

BASIC ELECTRONIC PROPERTIES AND OPTIMIZATION OF TCO/a-Si:H(n)/c-Si(p) HETERO SOLAR CELLS

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ABSTRACT

We report on a detailed analysis of the basic electronic properties and the optimization of amorphous/crystalline silicon heterojunction solar cells (a-Si:H(n)/c-Si(p)). The gap states density of the ultrathin a-Si:H emitter on c-Si was determined by photoelectron yield spectroscopy. By varying the a-Si:H film thickness the valence band offset was determined to about 0.45 eV. The density of states at the a-Si:H/c-Si interface amounts to about $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ at midgap. This result was obtained by field dependent surface photovoltage measurements. In addition, photoluminescence measurements were performed to investigate the recombination at the a-Si:H/c-Si interface. To gain an optimized solar cell performance the deposition temperature of the a-Si:H and the gas phase doping concentration was varied. These optimizations lead to a maximum efficiency of 17.2% for a TCO/a-Si:H(n)/c-Si(p)/a-Si:H(p) solar cell fabricated using low temperature processes only.

INTRODUCTION

Silicon heterojunctions produced by plasma enhanced chemical vapor deposition (PECVD) of thin (5-10nm) hydrogenated amorphous silicon (a-Si:H) layers on a crystalline silicon substrate attract more and more interest for low cost and high efficiency solar cells [1].

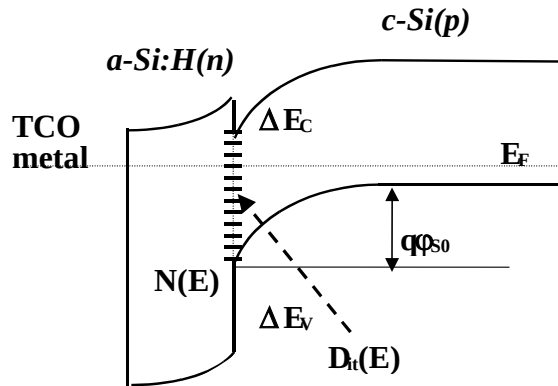


Fig. 1: Schematic band diagram of a-Si:H(n)/c-Si(p) heterojunction including band offsets, ΔE , the interface states density, D_{it} , and gap states density of a-Si:H, $N(E)$.

The main advantage of this kind of solar cell is the possibility of a complete low temperature processing when a BSF consisting of a-Si:H is implemented. This can be very important for temperature sensitive substrates like

thin mc-Si or EFG wafers and poly-Si on glass. In this paper we focus specially on the system a-Si:H(n)/c-Si(p) which is the inverse doping structure as reported by SANYO [1]. Fig 1 shows a schematic band diagram of the heterostructure. The transport through this kind of structure is determined by interface states, $D_{it}(E)$, band offsets, ΔE_V and ΔE_C , gap states density in the a-Si:H, $N(E)$, band bending, $q\phi_{s0}$, and diffusion length in the absorber. In this paper we present the determination of basic electronic properties of the heterojunction according to Fig. 1 and the optimization of the whole solar cell performance of TCO/a-Si:H(n)/c-Si(p)/a-Si:H(p) structure.

EXPERIMENTAL

Hydrogenated amorphous silicon is deposited by a plasma enhanced chemical vapor deposition process on p-type c-Si wafers. The thickness of the a-Si:H layer is 5 – 10 nm. Doping of a-Si:H is achieved by premixing silane with phosphine for n-type doping and with diborane for p-type doping. The solar cell structure is completed by a ZnO or ITO layer as transparent conductive oxide (TCO) and Al grids. For the rear contact also Al is used.

Using photoelectron yield spectroscopy with excitation by UV light (UV-PEYS), the density of occupied states in the band gap and the valence band close to the band edge were determined. Details of the experimental set-up can be found in [2]. At the low excitation energies of 4-7eV used in UV-PEYS, the information depth increases to 5-10nm, which is comparable to the thickness of the a-Si:H films under investigation. Moreover, due to the large information depth, the contribution of surface states to the photoelectron yield is negligible. Thus, UV-PEYS provides an integral measure of the density of occupied states in the bulk of the ultrathin film. In addition, the position of the Fermi level can be determined from the spectra.

