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Effect of the microstructure on the electronic transport in hydrogenated microcrystalline silicon

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Abstract

Undoped hydrogenated amorphous silicon layers deposited at different values of very high frequency (VHF) powers and silane to hydrogen dilution ratios possess various types of microstructures. Transport and defect measurements on layers suggest that structural properties (e.g., crystallite shape and size) do not significantly affect electronic properties. The latter depend mostly on defect density and on the Fermi level. The authors therefore suggest using the 'quality parameter' $\mu^0\tau^0$ for an unambiguous comparison between different μc-Si:H layers. Transport characterisation techniques in the direction perpendicular to the substrate and cell performance results corroborate the minor effect of microstructure on the bulk electronic transport properties.

1. Introduction

Microcrystalline hydrogenated silicon (μc-Si:H) is now internationally recognised as a promising material for the active layer of thin-film solar cells. It has been observed recently that this material is not unique, but that it may exhibit a wealth of different microstructures depending on the deposition conditions [1]. The substrates themselves have also been shown to critically control the structural orientation of the material [2,3]. Furthermore, the presence of an amorphous incubation layer (between the substrate and the growing μc-Si:H film) is sometimes observed [4]; the thickness of the incubation layer also depends both on the type of substrate and on the deposition parameters.

Despite its successful incorporation into solar cell devices, an important enigma persists concerning electronic transport in this material. While μc-Si:H solar cells performance clearly depends on the properties of the doped layers and quality of the p–i and n–i interfaces, the effect of the intrinsic (i-) layer and especially the effect of electronic transport within the i-layer on solar cell performance is still poorly understood. This is mainly due to the difficulty to directly study transport properties in this material, a material which does

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not possessed a unique and well-defined morphology, but can exhibit various forms of microstructure (depending on the deposition conditions and substrate). Therefore, one would expect that a variation in material morphology will affect the layer transport properties, the defect density as well as solar cell performance.

While the role of the microstructure and of the initial growth of the μc-Si:H i-layer (at the p–i interface of p–i–n) starts to be better understood, the factors limiting the transport within the i-layer remain controversial: some experimental evidence supports the idea that charge carrier transport is limited by the amorphous tissue surrounding the μc-Si:H crystallites [5], while other data suggest that transport is limited by the bulk of the crystallites [6]. The situation is rendered even more complicated by the regular presence of an incubation layer and by the evolution of the microstructure along the growth axis (starting from an amorphous incubation layer and ending with fully microcrystalline growth). Recently, local analysis of the conductivity with a scanning conductive atomic force microscope (AFM) tip has been proposed for charge transport investigation [7]. However, this innovative technique gives only local information on the surface and hardly gives access to transport in the bulk.

The objective of this paper is therefore to limit investigation methods to simple characterisation techniques, which are sensitive to the bulk of the material. We, thus, chose to look at individual i-layers and to study steady-state photoconductivity (SSPC) σ_{ph}, ambipolar diffusion length L_{amb} (measured from steady-state photocarrier grating (SSPG)) and to deduce $\mu^0\tau^0$ products as a tool for qualifying transport in the bulk of μc-Si:H layers. Diffusion length L_D (evaluated from surface photovoltage (SPV)) is used to analyse transport in the growth direction. These transport properties are then compared with sub-band gap absorption (which is sensitive to defects), and with the microstructural properties in order to get insight into the factors that limit transport. Finally, results on solar cell performance (incorporating i-layers deposited under identical plasma conditions) and the comparison with characteristics of individual layer are also discussed.

2. Experimental

All μc-Si:H samples studied here were grown by the very high frequency glow discharge (VHF-GD) deposition technique at temperatures around 200 °C. Two series of layers were deposited at a fixed VHF power (6 and 30 W) at various silane concentrations in hydrogen (1.25–8.6% and 5–8%, respectively), and two series were deposited at fixed silane concentrations (5% and 7.5%) but at various VHF powers (9–25 and 30–70 W, respectively). The 6 W power series was deposited at 110 MHz while all other series were deposited at 130 MHz. A gas purifier was used in order to limit the incorporation into the material of oxygen atoms coming from the gas source. An overview of the sample deposition conditions and resulting deposition rates of the layers is given in [8]. Note that some of the samples deposited at high silane concentrations and/or low powers are amorphous or have a large amorphous volume fraction.

