Internal Photoemission of Holes and the Mobility Gap of Hydrogenated Amorphous Silicon

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(Received 16 June 1989)

We report the first observation of the internal photoemission of holes into the valence band of hydrogenated amorphous silicon from metal contacts. This, together with the corresponding photoemission of electrons into the conduction band, is used to directly determine the room-temperature mobility gap of *a*-Si:H. The effective mobility gap is found to be 1.89 ± 0.03 eV which is 0.16 eV larger than its Tauc optical gap of 1.73 eV. The important implications of the results on the understanding of *a*-Si:H band structure, electronic properties, and devices are outlined.

PACS numbers: 71.55.Jv, 73.40.Ns, 73.60.Gx

The concept of mobility edges, which represent the transition from extended free-carrier states to those where carriers are localized, is central to the physics of amorphous semiconductors.[1,2] The corresponding mobility gap, E_μ, is of both fundamental and practical interest since it is directly related to free-carrier transport and electronic properties of amorphous semiconductors. Although there is a general agreement about the existence of mobility edges in amorphous materials, no definite correlation has been made between mobility gaps and commonly measured optical gaps. The optical gaps, $E_{\rm opt}$, as defined by Tauc's relation,[1,3,4] are an extrapolation of the optical transitions between parabolic bands associated with extended states. They normally give the energy separation between the exponential regions of the optical absorption but no information about mobility gaps. This is true even for hydrogenated amorphous silicon (*a*-Si:H) which has been extensively studied as a prototype amorphous semiconductor due to its technological applications. Its band gap is still an ill-defined parameter and is generally taken to be 1.7 to 1.8 eV as obtained from the Tauc relation.[3,4] There have been attempts to *indirectly* estimate the mobility gap of *a*-Si:H;[5-8] the reported values which are based on a variety of assumptions ranging from 1.7 to 2.1 eV and have large uncertainties associated with them. The absence of reliable values for E_μ seriously limits any rigorous treatment of *a*-Si:H semiconductor properties as well as understanding of the nature and location of the individual mobility edges. In this Letter we report the first *direct* determination of E_μ in *a*-Si:H using internal photoemission (IPE) of *both* holes and electrons from the metal contacts into the extended states. This was made possible by the ability to obtain and characterize IPE of holes into the extended valence-band states of *a*-Si:H for the first time and thus determine the separation of the valence-band edge from the metal Fermi level, Φ_{Bp}. Correspondingly, the separation of the electron mobility edge from the same metal Fermi level, Φ_{Bn}, was obtained from the photoemission of electrons.[9] We find that for intrinsic *a*-Si:H having a Tauc optical gap of 1.73 eV, the effective mobility gap, $E_\mu = \Phi_{Bn} + \Phi_{Bp}$, is 1.89 ± 0.03 eV at room temperature. This value of E_μ, as well as the significant difference from $E_{\rm opt}$, has direct consequences on the understanding of the band structure in *a*-Si:H, its alloys, the physics of heterojunctions and amorphous superlattices, as well as the characterization and design of *a*-Si:H-based devices.