The interface states density was obtained by measuring the surface photovoltage (SPV) under different bias conditions. For the SPV measurement the sample is sandwiched in an artificial metal/insulator/semiconductor structure using mica foil as insulator and TCO as the metal. The sample is excited by a short laser pulse ($\lambda = 932\text{nm}$, 150 ns pulselength) and the change in the band bending due to the generated excess carriers is measured. By applying a bias voltage the position of the Fermi energy at the interface or surface is changed. From the relationship between the change of the band bending, estimated from the SPV voltage, in dependence of the bias voltage the interface states density can be determined [3]. Photoluminescence measurements were performed using the 743 nm line of a pulsed dye laser.

RESULTS AND DISCUSSION

According to Fig. 1, the a-Si:H/c-Si heterostructure is determined by band offsets, the density of interface states and the density of states in the band gap of the amorphous emitter. In the first part of this paper these basic electronic properties will be characterized. In the second part the optimization of the heterostructure is shown.

The gap states density can be determined using PEYS. Fig. 2 shows the density of occupied states, $N(E)_{oc}$, as a function of the energetic position with respect to the valence band for a-Si:H(i)/c-Si(p) with three different a-Si:H layer thicknesses as shown in the figure. The valence band edge which is the origin of the x-axis is defined as the onset of the parabolic density of states distribution. A value of $2 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ is used at the valence band edge of a-Si:H. The spectra for layer thicknesses above 3 nm show similar characteristics as reported for a-Si:H on glass substrates [4]. A deep defect band is centred at about 0.5 eV above the valence band which originates from the Si dangling bonds. The exponential valence band tail, which is generated due to strained bonds, is characterized by an Urbach energy of about 70 meV. The Fermi energy lies independent of the a-Si:H layer thickness at about 1.25 eV above the valence band. For the sample with the thinnest a-Si:H layer the defect band stays unchanged but the slope of the valence band Urbach energy is enhanced compared to the samples with thicker emitters. This can be interpreted as follows. The information depth of the PEYS is about 5-10 nm. For thin a-Si:H layers also the occupied states of the c-Si valence band contribute to the signal. The contribution of the valence band states starts for $E - E_V < 0.45 \text{ eV}$ with respect to the valence band of the a-Si:H layer. Thus the valence band offset according to Fig. 1 can be estimated to about 0.45 eV. The conduction band offset amounts then to about 0.15 eV since the band gap of the a-Si:H was determined to be 1.7 eV.

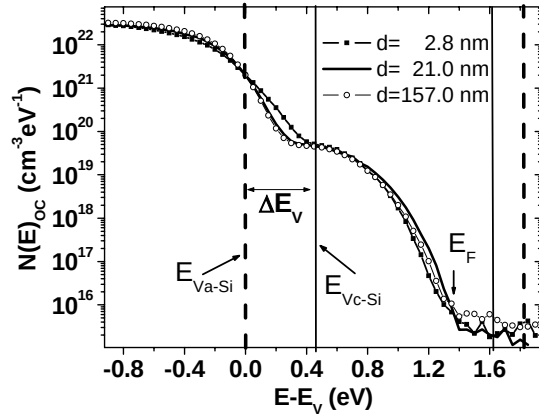


Fig. 2: Density of occupied states as a function of energy for different a-Si:H layer thickness. The energetic positions of the valence and conduction bands and the Fermi level are indicated.