SSPC and SSPG measurements were performed on layers deposited on glass (Schott AF45); σ_{ph} and L_{amb} were determined at a generation rate of $\approx 1.7 \times 10^{20}$ cm^{-3} s^{-1} using a Kr laser at a wavelength of 647 nm. For SPV measurements, layers were deposited on Asahi type U or ZnO-coated glass. True optical absorption spectra of all layers were measured using absolute constant photocurrent measurements (A-CPM) and taking into account light scattering effect [9].

The layers of the two series grown at the highest deposition rates (i.e., the 7.5% silane concentration power series and 30 W dilution series) were also incorporated (using identical deposition conditions) as i-layers of n–i–p cells. Experimental details and performance of these cells are given in [8].

3. Results

Fermi level position E_f in μc-Si:H layers is known to be very sensitive to oxygen content. Incorporation of oxygen either during growth or after growth (through a diffusion along the grain boundaries or cracks – so-called 'post-oxidation effect') results in a n-type doping of the material. Therefore, layers deposited under various

hydrogen dilutions of silane (parameter which controls the obtained microstructure and, thus, has an effect on oxygen diffusion into the sample [10]) as well as layers deposited at various rates (which affect the incorporation of oxygen during growth), exhibit large scattering in E_f and, correspondingly, in the values of dark conductivity (see [8] for more details on the dark conductivity, SSPC and SSPG data of the four series of layers studied in this paper).

E_f can be conveniently monitored by the parameter b, which is plotted on Fig. 1 for the four series of layers. High values of b (Note that $b \approx 1$ for intrinsic material) are obtained either for material deposited at high power, which is responsible for a structure in which oxygen can easily diffuse (high 'post-oxidation' as seen from SIMS spectroscopy [10]), or for material deposited at low rates with a high incorporation of oxygen during growth. Note that b was originally defined for amorphous hydrogenated silicon (a-Si:H) [11]; it is given by the ratio of densities band mobilities times the ratio of free carrier, $b = (\mu_n^0/\mu_p^0)(n_f/p_f)$. b has the advantage that it can be deduced directly from a combination of SSPC and SSPG measurements [11].

Due to the large scattering in b (as a function of the deposition parameters, cf. Fig. 1), the same picture is found for the mobility times recombination time products $\mu^0\tau^R$ for electrons or for holes as obtained from σ_{ph} or L_{amb}, respectively (see Fig. 2). In order to compare transport properties of samples exhibiting different values of E_f, we therefore introduce the quality parameter $\mu^0\tau^0$ which is independent of E_f (i.e., independent of b). Such a procedure was originally developed for a-Si:H [11] and appears to be also valid for μc-Si:H given the similarities in the transport properties [12,13]. If we now introduce $\mu^0\tau^0$ (cf. Fig. 3), the scattering between SSPC and SSPG transport data (see also [8]) for the four series disappears and we

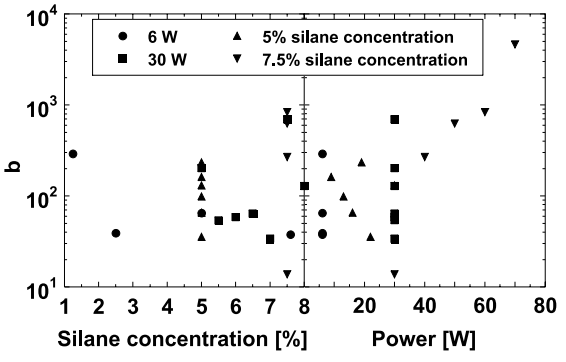

Fig. 1. Position of the Fermi level, evaluated by the parameter b, as a function of both silane concentration (left) and VHF power (right) for the four series of μc-Si:H layers investigated here. Note that $b \approx 1$ for a 'truly' intrinsic material (i.e., for a layer with E_f at mid-gap). The measurements errors for b are ±20%.