The separation of the conduction and valence band in single-crystal semiconductors has been measured using IPE of both electrons and holes where, to ensure efficient injection and collection of photoemitted holes, the values of Φ_{Bp} were obtained using *p*-doped crystals.[10,11] This approach, however, cannot be used to measure E_μ of intrinsic *a*-Si:H because doping leads to changes in $E_{\rm opt}$ and introduces large densities of defects[12] which makes it difficult to experimentally separate IPE currents from those generated in the *a*-Si:H. Consequently, in order to accurately determine E_μ it is necessary to measure both Φ_{Bp} and Φ_{Bn} for the same undoped *a*-Si:H material. This was accomplished by using p^+-*a*-Si:H/*i*-*a*-Si:H/metal structures in which the undoped layer was deposited at the same time as in the n^+-*a*-Si:H/*i*-*a*-Si:H/metal structures used to measure Φ_{Bn}.[9] These new structures, 0.4 μm thick, allow the efficient injection and collection of photoemitted holes due to a flat-band condition at the metal/*a*-Si:H contact resulting from the large built-in potential at the p^+/i junction and the low density of gap states in the intrinsic *a*-Si:H.[13] Furthermore, the collection of photoemitted holes could be enhanced by applying a positive bias to the metal without developing large dark currents. The p^+-*i* and n^+-*i* structures were deposited by glow-discharge decomposition of silane, as described elsewhere,[14] with intrinsic *a*-Si:H having an optical gap of 1.73 eV and a midgap density of states of $\sim 10^{15}$ cm^{-3}eV^{-1}. Rough (textured) conducting SnO$_2$ substrates were used to eliminate the large interference-fringe effects observed in the IPE on thin *a*-Si:H structures.[9] IPE was investigated using intimate metal/*a*-Si:H contacts which were simultaneously deposited onto both types of structures by vacuum evaporation of 100–150-Å-thick Al, Ni, Pd, and Pt films on top of the freshly etched undoped *a*-Si:H films. Both Φ_{Bn} and Φ_{Bp} were determined for all metal contacts at room temperature from the spectral dependence of photocurrents generated by photons incident on the metal in the photon energy range from 2.0 to 0.8 eV.[15]

An example of the photoemitted currents obtained from the p^+-i structures is shown in Fig. 1 where the yields for Pt and Al contacts, with +0.5 V applied to the metal, are plotted as a function of photon energy. For photon energies $\gtrsim 1.4$ eV the photocurrents exhibit the well-known exponential dependence on E which is associated with the optical-absorption edge in the valence-band tail states.[3] However, the spectral dependence of photocurrents for energies < 1.4 eV is quite different from that of the optical subgap absorption and carriers generated in the *a*-Si:H.[3] These photocurrents exhibit the characteristics expected for the internal photoemission of holes with a dependence on the metal contacts which is similar to that obtained for the IPE of electrons on n^+-i structures.[9,16,17] Furthermore, their dependence on positive bias to the metal is quite analogous to that obtained for IPE of electrons with negative bias to the metal contact.

Just as in the case of IPE of electrons, the spectral dependence of the results in Fig. 1 can be fitted by the Fowler-Nordheim relation for the photoemission of carriers from metals into semiconductors:[9,18]

$$Y(E) = C(E - \Phi_B)^2 \text{ for } E - \Phi_B > 3kT, \tag{1}$$

where $Y(E)$ is the yield, defined as the photocurrent per incident photon of energy E, and Φ_B is the separation of the conduction or valence band from the metal Fermi level. C is generally taken to be a constant reflecting the efficiency with which the carriers are generated in the metal and then injected into the semiconductor. The validity of Eq. (1) is limited to photon energies greater than $\Phi_B + 3kT$ because of the thermal distribution of carriers at the metal Fermi level which leads to a tail in the photoemitted currents. In the case of *a*-Si:H, this tailing in the lower photon energy range of $(\text{yield})^{1/2}$ data can be further enhanced by carrier injection into the localized states close to the mobility edges. However, the effect of this tailing is still small on values of Φ_B derived from the extrapolation of the yield at higher photon energies. There is also a more direct effect of the electric fields on the extrapolated values of Φ_B due to image-force lowering.[18] The decrease in Φ_B from its zero-field value, $\Delta\Phi_B$, due to a surface field E_s is given by

$$\Delta\Phi_B = \tfrac{1}{2}\,(qE_s/\pi\epsilon\epsilon_0)^{1/2}, \tag{2}$$

where ϵ is the dielectric constant of the material and ϵ_0 is the permeability in vacuum. We found that with surface fields up to $\sim 2\times10^4$ V/cm there was improvement in the collection efficiency of the photoemitted currents but the extrapolated values of Φ_{Bn} and Φ_{Bp} were within 10 and 20 meV, respectively.

