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## Hole drift-mobility measurements in microcrystalline silicon

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We have measured transient photocurrents on several *p-i-n* solar cells based on microcrystalline silicon. For two of these samples, we were able to obtain conclusive hole drift-mobility measurements. Despite the predominant crystallinity of these samples, temperature-dependent measurements were consistent with an exponential-bandtail trapping model for transport, which is usually associated with noncrystalline materials. We estimated valence bandtail widths of about 31 meV and hole band mobilities of 1–2 cm<sup>2</sup>/V s. The measurements support mobility-edge transport for holes in these microcrystalline materials, and broaden the range of materials for which mobility-edge transport corresponds to an apparently universal band mobility of order 1 cm<sup>2</sup>/V s. © 2005 American Institute of Physics. [DOI: 10.1063/1.1984087]

Microcrystalline silicon ( $\mu\text{c-Si:H}$ ) is a class of thin-film hydrogenated materials that are deposited under conditions fairly close to those that produce hydrogenated amorphous silicon (*a-Si:H*). One important application is as an optical absorber layer in solar cells, for which conversion efficiencies in single-junction cells based on this type of material have now reached 9.8%.<sup>1,2</sup> The device physics underlying these efficiencies has not yet been established, principally because we lack understanding of carrier transport and recombination. Indeed, carrier transport in  $\mu\text{c-Si:H}$  is of fundamental interest. The material is sufficiently ordered that its interband optical absorption is similar to that of crystal silicon (rather than the dramatically different optical properties of *a-Si:H*). However, disorder dominates sufficiently that transport properties have similarities to those of *a-Si:H*, as we shall show here.

In this letter, we present “time-of-flight” hole drift-mobility measurements<sup>3</sup> in several  $\mu\text{c-Si:H}$  samples from Forschungszentrum Jülich. Most amorphous semiconductors are well suited to the time-of-flight technique, but measurements in  $\mu\text{c-Si:H}$  have been inhibited by the relatively high dark conductivities. We were able to obtain hole drift mobilities conclusively in two of our samples. The hole drift mobilities are markedly higher than in *a-Si:H*, but the magnitude (<2 cm<sup>2</sup>/V s) remains far below the values for crystalline silicon ( $\approx 10^3$  cm<sup>2</sup>/V s). The hole drift mobilities were strongly temperature dependent and quite dispersive below room temperature. Some of these results differ from the conclusions of previous work (Refs. 4 and 5), which we discuss subsequently.

We found that the “exponential bandtail trapping” model that is commonly applied in amorphous semiconductors gave a fairly good account for our measurements, although the valence bandtail width and the attempt frequency were both markedly smaller than for holes in *a-Si:H*. In these models, the actual band-mobility is usually associated with a *mobility edge* (the level energy at which wavefunctions switch from localized to delocalized). Remarkably, the valence-band mobility  $\mu_0$  that we obtained was within the range of values around 1 cm<sup>2</sup>/V s that has been reported for *a-Si:H*. The similarity of the magnitudes in both  $\mu\text{c-}$  and *a-Si* suggests

that  $\mu_0 \approx 1$  cm<sup>2</sup>/V s may be a universal attribute of a mobility edge in silicon-based materials.

The samples used for our measurements were *p-i-n* structures prepared in a multichamber system using plasma-enhanced chemical vapor deposition (PECVD) at frequencies of 95 MHz (very high-frequency PECVD).<sup>1</sup> We used ZnO coated glass as a transparent, conductive substrate. The  $\mu\text{c-Si:H(B)}$  *p*-layers are about 20 nm thick; the films were doped by adding trimethylboron to the silane–hydrogen gas mixture. The intrinsic  $\mu\text{c-Si:H}$  layers were prepared using a silane–hydrogen mixture of 5–6%. The *n* layer (phosphine doped) was an *a-Si:H(P)* layer 30 nm thick. As top contacts, we used sputtered ZnO dots with diameters of 1–2 mm; we plasma-etched (SF<sub>6</sub>-gas process) the top surface of these structures to remove the *n* layer from regions not under the ZnO.

