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Hole Drift-Mobility Measurements and Multiple-Trapping in Microcrystalline Silicon

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ABSTRACT

We present photocarrier time-of-flight measurements of the hole drift-mobility in microcrystalline silicon samples with a high crystalline volume fraction; typical room-temperature values are about 1 cm^2/Vs. Temperature-dependent measurements are consistent with the model of multiple-trapping in an exponential bandtail. While this model has often been applied to amorphous silicon, its success for predominantly crystalline samples is unexpected. The valence bandtail width is 31 meV, which is about 10-20 meV smaller than values reported for a-Si:H, and presumably reflects the greater order in the microcrystalline material. The hole band-mobility is about 1 cm^2/Vs – essentially the same magnitude as has been reported for electrons and for holes in amorphous silicon, and suggesting that this magnitude is a basic characteristic of mobility-edges, at least in silicon-based materials. The attempt-frequency υ is about 10^9 s^{-1}; this value is substantially smaller than the values 10^{11} - 10^{12} s^{-1} typically reported for holes in amorphous silicon, but the physical significance of the parameter remains obscure.

INTRODUCTION

There have been several reports of drift-mobility measurements [1,2,3,4] in microcrystalline silicon in the last decade or so since it became clear that this material could be prepared with properties that are interesting for solar cells [5]. There is, of course, an enormous range of possible structures in microcrystalline silicon materials. For each sample there is a spectrum of sizes for the component nano & microcrystallites. Even more poorly understood, for each sample there is also a jumble of non-crystalline material that lies between the crystallites. Unsurprisingly, there has also been a very large spread in reported drift mobilities and transport properties.

In this paper we shall first summarize our recent hole drift-mobility measurements in a particular form of microcrystalline silicon that has been developed at Forschungszentrum Jülich as a solar cell absorber, and for which cells with 8.7% conversion efficiency have been reported [6]. We shall not offer a detailed defense of the measurements here, nor shall we offer an extended review and comparison with previous work on microcrystalline silicon; these will be presented elsewhere. Instead, we emphasize an unexpected aspect of the present measurements, which is that they exhibit the features of "exponential bandtail multiple-trapping."

Since its first successful application to amorphous semiconductors in the early 1980's (see Tiedje's review [7]), exponential-bandtail multiple-trapping (usually abbreviated as simply "multiple-trapping" or "MT") has become the standard approach to analyzing most transport experiments in hydrogenated amorphous silicon (a-Si:H) and related materials such as amorphous silicon-germanium alloys. The model assumes an exponential bandtail of localized states lying at the bottom of the conduction band, or at the top of the valence band. The application to transport also assumes the existence of a "transport edge," with the property that the only carriers that contribute to electrical transport are those occupying electronic states lying

above this edge (for electrons) or below it (for holes); it has generally been assumed that this edge is the "mobility-edge" dividing localized and extended electronic states.

In the present work we have found that multiple-trapping obtains for our measurements in a predominantly crystalline form of microcrystalline silicon. This form of microcrystalline silicon is apparently a far more ordered material than amorphous silicon, and certainly X-ray measurements, Raman scattering, and direct microscopy indicate that most of the volume is associated with small crystallites. One is naturally drawn to models for electrical transport that are based on the effective-mass theory, which would seem to apply at least within a crystallite. Indeed this approach has been applied recently to Hall mobility measurements in *n*-type microcrystalline silicon [8]. It is thus a bit of a shock to discover that the multiple-trapping model taken from amorphous semiconductors is a better description of microcrystalline silicon than is an effective-mass based approach – but this is the implication of our measurements. The multiple-trapping parameters in the microcrystalline material do differ in interesting ways from those that have been reported for a-Si:H, and we shall return to this comparison in the concluding section of this paper.

