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Hole Drift-Mobility Measurements in Contemporary Amorphous Silicon

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ABSTRACT

We present hole drift-mobility measurements on hydrogenated amorphous silicon from several laboratories. These temperature-dependent measurements show significant variations of the hole mobility for the differing samples. Under standard conditions (displacement/field ratio of 2×10^{-9} cm^2/V), hole mobilities reach values as large as 0.01 cm^2/Vs at room-temperature; these values are improved about tenfold over drift-mobilities of materials made a decade or so ago. The improvement is due partly to narrowing of the exponential bandtail of the valence band, but there is presently little other insight into how deposition procedures affect the hole drift-mobility.

INTRODUCTION

The drift of electrons and holes in electric fields is central to most electronic devices. While the fundamental physics of drift is fairly well established for most crystalline semiconductors, for hydrogenated amorphous silicon (a-Si:H) and other disordered semiconductors our understanding remains provisional. Experimentally, electron and hole drift are generally measured using "time-of-flight" measurements of the transit time t_T for a carrier across a specified displacement L and at a specified electric field E; by definition, the drift-mobility is

$$\mu_D \equiv \frac{L/E}{t_T} .$$

For a-Si:H and related materials, the drift-mobilities of electrons and holes in a given material can generally be understood using a "bandtail multiple-trapping" model that invokes a band mobility μ^0, the width ΔE of an exponential bandtail
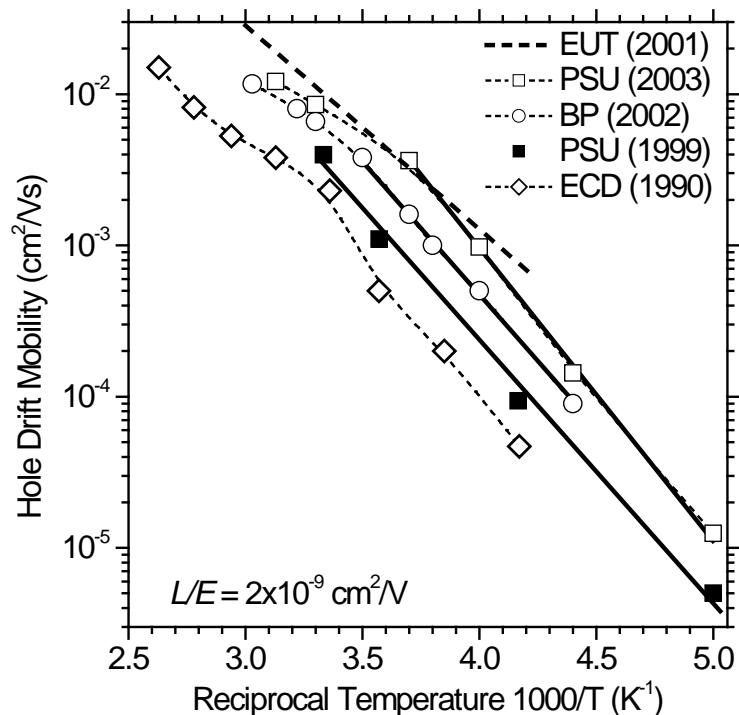

Figure 1: Temperature-dependent hole drift-mobilities for several a-Si:H materials; the mobilities correspond to a ratio $L/E = 2\times10^{-9}$ of the hole displacement L and the electric field E. The solid and dashed lines are fits to simply activated behavior.

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of localized states extending into the bandgap from the bandedge, and an attempt-frequency ν describing the trapping dynamics of mobile carriers by the bandtail states. The drift-mobility is generally much smaller than the band mobility. This property is the consequence of "multiple-trapping" – the successive capture and release of mobile carriers by the bandtail states.

This multiple-trapping parameterization is essentially phenomenological: we have very little understanding of the fundamental physics of exponential bandtails. For this reason it is important to study how changes in underlying materials affect drift-mobilities and the multiple-trapping parameters. For example, for electrons, alloying with germanium or carbon diminishes the drift-mobility substantially; this alloying effect appears to be due primarily to an alloying-induced broadening of the conduction bandtail [1,2]. Holes are typically several hundred times less mobile than electrons in amorphous-silicon based materials, but alloying effects are also much smaller than for electrons [2]. To the best of our knowledge, there is no theoretical understanding of these drift-mobility observations – neither the asymmetry of electron and hole drift mobilities in "standard" a-Si:H, nor their quite different alloying effects.