To determine the extent of crystallinity, Raman spectra were recorded from the *i* layer at spots right next to the ZnO contacts. The integrated intensity ratio  $I_C^{\text{RS}} = I_C / (I_A + I_C)$  was determined by deconvoluting the spectra into three signal peaks at 480 cm<sup>-1</sup>, 500 cm<sup>-1</sup>, and 520 cm<sup>-1</sup>. The first one can be attributed to a disordered structure, such as an amorphous phase or grain boundaries (*I<sub>A</sub>*), and the latter two are attributed to the crystalline phase (*I<sub>C</sub>*).<sup>6</sup> We were able to extract drift mobilities for samples C and D with the lowest crystalline volume fraction (Raman Ratios 0.60 and 0.61, and thicknesses 3.4 and 4.3  $\mu\text{m}$ , respectively). Two other samples with Raman ratios around 0.70 had depletion widths that were too small to permit accurate determinations of drift-mobilities.

Transient photocurrent measurements were done using a nitrogen-laser pumped dye laser with a pulse width of 3 ns. The samples were illuminated through the *n* layer using a laser wavelength of 500 nm, which corresponds to an absorption depth of about 160 nm. A step voltage bias was applied to the sample about 100  $\mu\text{s}$  before the laser pulse.

Figure 1 shows photocurrent transients measured at  $T = 250$  K on Specimens C and D for several applied bias voltages in the range  $V = 0$  V and  $V = 6$  V. The transient response at 0 V is due to the “built-in” electric field. At the shortest times ( $t < 3 \times 10^{-8}$  s), the 0 V transients are dominated by

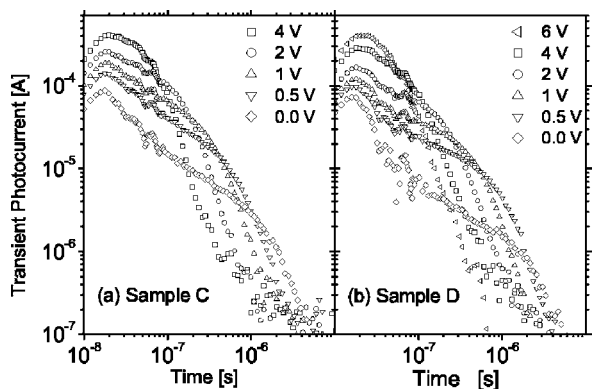


FIG. 1. Panels (a) and (b) show transient photocurrents taken at  $T=250$  K on Samples C and D for several applied bias voltages.

the very rapid collection of electrons. For longer times at 0 V, and throughout at the higher voltage, holes dominate the photocurrent. With this exception, these families of transients are consistent with standard “dispersive” hole drift mobilities. Each transient shows two segments: A “pretransit” regime with a fairly shallow power-law decay and the “posttransit” regime with a steep decay. With increasing voltage, the transit time occurs earlier, resulting in a “crossover” of the currents. Similarly dispersive transients have been presented many times before for amorphous semiconductors; we present these here to emphasize that a conventional drift-mobility interpretation does obtain in these microcrystalline samples.

Figure 2 shows the temperature-dependent hole drift mobilities  $\mu_D \equiv L/Et_T$  determined from transients such as those in Fig. 1;  $L$  is the photocarrier displacement at the transit time ( $d/2$ , if the entire sample is traversed), and  $E$  is the electric field (including an estimate of the effective, internal field).<sup>7</sup> The transit times were calculated using photocharge techniques<sup>8,9</sup> for the ratio  $L/E=7 \times 10^{-8}$  cm<sup>2</sup>/V. For reference, we show a multiple-trapping extrapolation of the hole drift mobility for one sample of  $a$ -Si:H;<sup>10</sup> it has not been feasible to directly measure  $\mu_D$  in  $a$ -Si:H for this value of  $L/E$  because of hole deep trapping by dangling bonds.