We simulated the complete solar cell structure including band offsets and interface states according to Fig 1 to elucidate the consequences of the asymmetry in the band offsets. Fig. 3 shows the simulated efficiency as a function of the band offset of the minority carriers for two densities of interface states, D_{it} . In the case of a-Si:H(n) on c-Si(p) the band offset for the minority carriers is the conduction band offset whereas for a-Si:H(p)/c-Si this is the valence band offset. The values for the band offsets of the two different structures are indicated in the figure. For small values of D_{it} ($D_{it} \approx 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$), the efficiency is independent of ΔE for $\Delta E < 500 \text{ meV}$ and then decreases rapidly for higher values. When there is a high amount of interface states the situation changes. For $D_{it} \approx 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ the efficiency decreases from 16% to 12% for low values of ΔE . As mentioned above the structure a-Si:H(n)/c-Si(p) exhibits a small value of ΔE . According to Fig. 1 the Fermi level for a structure of this doping sequence crosses the interface at around midgap. It is well known that the recombination via deep defects is highest when the defect is located near midgap and thus the efficiency is reduced. For the inverse doping structure ΔE amounts to 450 meV and the efficiency stays nearly constant with increasing D_{it} . The Fermi level for a a-Si:H(p)/c-Si(n) structure crosses the interface below midgap and thus this structure is less sensitive to interface states than a a-Si:H(n)/c-Si(p) heterojunction [5].

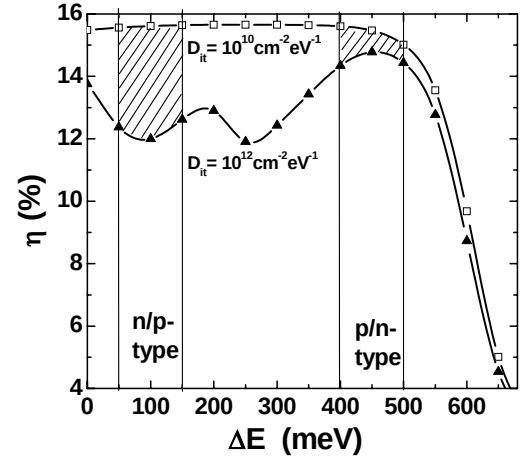


Fig. 3: Simulated efficiency of a-Si:H/c-Si solar cells as a function of the minority carrier band offset for two values of density of interface states. ΔE for a-Si:H(n)/c-Si(p) and Si:H(p)/c-Si(n) are indicated.

The interface states density can be determined by field dependent photovoltage measurements. This method was developed to investigate the electronic states of the crystalline silicon surface. One assumption of the determination of the surface or interface density of states is that during the measurement no electronic states are recharged. At room temperature this assumption is not fulfilled for a-Si:H/c-Si. There is a charge transfer into the amorphous layer causing the recharging effect probably due to phonon assisted tunneling or thermionic emission. To reduce

the recharging effect the measurements were performed at a temperature of 100K. Fig 4 shows $D_{it}(E)$ determined with field dependent SPV as a function of the energetic position in the band gap for a-Si:H/c-Si heterojunctions for three different a-Si:H deposition temperatures, T_S .

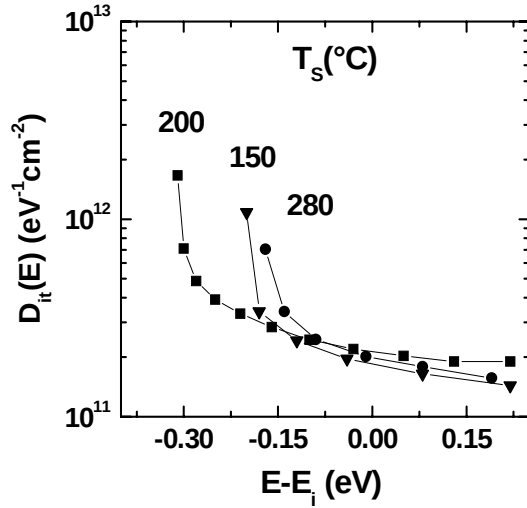


Fig. 4: Interface states density, $D_{it}(E)$, from SPV as a function of the position in the bandgap for different a-Si:H deposition temperatures.

