TRANSPORT PROPERTIES OF COMPENSATED μc-Si:H

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ABSTRACT

Electron and hole transport in completely microcrystalline silicon (μc-Si) p-i-n cells and in intrinsic or near intrinsic μc-Si layers have been investigated, for the first time, by time of flight (TOF) at temperatures between 100 and 400 K. At room temperature, both electron and hole drift mobilities were found to be between 0.2 and 1 $cm^2V^{-1}s^{-1}$. No trace of anomalous dispersive transport was observed, neither for electrons nor for holes, down to 100 K. A decrease of the drift mobility was observed when the temperature was raised from room temperature to 400 K as usually observed in crystalline semiconductors. However, these experimental values of the drift mobilities appear more puzzling than helpful for the comprehension of this "new" photovoltaic material.

INTRODUCTION

Compensated microcrystalline hydrogenated silicon (μc-Si:H) has recently successfully been used for the active layer (i-layer) of single and tandem solar cells [1-3]; compensation (i.e. shift of E_f to midgap) is obtained by a low level of boron doping [4]. As far as the optical properties are concerned, this "new" material, which has a very low amorphous phase fraction, exhibits an optical gap smaller than crystalline silicon (c-Si), an enhanced optical absorption in the visible (compared to c-Si) and a subgap absorption similar to that of a-Si:H [5].

In contrast to undoped μc-Si:H [6], both photoconductivity and ambipolar diffusion length are found to be generally higher in compensated μc-Si:H than in state-of-the-art intrinsic or compensated a-Si:H [7]. However, photoconductivity or ambipolar diffusion length are measured in a coplanar configuration, whereas in reality one should use characterisation techniques that analyse the transport in the same direction as the one that is determinant in a solar cell, i.e. in the direction perpendicular to the substrate. As a matter of fact, due to the particular growth of our μc-Si which is columnar [4], transport in μc-Si:H should be assumed, a priori, to be anisotropic. Thus, TOF measurements were selected, in order to better understand the exceptionally high collection of complete μc-Si p-i-n cells, even on devices with thicknesses in excess of 3 μm [8].

EXPERIMENTAL

All p-i-n μc-Si:H cells and μc-Si:H layers were produced by the VHF-GD deposition technique at 70 MHz. P-i-n cells were deposited on Ahsai type U substrates and the bottom n-layer was covered with an ITO transparent contact, in order to allow illumination through both top and bottom contacts. The material outside of the dots was then removed by plasma etching in order to have a well defined area of the structure. Layers were deposited on chromium- (Cr-) coated Corning glass; top semi-transparent Cr dots were then evaporated to form the metal-semiconductor-metal structures used for the measurement. The samples investigated were selected from a compensation series of slightly boron doped samples. Level of compensation were monitored by measuring the dark conductivity on a sample deposited on glass during the same deposition run. Thicknesses of the films and of the cells were between 1.7 and 2.3 μm.

TOF measurements were performed using 3 ns long light pulses at 550 nm from a nitrogen-pumped dye laser. Current transients were recorded with a Tektronix digital oscilloscope 2440 having a 350 MHz bandwidth. Measurements at temperatures below room temperature were done in an evacuated cryostat. In order to reduce the area of the structures used in TOF, the p-i-n diodes or the double Schottky structures were "sliced" by scratching the sample with a diamond tip. Drift mobilities were deduced from the slope of the data line in the plot of (thickness/field) versus transit time. This procedure was chosen in order to eliminate the need to

correct the time origin of the current transients (the time origin of the latter is, in our curves, simply defined by the oscilloscope trigger point). The transit times were defined as the width of the current transient at half of its maximum amplitude.

Estimation of the capacitance of the samples (from the measurement of the RC time constant of the sample/load resistor system) was obtained by measuring the current decay following the application of the external field on the sample.

RESULTS AND DISCUSSION

RC time constants and transit times

TOF measurements were found to be much more difficult to perform on μc-Si:H than on a-Si:H. As an example, hole current transients measured on a p-i-n diode (compensated i-layer) with an area of ≈5 mm^2 did not intersect, as expected, when near total collection is achieved. When the area of the diode is reduced to 1/4 of the initial area, reasonable transients are obtained (see Fig. 1b). One should note that this effect is due purely to the area of the diode (i.e. to its capacitance), and is not an effect of the total generated charge, as one could argue. From this example it seems that transients are in fact limited here by the RC time constant τ_{RC} of the sample-load resistor system. As a matter of fact, the capacitance of these μc-Si:H structures was found to be much higher than that of a-Si:H structures with the same geometry; the capacitance is, for μc-Si:H, roughly 10 times higher than the geometrical capacitance that can be calculated from the size of the sample. However, the observation on high capacitance samples that, for times greater than τ_{RC}, current transients are independent of the applied voltage, is puzzling and no clear convincing explanation could be found so far.