The results for Al, Ni, Pd, and Pt contacts, obtained with a positive bias of 0.5 V to the metal, are plotted in Fig. 2 as $(\text{yield})^{1/2}$ versus photon energy. A good fit of the data by Eq. (1) for IPE of holes is obtained. The data on IPE of electrons from the same metal contacts on n^+-i structures measured under short-circuit conditions are similarly presented in Fig. 3. (The tailing of IPE at $E \lesssim \Phi_B + 3kT$ is not included in the figures.) The values of Φ_{Bn} and Φ_{Bp} obtained from the data are listed in Table I. In Fig. 3 there is a systematic increase in Φ_{Bn} as the work function of the metal increases from 4.3 eV (Al) to 5.6 eV (Pt).[19] In direct contrast to this,

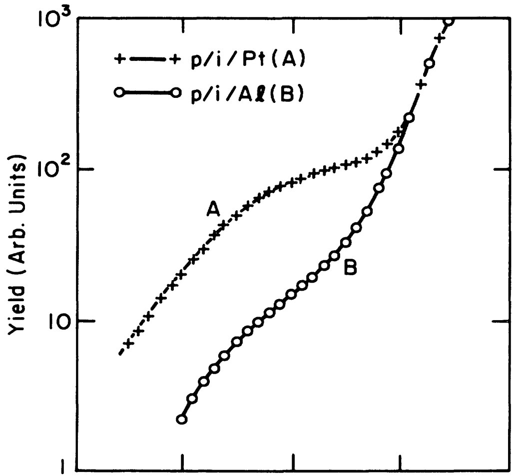

FIG. 1. The internal photoemission yield (current per incident photon) obtained from the p^+-*a*-Si:H/*i*-*a*-Si:H/metal structure for Pt and Al contacts, with +0.5-V bias applied to the metal.

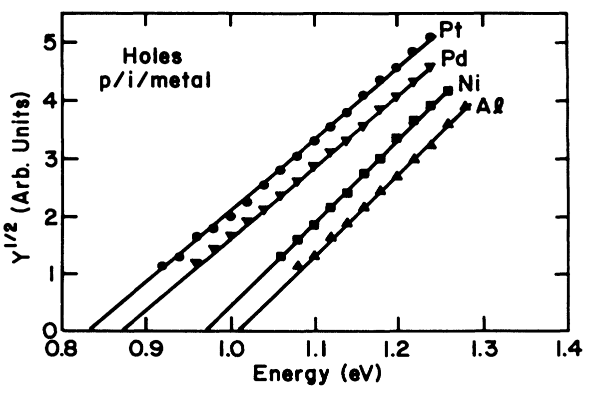

FIG. 2. $(\text{Yield})^{1/2}$ vs photon energy for the photoemission of holes from different metals into the valence band of intrinsic *a*-Si:H measured in a p^+-i structure.

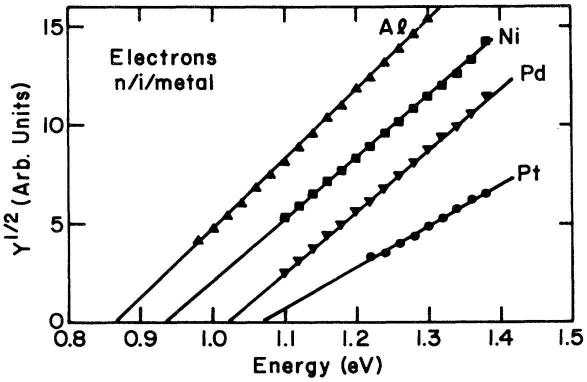

FIG. 3. (Yield)$^{1/2}$ vs photon energy for the photoemission of electrons into the conduction band of intrinsic a-Si:H for the same metal contacts as in Fig. 2, measured on a corresponding n^+-i structure.

TABLE I. The energy separation of the electron and hole mobility edges, Φ_{Bn} and Φ_{Bp}, from the metal Fermi level at four metal/undoped-a-Si:H contacts. The value of mobility gap, $E_\mu = \Phi_{Bn} + \Phi_{Bp}$, is also shown for the undoped a-Si:H having a Tauc optical gap of 1.73 eV.

