 times magnified.

The energy distribution from amorphous silicon presents a tailing towards high energies. The distribution from Ta also shows a tail, but much less pronounced; it is due to the finite resolution of the analyzer.[4] Since the tail in the semiconductor is much more pronounced, it cannot be ascribed to experimental effects alone.

The interpretation of the data of Fig. 1 (and of those presented by the Stanford group) requires some care. It is well known[7] that energy distributions obtained at $5 < h\nu < 6.5$ eV from crystalline semiconductors have shapes very similar to those of Fig. 1. In particular they also exhibit a high-energy tail that is far too pronounced to be due to experimental broadening. These tails are a consequence of $\vec{K}$-conserving selection rules: There is no direct optical excitation out of the top of the valence band. Thus in the crystalline case the shape of the energy distribution bears no resemblance to the density of states; the (sharp) top of the

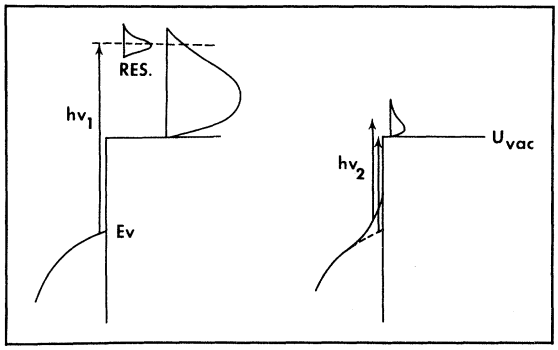

FIG. 2. Illustration of photoemission measurements. Left-hand side: large photon energy, sharp edge of the valence band. Finite analyzer resolution introduces spurious tail. Right-hand side: At low enough photon energy emission is only possible from real high-energy tail in density of states, independent of resolution of the energy analyzer.

valence band is located at or above the extremity of the tail.[6] It has been shown experimentally[4,5] that selection rules based on k-vector conservation do not exist in amorphous semiconductors. Thus, the upper half of the energy distributions of Fig. 1 is an image of the density of states near the top of the valence band and the tails observed (Fig. 1) represent a tail in the density of states.

The correct test for the existence of a tail in the density of states of the solid is illustrated in Fig. 2. The left-hand side shows the density of states with a sharp edge at the top of the valence band. The experimental smearing indicated as RES produces a spurious tail. We reduce the photon energy to values below $h\nu_2$ on the right-hand side of Fig. 2. In the absence of a tail, no electrons will be emitted. Conversely, electrons that are emitted at these low photon energies constitute a proof that there are indeed electrons with energies above the top of the valence band. Figure 1 shows such an energy distribution, obtained at $h\nu = 5.39$ eV, that is entirely made up of electrons excited out of states located in the high-energy tail. The latter is thus a real property of amorphous silicon.

Thus we come to the conclusion that amorphous silicon films prepared under different conditions in our laboratory all present evidence for a tailing in the density of states. (We have consistently made this observation on about fifty films for which electron diffraction and Auger spectroscopy showed that they were amorphous and pure silicon.) The discrepancy with the conclusions of the Stanford group may lie in the fact that their films were prepared in still another manner. But, according to the discussion presented above, direct comparison of distributions at high photon energies ($h\nu = 8.5$ eV) between amorphous and crystalline silicon is not the proper way of investigating the existence of the disputed tail. We recall that the density of states in the tail[1] as well as the position of the Fermi level depend on annealing. The data presented by Pierce and Spicer resemble the data we obtained after annealing our amorphous films to 500°C. For such films our data agree with Pierce and Spicer's upper limit of 3×10^{19} cm^{-3} states although we clearly see their presence.

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