Table I: Sample Properties

Sample	*Raman Ratio* I_C^{RS}	*i-layer thickness* d (μm)
B	0.71	4.0
D	0.60	3.4
E	0.61	4.3

SAMPLES

The samples used for our measurements were *pin* structures prepared in designated chambers of a multi-chamber system using plasma-enhanced chemical vapor deposition at frequencies of 95MHz (VHF-PECVD) [6]. We used ZnO coated glass as a transparent, conductive substrate. The μc-Si:H(B) *p*-layers are about 20nm thick; the films were doped by adding trimethylboron to the silane-hydrogen gas mixture. The intrinsic μc-Si:H layers were prepared using a silane-hydrogen mixture of 5-6%. The n-layer (phosphine doped) was an amorphous 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_6-gas process) the top surface of these structures to remove the n-layer from regions not under the ZnO.

In this paper we present measurements on three samples summarized in Table I. 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 $I_C^{RS} = I_C/(I_A+I_C)$ was determined by deconvoluting the spectra into three signal peaks at 480 cm^{-1}, 500 cm^{-1} and 520 cm^{-1}. The first one can be attributed to a disordered structure like an amorphous phase or grain boundaries (I_A), and the latter two are attributed to the crystalline phase (I_C) [9].

DRIFT-MOBILITIES

The transient photocurrents were measured in the *pin* diodes following illumination by a 3 ns laser pulse (wavelength $\lambda = 500$ nm) through the *n*-layer. The photocurrent transients were consistent with a conventional interpretation in terms of hole time-of-flight. In particular, the photocharge was independent of the applied voltage, and a transit-time was discernible in the transient. Additionally, the photocurrent at short times was linear in the applied voltage, which is consistent with transport that is linear with electric field.

In Fig. 1 we present our temperature-dependence measurements of the hole drift-mobility for 3 samples [10] corresponding to a particular "displacement/field" ratio $d^2/2V = 7\text{x}10^{-8}$ cm^2/V of sample thickness d and applied field (V/d). The activation energy (0.13 eV) is illustrative only,

and does not indicate any particular depth for the bandtail traps. These average drift-mobilities, determined using $\mu_D = d^2/(Vt_\tau)$, are much larger than typically obtained in a-Si:H [11], although a direct experimental comparison at the same value for d^2/V is not possible. We compare multiple trapping fitting parameters shortly.

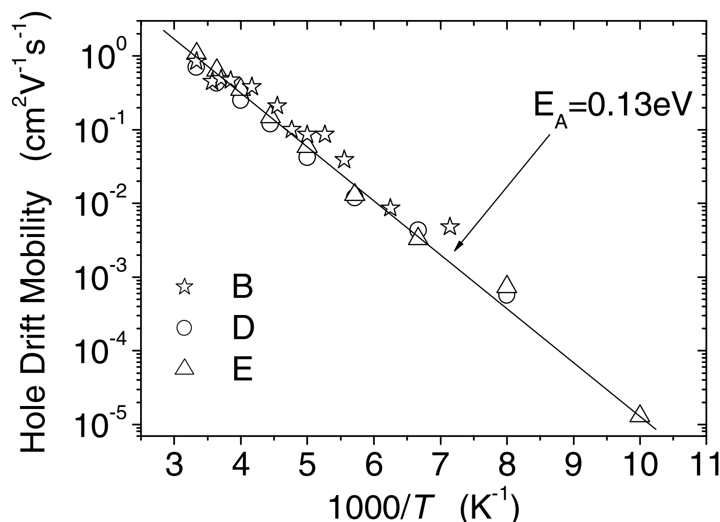

Fig. 1: Hole drift-mobilities measured for three microcrystalline silicon materials (cf. Table I) determined with a displacement/field ratio $d^2/2V$ = 7.8 x 10^{-8} cm^2/V.

MULTIPLE-TRAPPING FITS

Our procedure for fitting to the multiple-trapping model starts with the transient photocharge $Q(t)$ (the time-integral of the photocurrent $i(t)$). In particular, we fit to the time-dependence of the normalized photocharge $Q(t)d^2/Q_0(V+V_{bi})$, where Q_0 is the total photocharge of holes generated by the laser pulse, V is the bias voltage, d is the i-layer thickness, and V_{bi} is a correction for the internal field. We have illustrated the photocharge measurements in Fig. 2 for seven temperatures. For clarity, we have removed sections of the transient for $Q(t) > Q_0/2$; these portions of the transient are past the "transit time," and are not used in our multiple-trapping fitting procedure. We have also removed early-time portions of the transients that are clearly