The fact that alloying does not significantly affect hole drift mobilities suggested that there was little that might be done to improve them, but starting in the mid-1990's there have been several reports of significant increases in hole mobilities in "contemporary" materials. We summarize some of these measurements, including those being reported here, in Figure 1. The lowest curve, denoted ECD(1990), was reported in ref. 2; the curve was measured on a sample prepared at Energy Conversion Devices, Inc., and is quite close to measurements on samples made prior to 1990 in several laboratories. In 1995, Ganguly and Matsuda [3] published hole drift-mobilities on several samples of a-Si:H showing a *much* higher drift-mobility than the 1980's baseline. This material has not yet been reproduced by other laboratories, but the indication that significant improvement in hole drift-mobilities is possible in a-Si:H is consistent with more modest improvements reported subsequently. In Figure 1, we have shown drift-mobilities based on previously published measurements on "expanding thermal plasma" material [4] made at Eindhoven University of Technology (denoted EUT(2001)). We also show measurements that are newly reported here on materials prepared at Pennsylvania State University (denoted PSU(1999) and PSU(2003)) and at BP Solar, Inc. (denoted BP(2002)).

In this paper we next present some additional details on the samples. We then describe for one sample how we obtain drift-mobilities from transient photocurrent measurements. We also briefly discuss fitting of multiple-trapping fitting parameters to the transient measurements. We conclude with a discussion of future directions for hole drift-mobility research.

SAMPLES

Several Schottky barrier diode samples were made in 1999 at Pennsylvania State University; substrates were SnO_2-coated glass. A 35 nm n^+ a-Si:H contact layer was first deposited onto the substrate. The undoped a-Si:H layer was then plasma-deposited (13.56 MHz) at a substrate temperature of 200 C and a hydrogen/silane dilution ratio R of 10:1. A top, semi-transparent Schottky barrier was formed by thermal evaporation of Ni onto the intrinsic layer; the top surface was briefly etching with buffered hydrofluoric acid prior to the evaporation step. The measurements reported here were on a sample with an intrinsic layer thickness of 1.47 µm.

Two additional samples were made at Pennsylvania State University in 2003 using similar substrates. These samples were *pin* structures: 25 nm a-SiC:H *p*-layer, a-Si:H intrinsic layer, 35 nm nanocrystalline Si *n*-layer, semitransparent Cr top contact. The intrinsic layer of one sample was made using $R = 10$ dilution (thickness 0.53 µm); the second was made without hydrogen

dilution (intrinsic layer thickness 0.69 μm). We have shown measurements for the undiluted sample, which had a somewhat larger hole drift-mobility than the diluted one.

The sample prepared at BP Solar, Inc. that was used in Figure 1 was prepared using DC plasma deposition; the intrinsic layer was prepared using a dilution ratio of 10, and was 0.91 μm thick . The sample had a *pin* structure (a-SiC:H *p*-layer), and was deposited onto SnO_2 coated glass. A semitransparent ZnO electrode was deposited onto the top *n*-layer. The sample was prepared under conditions similar to those used in the solar cell factory operated by BP Solar in Toano, Virginia. A second sample from BP Solar prepared in 1999 had quite similar drift properties; we don't report these here.

HOLE DRIFT MEASUREMENTS AND BANDTAIL MULTIPLE TRAPPING

In this section we provide details of the measurements and analysis for the sample denoted PSU(1999) in Figure 1. Transient photocurrent measurements are shown for three temperatures in the upper panel of Figure 2. These measurements were done using a dye laser (3 ns pulsewidth, 500 nm). The sample was illuminated through the *n*-layer. The normalization $i(t)d^2/Q_0V$ involves the thickness of the *i*-layer *d*, the reverse bias voltage *V* across the diode, and the total photocharge generated in the diode Q_0 (as estimated by integrating the transient photocurrent); the normalized photocurrent has the dimensions of a mobility (cm^2/Vs).

The photocurrent at 300 K shows an initial feature peaking at about 20 ns. This feature is due to the motion of electrons that are photogenerated in the top 10% (150 nm) of the sample. The electrons are swept to the top interface faster than can be resolved by the electronics, which had a response time of 60 ns for this sample. The longer-time photocurrent is due to the motion of holes. The "kink" in the hole-dominated section that occurs at a delay of about 1 μs corresponds to the time at which about half of the photogenerated holes
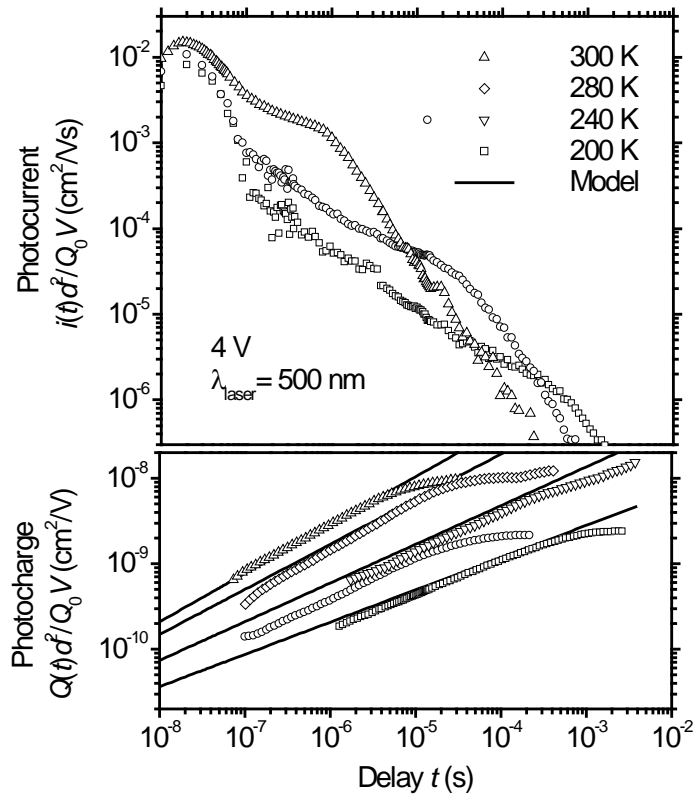