At midgap $D_{it}(E)$ amounts to about $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ independent of T_S . This value is comparable to a silicon surface passivated by hydrogen. However, recharging effects at 100K cannot be completely neglected. A detailed analysis devoted that recharging causes an overestimation of $D_{it}(E)$ and thus the determined $D_{it}(E)$ in Fig. 4 is an upper limit. Towards the band edge $D_{it}(E)$ increases. The onset of the increase depends on the deposition temperature. For $T_S = 200^\circ\text{C}$ this onset starts at $E - E_i = -0.3 \text{ eV}$ whereas for higher and lower T_S the onset is closer to midgap. To determine the consequences of these results on the recombination at the a-Si:H/c-Si interface we performed photoluminescence measurements.

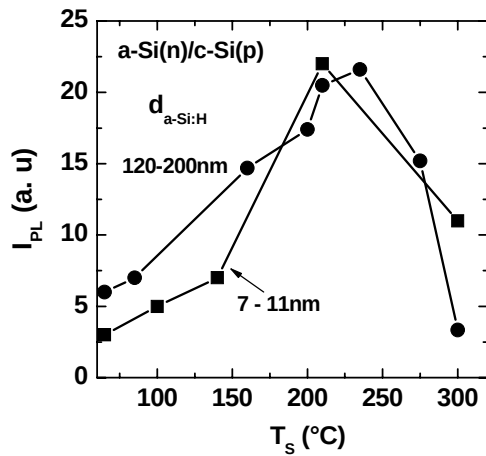


Fig. 5: Photoluminescence intensity, I_{PL} , as a function of the deposition temperature for samples with different thickness.

Fig. 5 shows the photoluminescence intensity, I_{PL} , measured at $E = 1.2 \text{ eV}$ as a function of T_S for two different a-Si:H layer thickness ranges. I_{PL} shows a maximum for $T_S = 210 - 230^\circ\text{C}$. The obtained maximum is independent of the layer thickness. This shows that photoluminescence is an interface sensitive method. The photoluminescence intensity is a measure for the splitting of the quasifermi-niveaus and thus for the maximum achievable open circuit voltage. The optimum deposition temperature of the a-Si:H layer is about 210°C . This result is supported by these samples having the smallest value of D_{it} close to the band edge for $T_S = 200^\circ\text{C}$.

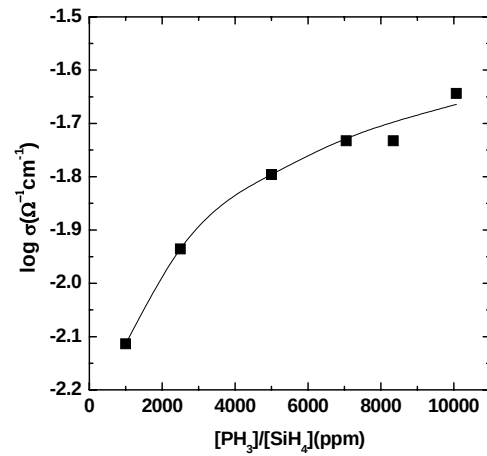


Fig. 6: Conductivity of a-Si:H on glass substrates as a function of the gas phase doping concentration ($d \approx 100 \text{ nm}$).

To obtain a maximum band bending in the c-Si absorber, the Fermi energy of the amorphous emitter should be as close to the conduction band as possible. For this purpose we look at the maximum conductivity of a-Si:H on glass substrates. Fig. 6 shows the conductivity as a function of the gas phase doping concentration which is defined as: $N_G = [\text{PH}_3]/[\text{SiH}_4]$. The maximum conductivity is obtained for $N_G = 10\,000 \text{ ppm}$ and the best solar cell should be obtained using this gas phase doping concentration. This is tested in a solar cell structure without using a BSF. Fig 7 shows the obtained efficiencies as a function of the gas phase doping concentration. The efficiency increases with increasing N_G up to 13 % for $N_G = 2000 \text{ ppm}$ and decreases with a further increases of N_G . Contrary to the results from the conductivity measurements the best solar cell is obtained for $N_G = 2000 \text{ ppm}$. The open circuit voltage follows the same trend as the efficiency. Also the short circuit current increases with increasing N_G until $N_G = 2000 \text{ ppm}$ and stays approximately constant with a further increase of N_G . This result can be interpreted as follows. It is well known that substitutional doping of a-Si:H on glass substrates leads to the creation of deep defects. This leads to a self compensation effect in a-Si:H. However, the maximum conductivity for P-doped a-Si:H is reported for $N_G = 10\,000 \text{ ppm}$ [6] a result that is supported by our findings (Fig. 6). For amorphous silicon on crystalline silicon the initial growth of a-Si:H might be different to the case of a-Si:H on glass substrates. Due to the doping defects are