In order to be able to trust our measurements of drift mobility, we tried to insure that both the RC time constant of the sample was much lower than the determined transit time measured for near total collection and that the transients did exhibit shapes and intersections similar to those in Fig. 1b. This appeared to be difficult for most of the samples, either for one type of carrier or both. Reduction of the sample area could be performed (within this study) only down to a value of roughly 0.4 mm^2. This reduction in area usually did shorten the apparent transit time, but did not always produce transients that were similar to those of Fig. 1b. Generally, slight intersections could only be obtained for the transients of the majority carrier. On the same sample as in Fig. 1 (p-i-n diode with compensated i-layer), reduction of the sample area up to a factor of 4 narrowed the electron transients without producing an intersection of the transients (see Fig. 2a); further decrease of area (up to a factor of 10 of the initial area) did not produce any noticeable change in the transient shape. On the other hand, "better" current transient shapes for electrons could be obtained on slightly n-type layers (Fig. 2b).

Most of the samples measured during this study appeared to have a rather large leakage

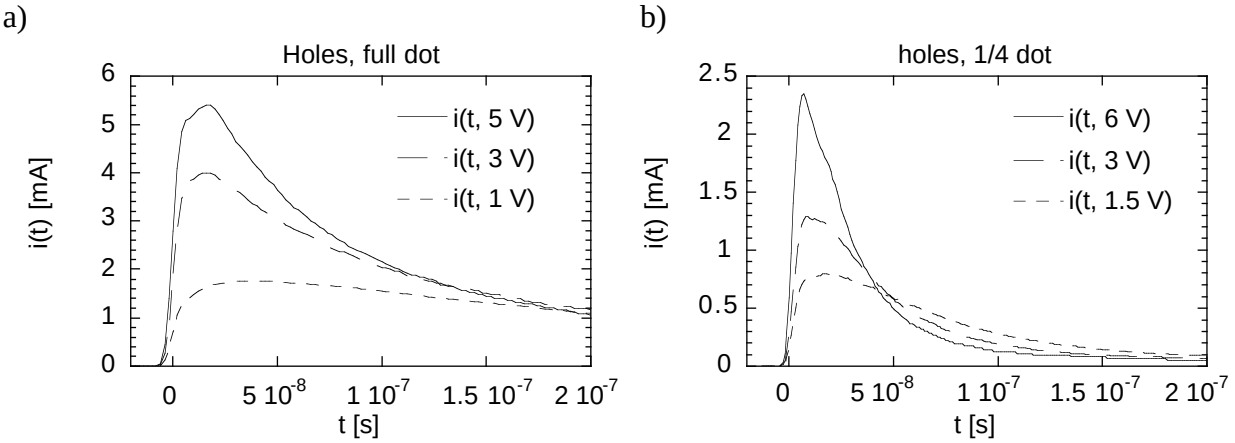

Figure 1: Hole current transient at selected applied voltages for (a) the full dot area (4.9 mm^2), (b) a dot area reduced to 1/4 of the initial value in a 1.7 μm thick p-i-n microcrystalline cell (sample H030294B).