Figure 2: Normalized photocurrent ($i(t)$) and photocharge ($Q(t)$) transient measurements in one a-Si:H sample (PSU 1999) are shown at several temperatures as the open symbols. The photocurrent transients show an electron-transport feature peaking at about 20 ns that is due to the finite absorption-length of the laser; the longer-time behavior is the dispersive drift and sweepout of holes. We have subtracted the electron feature from the photocharge transients in the lower panel. The solid lines in the lower panel represent a fitting to the photocharge measurements using the bandtail multiple-trapping model.

have crossed the sample; this kink is often used to define a transit-time for calculating a hole drift-mobility.

These same features are also apparent in the transients at 240 K and 200 K. As the temperature falls, the "electron" feature becomes more prominent. This effect occurs because hole mobilities decline more with falling temperature than do electron mobilities. Following the electron feature, the hole photocurrent declines as a power-law ($t^{-0.44}$ at 240 K) through the kink (at

Table I: Valence Bandtail Parameters from Hole Drift-Mobility Measurements			
Sample	ΔE_V (eV)	ν (s^{-1})	μ_h^0 (cm^2/Vs)
PSU (1999)	45	1.0×10^{12}	0.7
ECD (1990)	48	7.7×10^{10}	0.27

the transit time). A power-law decay of the photocurrent $t^{-(1-\alpha)}$ is the defining attribute for "dispersive" transport, where a is termed "the dispersion parameter;" in principle, the photocurrent following the transit time should fall as $t^{-(1+\alpha)}$. For the bandtail multiple-trapping model, $\alpha = kT/\Delta E_v$.

In the lower panel of the figure, the open symbols indicate the transient photocharge $Q(t)d^2/Q_0V$ calculated by time-integration of the photocurrent. The transients which saturate near the value 10^{-8} cm^2/V were recorded for 2 V bias. The transients saturating at 2.5×10^{-9} cm^2/V were recorded at 8 V bias; we generally use high bias voltages to estimate the total photocharge Q_0. For this panel, we have also subtracted the early-time photocharge that is primarily due to electron motion.

We use photocharge transients such as these to calculate drift-mobilities; we have previously shown that this procedure is consistent with methods using direct transit-time measurements [1]. The virtue of the method is that, in a single measurement, one obtains drift-mobilities for a continuum of displacement-field ratios. Prior to the directly-measured transit-time, the normalized photocharge may be interpreted as the ratio $L(t)/E$ of the mean displacement $L(t)$ of holes to the electric field E. The delay t corresponding to a specific displacement-field ratio L/E is then used to calculate the drift-mobility from the definition $\mu_D = (L/E)/t$.[*] The hole drift-mobilities in Figure 1 all correspond to the particular value $L/E = 2 \times 10^{-9}$ cm^2/V; because of dispersion, it is essential in comparing the drift-mobilities for different materials to use a common value for L/E.

The solid lines in Figure 2 are a fit to the experimental measurements based on the bandtail multiple-trapping model. This model has been described elsewhere; the three parameters that are involved in the fitting are the width of the exponential bandtail of the valence band ΔE_V, the band mobility of holes μ_h, and the escape frequency ν describing hole trapping dynamics. The particular parameters chosen for Figure 2 are summarized in Table I, along with the parameters published for a sample (ECD 1990) prepared about ten years ago [2]. The equation to which these parameters apply is

$$L(t)/E = K(\mu_h/\nu)(\nu t)^{kT/\Delta E_V} \ , \tag{1}$$

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[*] Drift mobilities are often calculated using the conventional equation $\mu_D = d^2/Vt_T$, where t_T is the transit time actually observed as a breakpoint or kink in a photocurrent transient. Such mobilities are twice as large as drift-mobilities calculated using the "L/E" procedure used here. We prefer the "L/E" definition. For dispersive transport, the photocharge at the breakpoint has reached only half its saturation value. This implies that the mean displacement of carriers is half the sample thickness at the time at which the breakpoint occurs, so $L/E = d^2/2V$, and $\mu_D = d^2/2Vt_T$.