We briefly compare the present measurements with previous experiments on drift mobilities in  $\mu c$ -Si:H. One experimental problem has been the large dark conductivity of many of the microcrystalline materials, which militates against conventional photocarrier time-of-flight estimation of drift mobilities. Hole drift mobilities using conventional time-of-flight measurements were reported previously for

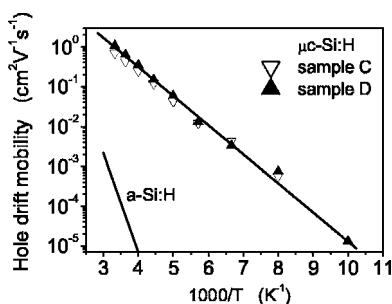


FIG. 2. Temperature dependence of the average hole drift mobility  $\mu_{d,h}$  for Samples C and D;  $\mu_{d,h}$  was evaluated at a displacement/field ratio  $L/E=7 \times 10^{-8}$  cm<sup>2</sup>/V. A typical hole drift mobility for  $a$ -Si:H extrapolated to this value of  $L/E$  is shown for reference.

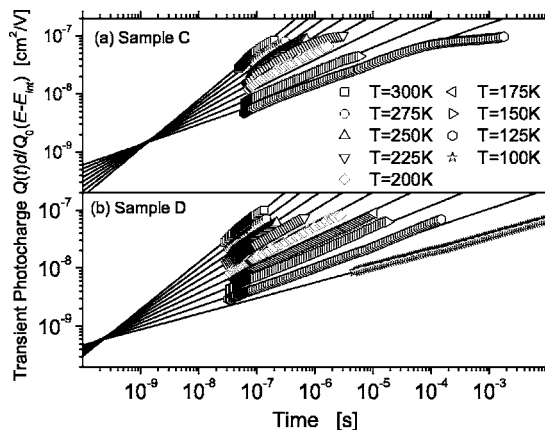


FIG. 3. Fittings of the bandtail multiple-trapping model to the transient photocharge measurements for Samples C (panel a) and D (panel b).

samples that were compensated to reduce their conductivity.<sup>4</sup> While the magnitude of the hole drift mobilities at room temperature was similar to those reported here, there was essentially no temperature dependence found between 100–400 K. Hole drift mobilities in intrinsic, but conductive,  $\mu c$ -Si:H have also been reported based on an unconventional “photo-CELIV” approach;<sup>5</sup> hole transport was reported to have a strong electric-field dependence which has not been found by other techniques. On a sample prepared under similar conditions as in the present study, electron and hole drift mobilities of 2–4 cm<sup>2</sup>/V s and 2 cm<sup>2</sup>/V s, respectively, were reported, which were also found to be thermally activated.<sup>11</sup> In this report, not only are the hole drift properties in a wide temperature range presented, but also the underlying transport mechanism are studied. Field-effect hole mobility measurements have been reported with a room-temperature magnitude of 0.2 cm<sup>2</sup>/V s,<sup>12</sup> which appears consistent with the present work.

We have applied the model of multiple trapping in an exponential bandtail to these hole drift-mobility measurements. The fundamental assumption of this model is that the valence-band density-of-states  $g(E)$  states may be divided at some level energy  $E_V$  into transport states (where the charge carriers are mobile) and traps (which immobilize the charge carriers until they are thermally re-emitted into transport states).  $E_V$  is commonly assumed to be the mobility edge<sup>13</sup> dividing localized and delocalized electronic states. In Fig. 3, the open symbols represent normalized transient photocharge measurements  $Q(t)d/[Q_0(E-E_{int})]$  for several temperatures.  $E$  is the electric field across the intrinsic layer, and  $Q_0$  is the total charge of holes estimated from the asymptotic value of  $Q(t)$ . The contribution of electrons has been subtracted, and a correction was taken to account for the built-in field  $E_{int}$ . The portions of these transients at early times close to the electronic rise time ( $t < 5 \times 10^{-8}$  s) have been excised, as have the late-time portions  $t > t_T$  where most holes have been collected.

As discussed by Wang *et al.*,<sup>8</sup> for times prior to the transit time  $t_T$ , the normalized charge  $Q(t)d/(Q_0E)$  estimates the ratio  $L(t)/E$  of the mean hole displacement  $L(t)$  to the electric field  $E$ . The bandtail multiple-trapping model predicts  $L(t)/E$ , and we used the following form for  $L(t)/E$  to fit the photocharge measurements:<sup>7,10</sup>

TABLE I. Multiple-trapping fitting parameters.