created which are located at the interface and in the a-Si:H layer. The optimal gas phase doping concentration is obtained when the Fermi energy in the a-Si:H layer is sufficiently close to the conduction band and the defect density is still considerably low. Obviously the optimum gas phase doping concentration for a-Si:H/c-Si solar cells is about 2000 ppm.

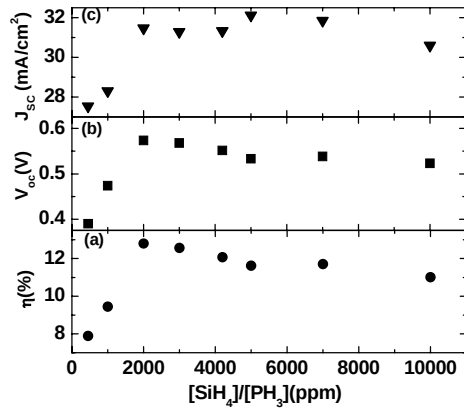


Fig. 7: Solar cell parameters of TCO/a-Si:H(n)/c-Si(p) solar cells with varying gas phase doping concentrations of the a-Si:H layer.

Using optimized deposition conditions a maximum efficiency of 17% on a flat c-Si substrate with diffused back surface field was obtained (Fig. 8). For this heterojunction solar cell a thin (3nm) intrinsic amorphous layer was used. Additionally we fabricated solar cells with a-Si:H(p) back surface field on a textured substrate but without special antireflex coating using only low temperature process steps. Without an intrinsic a-Si:H layer a maximum efficiency of 17.2 % was obtained (see Fig. 8). This is the highest efficiency of a complete low temperature a-Si:H(n)/c-Si(p)/a-Si:H(p) solar cell reported so far.

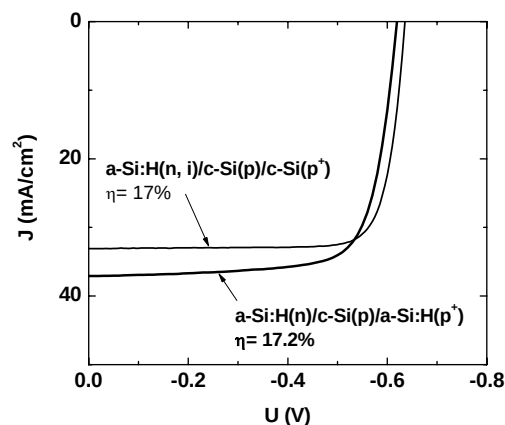


Fig. 8: Best solar cells using a diffused BSF (c-Si(p⁺)) and a low temperature a-Si:H(p) BSF.

CONCLUSION

The basic electronic properties of a a-Si:H/c-Si heterojunction were measured using PEYS and SPV. The valence band offset was determined to 0.45 eV. Simulations show that the interface states density of a a-Si:H(n)/c-Si(p) has a major impact on the cell efficiency and must be as low as possible. For the inverse doping structure D_{it} plays a minor role. However, with a D_{it} of about $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ a high efficiency TCO/Si:H(n)/c-Si(p) cell is achievable. Using optimized deposition conditions with respect to the deposition temperature and the gas phase doping concentration a complete low temperature processed solar cell with an efficiency above 17 % was processed.

ACKNOWLEDGEMENTS

This work is supported by the Bundesministerium für Bildung und Forschung. Contract number FKZ01F0012-19

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