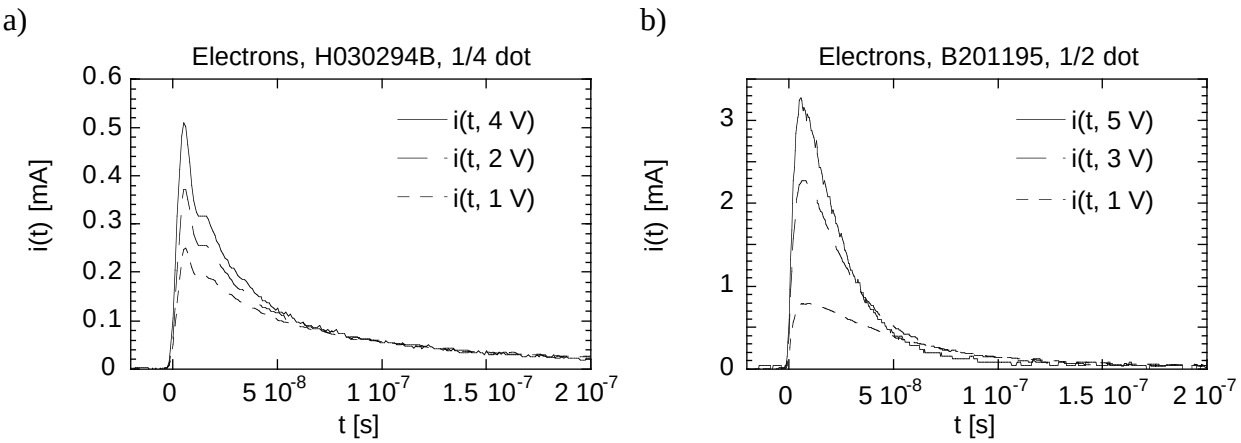

Figure 2: Electron current transients at selected applied voltages in (a) a 1.7 µm thick p-i-n microcrystalline cell with a compensated i-layer (sample H030294B) and a dot area reduced to ≈1 mm^2 (1/4 of the initial value), (b) a slightly n-type 2 µm thick µc-Si:H layer (sample B201195) with a ≈0.4 mm^2 dot area (1/2 of its initial area).

current, which prevented us from measuring some samples, especially with respect to both types of carriers. This leakage current was due, on one hand, to the rather high dark conductivity of µc-Si:H (present even for compensated µc-Si:H) coupled to the low barrier height of the Cr Schottky contacts, and on the other hand to the rather crude way used by us to reduce the dot area: Mechanical scratching generally increased significantly the leakage current. Both problems should be corrected in the future to insure more reliable structures for better characterisation possibilities.

Drift mobility measurements at room temperature

Here, a single p-i-n diode with a compensated i-layer and several layers with various compensation levels were investigated by TOF. Reasonable current transients were generally only obtained for the majority carriers. However, on individual layers, electron current transients of compensated or (of slightly) p-type appear reliable. The highest measured drift mobilities for electrons μ_e (≈1 cm^{2}V^{-1}s^{-1}) and for holes μ_h (≈0.6 cm^{2}V^{-1}s^{-1}) are shown on Fig. 3. All the measurements at room temperature are summarised in Table 1. One can observe that both holes and electrons are quite comparable from one sample to the other, without showing a dependence

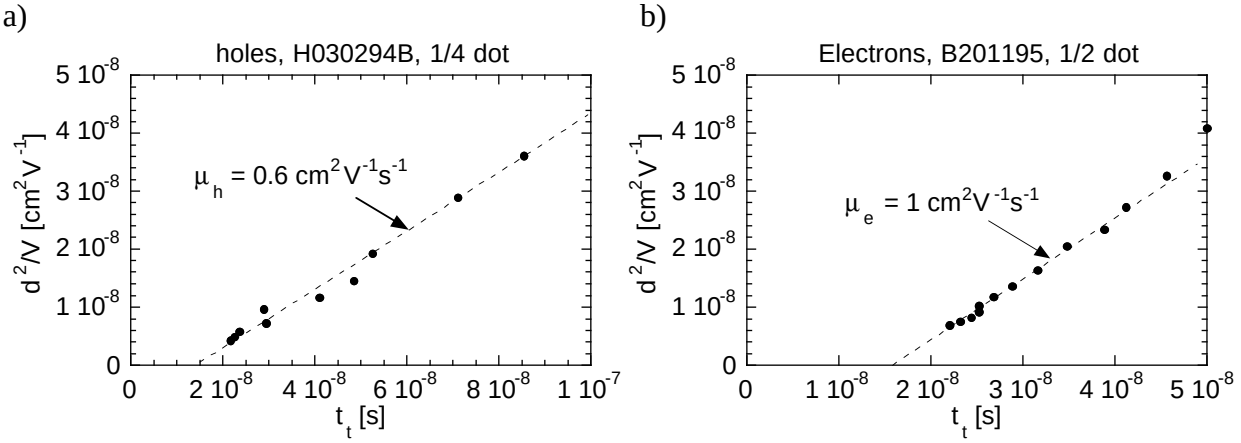

Figure 3: Values of the transit time at various voltages and deduced (a) hole drift mobility μ_h in a 1.7 µm thick p-i-n microcrystalline cell with compensated i-layer (sample H030294B, with a dot area reduced to ≈1 mm^2), (b) electron drift mobility μ_e in a slightly n-type 2 µm thick µc-Si:H layer (sample B201195, with a ≈0.4 mm^2 dot area).