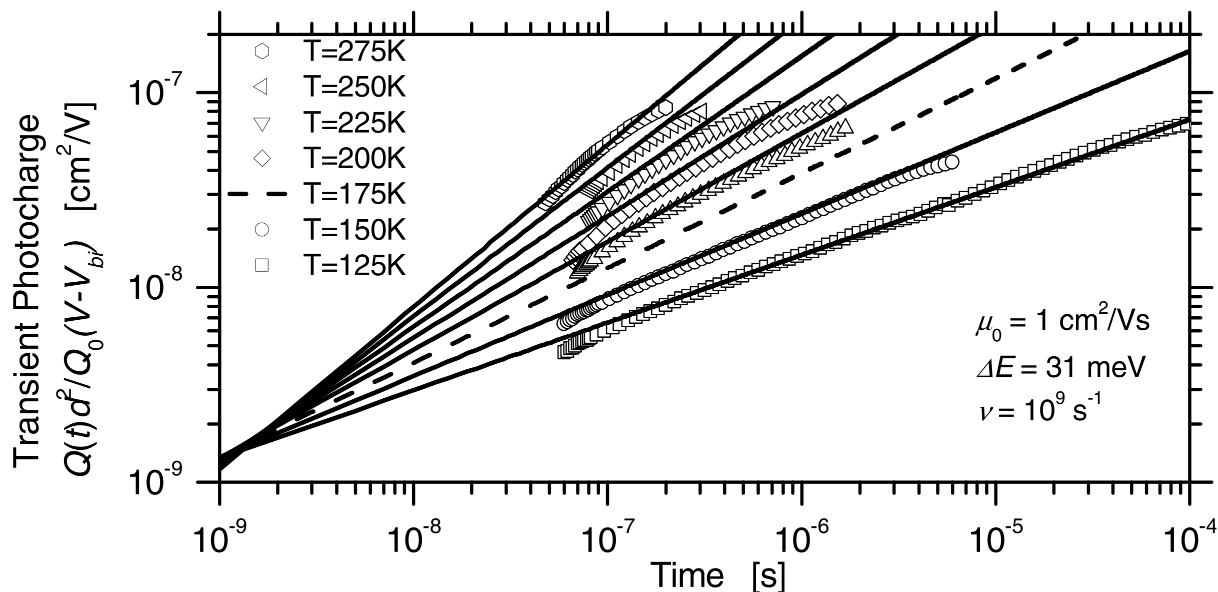

Fig. 2: The symbols are normalized photocharge transients measured in one microcrystalline silicon sample ("D" in Table I); the solid lines are the corresponding calculations using the exponential bandtail multiple-trapping model with the parameters indicated.

dominated by response-times of the measurement.

The solid lines in Fig. 2 are the multiple-trapping fittings. The actual equation that was fitted to the normalized photocharge is [11]:

$$L(t)/E = K\left(\mu_0/\nu\right)(\nu t)^{\alpha(T)}. \quad (1)$$

$L(t)$ is the mean displacement for photocarriers after a delay time t and with electric field E. The dispersion parameter $\alpha = kT/\Delta E_V$, where ΔE_V is the width of the exponential, valence bandtail, μ_0 is the valence band-mobility, and ν is an "attempt-to-escape" frequency characterizing the rate of release of holes from the bandtail traps. The constant $K = \sin(\alpha\pi)/(\alpha\pi(1-\alpha))$ is of order unity. The multiple-trapping parameters we chose (and that are the basis for the solid lines shown in Fig. 2) are given in Table II below, along with some results for a-Si:H [11,12].