Multiple-trapping parameters	Sample C	Sample D
Band-mobility $\mu_0$ (cm <sup>2</sup> /V s)	1.0	2.4
Bandtail width $\Delta E_V$ (meV)	31	32
Attempt frequency $\nu$ (s <sup>-1</sup> )	$9 \times 10^8$	$5 \times 10^9$

$$\frac{L(t)}{E} = \frac{\sin \alpha \pi}{\alpha \pi (1 - \alpha)} \left( \frac{\mu_0}{\nu} \right) (\nu t)^\alpha, \quad (1)$$

where  $\mu_0$  is the ‘band mobility’ for the holes,  $\Delta E_V$  is the width of the exponential bandtail, and  $\nu$  is the attempt-to-escape frequency that characterizes thermal re-emission of holes from a valence band-tail trap back to the valence band. This particular form assumes that the mobility-edge lies within the exponential region of the bandtail. The solid lines in Fig. 3 are our proposed fits; the associated parameters are listed in Table I. The bandtail multiple-trapping model appears to account well for the temporal and thermal variations of the hole displacement.

Bandtail states have previously been proposed to account for electron paramagnetic resonance spectra,<sup>14,15</sup> for photocarrier recombination experiments,<sup>16</sup> and transient photoconductivity measurements<sup>17</sup> in  $\mu\text{-Si}$ . One paper—reporting temperature-dependent ambipolar diffusion lengths<sup>16</sup>—estimates an exponential valence bandtail width of 26 meV, which seems reasonably consistent with the estimates of 31–32 meV in the present work. These valence bandtail widths for  $\mu\text{-Si:H}$  are substantially lower than those (40–50 meV) reported for  $a\text{-Si:H}$ .<sup>9,10</sup> While this seems unsurprising, these valence bandtails are actually wider than conduction bandtails (20–25 meV) in  $a\text{-Si:H}$ .<sup>18</sup> In this context, it may be useful to make one observation regarding the microscopic character of bandtail states in  $\mu\text{-Si:H}$ . Theoretical studies of bandtail states near a mobility edge, such as those probed by drift-mobility measurements, show that these states are not strongly localized on a defective configuration of a few atoms, but are spread over a broad region<sup>13</sup> and possibly with an intricate ‘‘spongelike’’ spatial structure.<sup>19</sup>

It is interesting that the attempt-to-escape frequency estimates  $\nu \approx 10^9 \text{ s}^{-1}$  for bandtail-trapped holes in  $\mu\text{-Si:H}$  are lower than most values reported for holes in  $a\text{-Si:H}$  ( $\nu \approx 10^{11} - 10^{12} \text{ s}^{-1}$ ). We would speculate that these lower values of  $\nu$  in  $\mu\text{-Si:H}$  indicate a lower total density of bandtail states in the more ordered material. However, the physical significance of  $\nu$  is not well established, and even the assumption that its value is independent of trap level energy has been challenged.<sup>20</sup>

Our estimates of the valence band mobility  $\mu_0 \approx 1 - 2 \text{ cm}^2/\text{V s}$  for  $\mu\text{-Si:H}$  are similar in magnitude to estimates of  $\mu_0$  for holes and for electrons in  $a\text{-Si:H}$  and  $a\text{-SiGe:H}$ .<sup>18</sup> Bandtail widths associated with these estimates in  $a\text{-Si:H}$  vary from 20 to 50 meV, and es-

timates of  $\nu$  vary over several orders of magnitude. The near constancy of  $\mu_0$  across such a broad range of materials suggests to us that  $\mu_0$  is a fundamental property of band transport and of the mobility edge for disordered silicon-based materials, and perhaps even more broadly. This conclusion is likely inconsistent with the first interpretation of the mobility edge in terms of a minimum metallic conductivity;<sup>13</sup> computational work addressing this issue is in its infancy,<sup>21</sup> and it will be interesting to see if the proposal of a universal value for  $\mu_0$  based on experiment ultimately finds theoretical support.

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