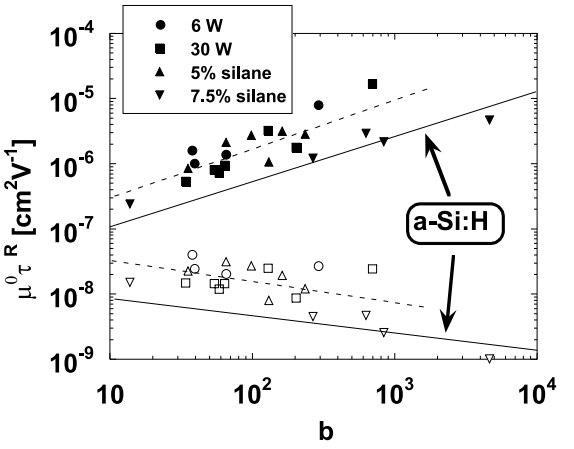

Fig. 2. Mobility × recombination time product $\mu^0\tau^R$, for electrons (solid marks) and holes (opened marks), as a function of b (which indicates the position of the Fermi level); $b \approx 1$ for intrinsic material for the four series of μc-Si:H samples. The measurements errors are ±20% for b and ±5% for $\mu^0\tau^R$.

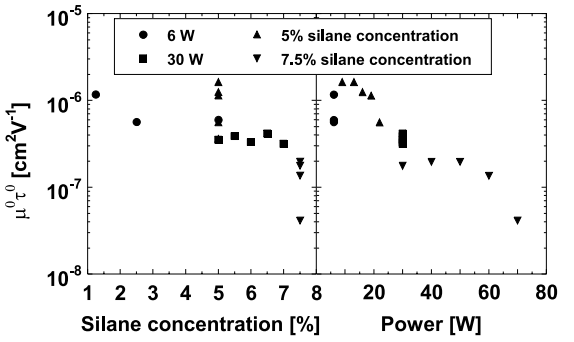

Fig. 3. Quality parameter $\mu^0\tau^0$ as a function of both silane concentration (left) and VHF power (right) for the four series of samples. The measurements errors for $\mu^0\tau^0$ are ±10%.

observe a smooth change in $\mu^0\tau^0$ as a function of the deposition parameters: $\mu^0\tau^0$ values decrease for both an increase in silane concentration and for an increase of the deposition power.

4. Discussion

Variations in $\mu^0\tau^0$ as a function of deposition parameters can be explained by a change of the microstructure, which affects the mobility μ^0, and/or by defects, which affect the lifetime τ^0. Defect densities in our layers were estimated from the 'true' optical absorption at an energy of 0.8 eV [14]; α (0.8 eV) is plotted for our series of samples on Fig. 4. If we now try to correlate $\mu^0\tau^0$ values with the defect densities we obtain the plot given in Fig. 5. $\mu^0\tau^0$ is found to be roughly inversely proportional to the defect density; this indicates that changes in mobility only plays a marginal role. One should note here that while no important change in the mobility is observed, microstructure varies indeed significantly with a modification of silane concentration [1]. In other words, we can conclude that crystallite size and shape does not play an important role. This observation suggests that the amorphous tissue surrounding the grains

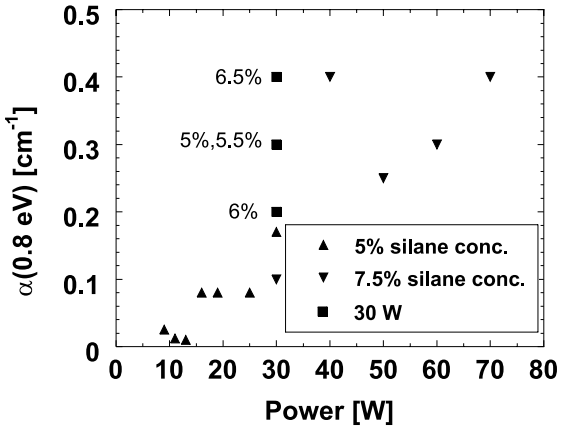

Fig. 4. 'True' optical absorption coefficient α (0.8 eV) at an energy of 0.8 eV for the two power series and the 30 W dilution series of μc-Si:H samples. Note that α (0.8 eV) can be used as a measure of the defect density in the material, and was deduced from A-CPM and corrected for the effect of light scattering in the layers. The measurements errors for α (0.8 eV) are ±4%.