Sample	Structure	Thickness [μm]	Type	σ_d [$\Omega^{-1}cm^{-1}$]	μ_e [$cm^2V^{-1}s^{-1}$]	μ_h [$cm^2V^{-1}s^{-1}$]
B311095	layer	2.11	<p>	$5x10^{-5}$	0.7-1	0.5
B271195	layer	2.3	compensated	$1.5x10^{-7}$	0.9	0.3-0.6
B291195	layer	2.3	<n>	$7x10^{-7}$	0.7-0.9	
B201195	layer	2.02	<n>	$8x10^{-7}$	1.1	
H030294B	p-i-n	1.7	compensated	n.a.	(1.2)	0.3-0.5

Table 1: Summary of the electron and hole drift mobilities measured on four μc-Si:H layers with various compensation levels by boron doping (from under- to over-compensation), and of a single μc-Si:H p-i-n diode with a compensated i-layer. Values in parenthesis or absent values indicate measurements where only poor intersections of the current transients, or where no intersection at all, respectively, were obtained. For some samples, a range of drift mobilities is indicated where significant scattering of the values (measured on different sample contacts) were observed.

on the Fermi level position (or on the doping level). μ_e exhibits a surprisingly low value, similar to hydrogenated amorphous silicon (a-Si:H). Since the measurement is performed in the direction that of perpendicular to the substrate (i.e. in the direction of the columnar growth), and since this material has a very low content of amorphous tissue (<10 %), we expected a significantly higher value for μ_e. In contrast, μ_h exhibited a much larger value than that found in a-Si:H, and it was roughly equal to half of the value found for μ_e; the ratio is close to the ratio of 3 between μ_e and μ_h observed in crystalline silicon.

Drift mobilities as a function of temperature

Measurements of the drift mobility as a function of temperature were also performed for most of the samples; the results are presented in Fig. 4 for the drift mobility of electrons μ_e and in Fig. 5 for the drift mobility of holes μ_h. As one can observe, μ_e exhibits a rapid drop of its value as the temperature is raised above 300 K, as is seen also in crystalline silicon [8]. One should note that this observation is not due to a screening of the electric field inside the μc-Si:H layer (for some samples at elevated temperatures the rule that the transit time must be smaller than the dielectric relaxation time τ_{diel} is not satisfied anymore); for every temperature above 300 K, we checked that the current transients were not affected by the decreased value of τ_{diel}. On the other hand, on the only sample that we could measure reliably below room temperature, to our surprise, no change was observed in this temperature range. It is here quite premature to

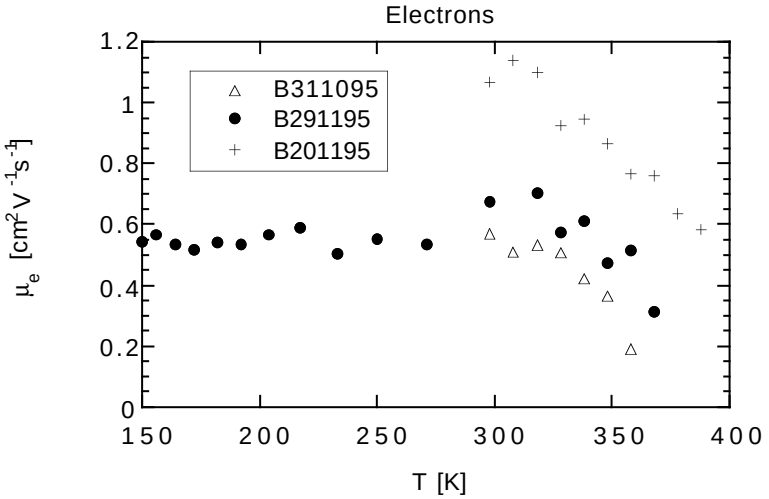

Figure 4: Electron drift mobility μ_e as a function of temperature for some of the samples presented in Table 1.

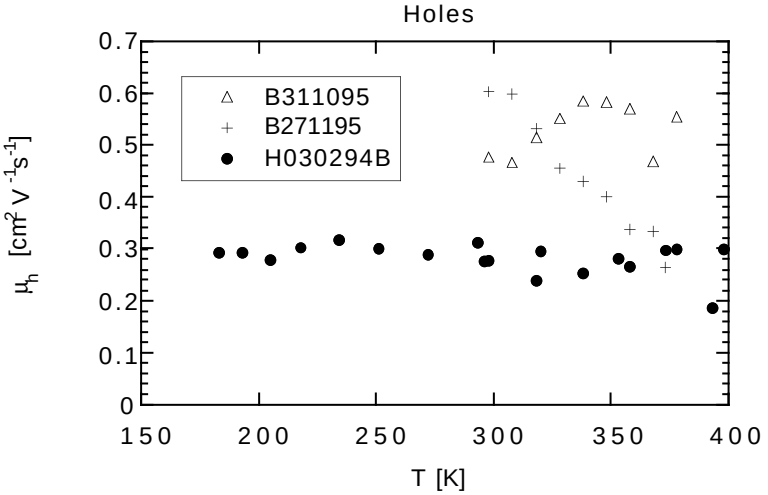

Figure 5: Hole drift mobility μ_h as a function of temperature for some of the samples presented in Table 1.

try to give any definitive explanation after the measurement of just one sample, but this behaviour still seems to us to be an indication that no significant potential barriers are present along the transport path.