Table II: Multiple-trapping fitting parameters

Multiple-trapping parameter	*μc-Si:H* (this work)	*a-Si:H* (ref. 11)	*a-Si:H* (ref. 12)
Valence band-mobility μ_0 (cm^2/Vs)	1.0	0.7	0.3
Bandtail width ΔE_V (meV)	31	45	48
Attempt-frequency ν (s^{-1})	9×10^8	1×10^{12}	8×10^{10}

MEANING OF MULTIPLE TRAPPING IN MICROCRYSTALLINE SILICON

One approach to analyzing mobilities in polycrystalline materials is to invoke the effective masses that would obtain for electrons and holes in the single crystal, and assume that the grain boundaries act as scatterers or barriers and as the locus for traps for the carriers [8]. It is instructive to use this approach crudely to calculate an "effective-mass carrier mobility" for holes $\mu_h^{e.m.}$ utilizing the expression $\mu_h^{e.m.} = v_{th} l/(kT/e)$, where v_{th} is the "thermal velocity" for holes (about 10^7 cm/s in c-Si near room-temperature) [13] and l is a scattering length. If the scattering length is identified with a typical crystallite size of 3 nm, we infer $\mu_h^{e.m.} = 120\,cm^2$/Vs, or about 100 times larger than the estimate in Table I. The effects of traps and barriers seem unlikely to explain the discrepancy for our samples, since these were already (implicitly) incorporated in the analysis that led to the estimate $\mu_0 = 1$ cm^2/Vs.

We suggest that, for our samples of microcrystalline silicon, the disorder is sufficient to strongly alter the bandedge states from their crystalline counterparts. In particular, we suggest that the bandedge states of the crystal have been transformed into a bandtail (ie. that the density-of-states $g(E)$ has been altered), and that a *mobility-edge* has formed within the bandtail [14] (ie. states lying deeper in the energy gap are localized).

The mobility-edge has been widely applied to amorphous semiconductors [7,15], and has recently been applied to microcrystalline samples with a larger fraction of amorphous "tissue" [16]. Here we are suggesting that it be applied to samples that are predominantly crystalline. In the mobility-edge model, hole states with energy levels below the mobility-edge ($E < E_V$) are completely delocalized (by definition), although with very different wavefunctions than the effective-mass states of crystals. Hole states lying above the mobility-edge ($E > E_V$) are localized. Both analytical and computational studies of mobility-edges [17,18] indicate that the localization radius for a hole state grows very rapidly, and may even diverge, as the state's

energy approaches the mobility-edge. It isn't clear theoretically how particular atomic-scale features such as "strained bonds" are incorporated into the bandtail states.

With this perspective, we first discuss the bandtail width ΔE_v. The estimate of 31 meV for the microcrystalline material seems unremarkable in the context of work on holes in amorphous silicon, which yield values in the range 40 – 50 meV. It is worth noting that disorder affects holes and electrons very differently. The conduction bandtail in amorphous silicon has a width around 22 meV [7,15]. Electron properties in samples quite similar to the present ones have been studied using post-transit time-of-flight [16]; bandtail multiple-trapping did not apply for these transients. An interesting possibility is therefore that electron transport may be governed by effective masses in exactly the same material for which holes require a mobility-edge approach.

The fact that the hole band-mobility μ_0 is about the same in the present microcrystalline samples and in amorphous silicon seems to support the mobility-edge interpretation, and more broadly suggests that a value near 1 cm^2/Vs may be a universal property of a mobility edge. Such "universality" is also suggested by the fact that electron band-mobilities in amorphous silicon are also around 1 cm^2/Vs [7,15]. Interestingly, a band mobility of 1 cm^2/Vs is *not* an obvious implication of the existing theoretical treatments of mobility-edges.

Finally, we turn to the attempt-frequency ν. It is quite interesting that the value for microcrystalline silicon is substantially (about 100 times) smaller than the lower values reported for a-Si:H. However, even for a-Si:H, there is no well-accepted physical interpretation for this parameter. One often-mentioned interpretation is that ν be identified as a "typical phonon frequency," but this association fails to explain either the very low magnitudes or the enormous range of magnitudes that have been reported experimentally [19]. Yelon and Movaghar have suggested that multi-phonon effects lead to the variations, and this perspective has been applied by Chen, *et al.*, to drift-mobility measurements [20]. Another possibility originating with high-field drift-mobility measurements in a-Si:H has been that ν reflects the bandedge density-of-states $g(E_V)$ [21], which suggests that the present measurements be interpreted as indicating a substantially lower value for $g(E_V)$ in microcrystalline than in amorphous silicon. Plainly, we need more clues from experiment about the meaning of this parameter; it seems possible that its dramatic lowering in microcrystalline silicon could be providing it.

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