where $K = \sin(\alpha\pi)/(\alpha\pi(1-\alpha))$ [5], and $\alpha \equiv kT/\Delta E_V$. While the fit in Figure 2 is imperfect, it is worth noting that it does account fairly well for measurements over a range of nearly 10^4 in time and 10^2 in photocharge. Hole drift is enhanced by increases in μ_h and by decreases in ΔE_V; increases in ν diminish drift. We have not made a careful study of the errors in these fitting parameters.

DISCUSSION

We first comment again on the measurements of Figure 1. The drift-mobilities at lower temperatures are simply activated, as we have illustrated with the heavy solid lines. For the higher temperatures, the drift-mobilities are generally lower than expected from this activated behavior; in this regime, the electrical response times of the samples (typically 50-100 ns) were approaching the times used to calculate the drift-mobilities. We haven't tried to deconvolute these response-time effects from the measured photocurrent transients, although it is possible to do so [6]. We think it plausible that the deviation from activated behavior at higher temperatures is attributable to these electrical response times; the alternative, which needs further exploration, is that simply activated behavior – and the bandtail multiple-trapping model – fails.

It is curious that the activation energies for the various samples, excepting the Eindhoven sample, are so similar. For the bandtail multiple-trapping model, this activation energy is $(\Delta E_V)\ln(L\nu/\mu_h E)$. If the improvement in hole drift-mobilities were due exclusively to narrowing of the valence bandtail width, and not to changes in the band mobility or attempt frequency, we would expect the samples with superior drift-mobilities to have noticeably smaller activation energies. This perspective, applied to the conduction bandtail, was actually quite successful in explaining the alloy-effect on electron drift-mobilities in a-SiGe:H [1]. However, for the present measurements on holes, it seems that the improvement in hole drift-mobilities must reflect changes in at least one other of the multiple-trapping parameters; the results in Table I suggest that ν varies substantially.

The drift-mobility measurements for the Eindhoven material indicate a much shallower activation energy than for the other samples. At first glance, this suggests a very different set of multiple-trapping parameters. In conjunction with the large dispersion parameter (0.7) reported for this material near room-temperature, one might conclude from the bandtail multiple-trapping expression $\alpha = kT/\Delta E_V$ that the samples had valence bandtails of width about 36 meV. This conclusion leaves unexplained the fact that the actual magnitudes of the drift-mobilities are fairly similar to the other samples over the range of measurement.

We draw two conclusions from the present work. First, contemporary materials generally have better hole drift mobilities than materials prepared ten to fifteen years ago. This improvement is not found only in "special" materials prepared under research conditions; the sample from BP Solar is typical of materials which that company used in its solar cell factory. Second, there is substantial, unexplained variation in hole drift mobilities. At present, we do not know which aspects of deposition cause this variation, nor do we know whether there are structural probes that would correlate well with the variations in hole properties. For example, we had anticipated that hydrogen-dilution of silane during plasma deposition might be essential to obtaining improved properties, but the highest mobility curve in Figure 1 corresponds to a sample made without dilution. This lack of insight into hole drift-mobilties, and presumably into the structure of the valence bandtail, is regrettable both scientifically and technically. In particular, we consider it possible that further improvement in hole drift-mobilities would further improve solar cells – but the program of hole drift-mobility measurements does not yet point in

any particular direction for changing the deposition conditions in order to realize such improvements.

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5. The constant K is based on two sources. One is the expression connecting the transient photocurrent before carrier transit to the multiple trapping parameters (E. A. Schiff, *Phys. Rev. B* 24, 6189 (1981) – equation (6)); after integration, this expression yields:

$$Q(t)d^2 \Big/ Q_0 V = \left(\mu_h^0/v\right) \frac{N_V}{kTg_V^0} \frac{\sin(\alpha\pi)}{\alpha\pi} (vt)^\alpha \ ,$$

where $\alpha = kT/\Delta E_V$, N_V is the effective density of states of the valence band, and g_V^0 is the density-of-states (cm^{-3}eV^{-1}) for the valence bandtail at the upper edge of the valence band. The second source is the relationship $N_V/g_V^0 = kT/(1-\alpha)$ that obtains from the assumption that the valence band edge lies within the exponential bandtail (E. A. Schiff, *Solar Energy Materials and Solar Cells* **78**, 567-595 (2003).
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