Metal	Φ_{Bn} (± 0.01 eV)	Φ_{Bp} (± 0.02 eV)	E_μ (± 0.03 eV)
Al	0.87	1.01	1.88
Ni	0.93	0.97	1.90
Pd	1.02	0.87	1.89
Pt	1.07	0.83	1.90

the systematic changes in Φ_{Bp} seen in Fig. 2 correspond to a decrease in Φ_{Bp} with increasing metal work function. The relatively small changes in both Φ_{Bn} and Φ_{Bp} result from the pinning of the metal Fermi level at the semiconductor interface by large ($\sim 10^{12}$ cm^{-2}) density of interface states. The effects of these interface states on IPE currents can, however, be ignored because of the much larger densities of states in the metal ($\sim 10^{22}$ cm^{-3} vs $\sim 10^{19}$ cm^{-3}). The effect of pinning of the metal Fermi level is eliminated by measuring both Φ_{Bn} and Φ_{Bp} for the same metal contacts.

The results presented here on the IPE of holes and electrons for the four different metals allow us to determine the effective mobility gap, E_μ, of intrinsic a-Si:H. The intimate metal/a-Si:H contacts make it possible to associate Φ_{Bn} and Φ_{Bp} with the energy difference between the metal Fermi level and the mobility edges of the a-Si:H so that $\Phi_{Bn} + \Phi_{Bp} = E_\mu$. This is further confirmed by the fact that as Φ_{Bp} decreases, there is a concomitant increase in Φ_{Bn} which yields the constant value for E_μ listed in Table I. The absence of changes in Φ_{Bn} and Φ_{Bp} with the low fields used shows that the *effective* mobility gap at room temperature in intrinsic a-Si:H having a Tauc optical gap of 1.73 eV is 1.89 ± 0.03 eV. This is not surprising since mobility edges are expected to lie in a high density of states.[4] Further, this gives direct experimental support to the theoretical suggestion,[20] based on scaling arguments, that the mobility edges are roughly 0.1 eV away from the exponential tail regions. It is also interesting to note here that the value of E_μ is close the the energy where $\alpha = 10^4$, the energy that is often used to characterize the gap in amorphous semiconductors.[21]

The ability to obtain the photoemission of holes and electrons into the valence and conduction bands of a-Si:H offers an opportunity to address problems concerning the physics of localization in disordered systems related to the nature of mobility edges, their position, and their dependence on external parameters like temperature and pressure. Also, the detailed field dependence of Φ_{Bp} and Φ_{Bn} will yield information about the nature and densities of localized states in the vicinity of the mobility edges, states whose effects have to be taken into account in the interpretation of measurements involving transport of thermally or optically generated carriers particularly at low temperatures.[8] In addition, IPE of electrons and holes can be used to understand the role of structural and chemical disorder on the conduction- and valence-band mobility edges by extending these studies to different amorphous silicon alloys (e.g., H, C, Ge, N, etc.) as well as other amorphous semiconductors. The value obtained for the mobility gap reported here and the clearly established difference of ~ 0.2 eV between E_μ and the exponential absorption regions associated with disorder have practical and theoretical implications for a-Si:H-based heterojunctions and devices. For example, the understanding, the realistic modeling, and the design of a-Si:H solar cells has to be based on the correct value of E_μ. The results reported here show that the presently achieved open-circuit voltages are substantially lower than those limited by the mobility gap of 1.9 eV and the exponential band edges.[22] This strongly suggests that their open-circuit voltages and power conversion efficiencies can still be significantly improved.

We gratefully acknowledge the helpful discussion with S. Fonash, P. McElheny, and M. Vanecek. We are also grateful to C. M. Fortmann and Solarex Thin Film Division for supplying the a-Si:H structures. This work was supported by the Electric Power Research Institute and in part by The Ben Franklin Technology Center of Central and Northern Pennsylvania.

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