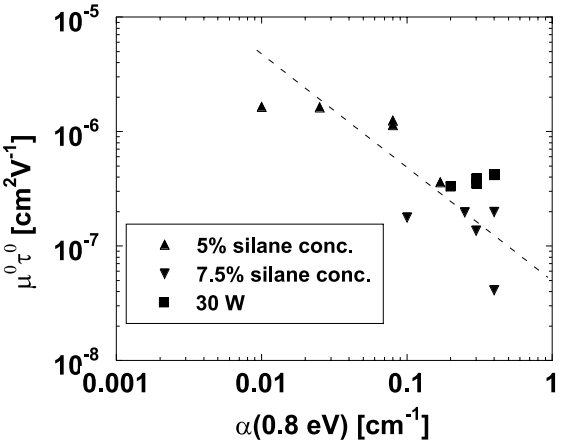

Fig. 5. Quality parameter $\mu^0\tau^0$ as a function of defect density, the latter being evaluated by the 'true' optical absorption coefficient α (0.8 eV) (see Fig. 4), for the two power series and for the 30 W dilution series. The dashed curve indicates the observed correlation for μc-Si:H samples and corresponds to a power-law with a −1 exponent. The measurements errors are ±4% for α (0.8 eV) and ±10% for $\mu^0\tau^0$.

controls charge transport and it explains why transport in μc-Si:H is so similar to that in a-Si:H.

At this point, we only discussed transport properties parallel to the surface, since SSPC and SSPC measurements are performed in the coplanar configuration. In order to get information on transport in the transverse direction (perpendicular to the surface), one may, e.g., use time-of-flight (TOF), ac conductivity or SPV techniques. However, most of these techniques are rather problematic for μc-Si:H: it is difficult to satisfy the TOF experimental conditions, ac conductivity may be strongly affected by the evolution of the microstructure with growth, and SPV is sensitive to 'post-oxidation' of the surface region. Strong post-oxidation (as observed on samples deposited at high plasma power) may adversely affect the measured value. L_D values measured on most samples of the 5% silane concentration series are generally close to the values obtained for L_{amb} (except for the samples deposited at power below 15W where some anisotropy is observed [8]). On the other hand, samples deposited at 30 W and higher silane concentration show L_D values between 60 and 100 nm which are much lower than the values of 200–250 nm observed for L_{amb}; higher

deposition powers reinforce the discrepancy between L_D and L_{amb} values. Decrease of L_D with time is also observed on some samples. Despite the difficulty of performing transport measurements in transverse configuration, the following observations could be made: (1) $\mu\tau$ products measured by TOF [10] correlate with those obtained by SSPC and SSPG (cf. Fig. 2) while (2) electron drift mobility values (as measured by TOF) vary only by a factor of 3 over the studied range of silane concentrations [15], (3) the anisotropy of the transport properties is found to be small or inexistent as seen from comparisons of SSPG and SPV measurements [8,16]. As a further indication of both (a) a rather weak transport anisotropy and (b) a minor effect of structure on transport properties, one observes that (thick) n–i–p cell performance satisfactorily correlates with $\mu^0\tau^0$ values of i-layers (deposited in the same conditions) [8], despite the fact that the different substrate types used for cells and layers induce different microstructures [2].

5. Conclusions

In this paper, we have shown that transport properties of μc-Si:H layers can be conveniently described by the quality parameter $\mu^0\tau^0$. This procedure, originally developed for a-Si:H, allows one to unambiguously compare samples having different impurity contents (such as oxygen incorporated during growth or by post-oxidation) and, therefore, exhibiting different E_f values. A study of various series of samples deposited under a wide range of silane concentration in hydrogen and of VHF power values suggests that transport properties depend mainly on E_f and on the defect density, and are almost independently of crystallites size and shape. This support the hypothesis that the amorphous tissue surrounding the grains plays a major role in determining transport in μc-Si:H; it also explains the transport similarities between a-Si:H and μc-Si:H.

The same conclusion seems also to be valid for transport in the transverse direction (perpendicular to the substrate) since only small or negligible anisotropy is observed in the transport properties. The latter observation is also supported by the satisfactory correlation between cell performance and corresponding layer transport properties. However, one should note here that such a correlation has been obtained on relatively thick n–i–p where the effects of the substrates as well as the effect of the quality of the p–i interface on the cell performance are maybe less pronounced. In thinner cells, changes in the microstructure of the intrinsic layer close to the n–i or p–i interface strongly affects the cell characteristics.

Acknowledgements

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