As far as the hole drift mobility μ_h is concerned, the situation is more confusing: A decrease of μ_h is observed only for one sample (the compensated one), when the temperature is increased above 300 K. For the others, μ_h remains fairly constant. At lower temperatures, no change of μ_h was found for the only sample which could be measured.

A interesting point to mention here, is that no trace of anomalous dispersive transport was observed at 150 K, as one can see in Fig.6 (and this even down to 100 K), neither for electrons nor for holes, despite the presence in this material of an exponential tail in the absorption spectra, for energies below the value of the indirect gap [5]. This indicates that transport is not controlled, even at low temperatures, by the small amount of amorphous tissue present in the material, but rather by the crystalline phase and by the grain boundaries.

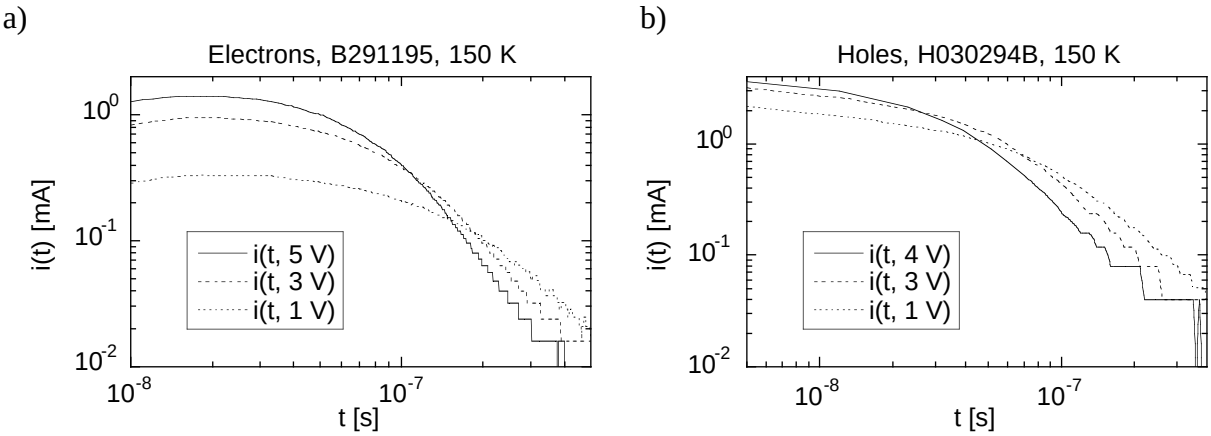

Figure 6: Current transients at selected voltages measure at 150 K for (a) electrons (sample B291195) (b) and for holes (sample H030294B).

CONCLUSIONS

It has been recently demonstrated that compensated microcrystalline silicon is a very interesting and valuable low-gap photovoltaic material. Opto-electronic properties of this material differ in general quite significantly from those already measured in "conventional"

undoped μc-Si:H; the latter exhibits a rather pronounced n-type character and no visible Urbach slope in the absorption spectra. As far as transport in compensated μc-Si:H is concerned, these first data show that this material is, in some aspects, very different from a-Si:H (with respect to hole drift mobility and temperature dependence of the drift mobilities). At the same it exhibits, however, comparable values at room temperature for the electron drift mobility as well as for the photoconductivity and the ambipolar diffusion length (the latter two parameters being measured in a coplanar configuration). This observation is quite puzzling, when one tries to understand why collection in thick (> 3 μm) μc-Si:H solar cells is, in fact, (much) better than in comparably thick a-Si:H diodes.

To better understand the transport and the collection in entirely μc-Si:H solar cells and in order to optimise further these cells, a more comprehensive study is needed. In particular, other characterisation techniques that are able to measure the transport along the same direction as the one in which collection occurs in solar cells, should be applied. However, as has been observed during this study, a new material usually also necessitates new or modified experimental conditions which can be sometimes difficult to satisfy.

ACKNOWLEDGEMENTS

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