

IP-D3-03

AMORPHOUS / CRYSTALLINE SILICON HETEROJUNCTION SOLAR CELLS WITH INTRINSIC BUFFER LAYER

A. M. Froitzheim¹, M. L. D. Scherff², A. Ulyashin², O. Milch¹, M. Schmidt¹, W. R. Fahrner², W. Fuhs¹

¹ Hahn-Meitner-Institut Berlin, Abteilung Silizium-Photovoltaik, Kekuléstr. 5, D-12489 Berlin
Tel.: +49/30/67053-350, Fax: +49/30/67053-333, e-mail: froitzheim@hmi.de

² University of Hagen, Department of Electrical Engineering Haldener Str. 182, D-58084 Hagen,
Tel.: +49/2331/987-4012, Fax: +49/2331/987-321, e-mail: maximilian.scherff@fernuni-hagen.de

ABSTRACT

Simple structure TCO/a-Si:H(n)/c-Si(p) heterojunction solar cells with varied emitters are investigated by current-voltage-characteristics (IV), photoluminescence (PL) and ultra violet photo electron spectroscopy (UPS). A confirmed efficiency of 16.2% on flat substrates is reached. Additionally, cells have been prepared with intrinsic a-Si:H(i) buffer layers, in order to passivate the proper pretreated wafers. This passivation results in an enhanced PL signal and UPS measurements indicate a reduced density of defect states in ultra thin a-Si:H(i) compared to a-Si:H(n) layers.

1. INTRODUCTION

Heterostructures such as TCO (transparent conductive oxide) / a-Si:H / c-Si have a considerable potential for cost-effective high efficiency solar cells processed at low temperatures [1,2]. The implementation of high technology features such as the use of an intrinsic buffer layer and surface texturing for a-Si:H(p)/c-Si(n) structures led to efficiencies up to 20.7 %. Up to now the attained efficiencies are lower for the inverse structure with n-type emitter on a p-type Si-wafer, a-Si:H(n)/c-Si(p). Scherff et. al. [3] reported a confirmed efficiency of 16.2 % on flat Fz-Si wafers. Borchert et al. [4] reported on an efficiency of 15.3 % on textured Cz-Si substrates. In a previous work we compared the a-Si:H(n)/c-Si(p) structure with the inverse heterostructure by simulation studies and intrinsic differences of these structures [5]. A significant intrinsic disadvantage of a-Si(n)/c-Si(p) consists in the stronger influence of defect states at the interface on the cell efficiency. The aim of the present paper is to investigate the recombination at the interface with and without intrinsic buffer layer.

In [3] we reported on a-Si:H(n)/c-Si(p) solar cell with a certified efficiency of 16.2 %. Analysing this cell in detail we concluded that the cell efficiency is mainly limited not by the a-Si:H(n)/c-Si(p) interface, but rather by the c-Si bulk properties and the rear contact. To further enhance the cell efficiency we proclaimed to incorporate a thin intrinsic buffer layer, as it was done by Sanyo for the inverse structure a-Si:H(p)/a-Si:H(i)/c-Si(n). Other ways to enhance cell efficiency would be to use similar methods as for classical diffused crystalline

silicon p/n-junctions such as texturing for light trapping and the use of point contacts in order to reduce rear contact recombination. In this work the incorporation of an intrinsic buffer layer is investigated and evaluated by means of PL and UPS measurements.

2. EXPERIMENTAL

2.1 Methods

Measurements of IV-characteristics and of quantum efficiency have been performed. In order to investigate the a-Si:H interface we applied photoluminescence-measurements (PL) using the pulsed techniques, first introduced by Timoshenko et al. [6]. This techniques supplies information on defect concentrations at the interfaces of a silicon absorber, by exciting charge carriers in crystalline silicon with a pulsed laser source (1 ns, 100μJ). The measured PL intensity at a certain wavelength λ consists of all photons, emitted by the cell, in the solid angle $d\Omega$ after the illumination of the cell (integration over time). In order to get more information about the ultra thin a-Si:H layers (5-10 nm) on crystalline silicon we used UPS measurements with an excitation energy of $h\nu = 6.5$ eV. In this energy range the layer thickness corresponds to the emission depth of the photoelectrons (10 nm) [7].

2.2 Preparation

Fig. 1 shows a cross section of the produced n/p-type heterojunction solar cells. As absorber we use a 350 μm thick (111) monocrystalline FZ silicon wafers ($0.5 - 2 \Omega\text{cm}$) with diffused back surface field on which the amorphous layer is deposited. The transparent conducting oxide (TCO) is used to enhance the lateral conductivity and to minimise reflection losses. Indium tin oxide (ITO) layer is used with a thickness of 80 nm. Control ITO layers which are deposited on glass substrates have an integral transmission of 86 % and a specific resistance of $3 \times 10^{-4} \Omega\text{cm}$. Finally the front and rear contacts are prepared by thermal evaporation. 30 nm Cr and 3 μm Ag layers structured with photolithography are used on the emitter and 2 μm Al (full area) are deposited on the backside. On each 3" wafer we prepare 9 cells with an area of 1 cm². The separation of the cell is done wet chemically by etching the ITO in order to separate the cells. More details of the preparation can

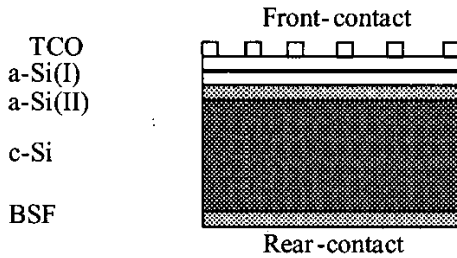


Fig. 1: Schematic structure of the prepared heterojunction solar cell. TCO is an 80 nm thick ITO, a-Si(I) is highly phosphorus doped a-Si:H(n), a-Si(II) is intrinsic a-Si:H(i), BSF is a boron diffused back surface field. The a-Si:H emitters have been prepared with and without the intrinsic buffer layer.

be found elsewhere [3]. It is important to note, that all the samples were prepared from the same wafer series, such that differences in the properties investigated, can be attributed to the different emitters and interfaces of the solar cell.

3. RESULTS AND DISCUSSION

3.1. Solar Cell Analyses

The IV characteristics of the solar cell with an 5 nm thick a-Si:H(n) emitter is displayed in Fig. 2. An efficiency of 16.2 % with a short circuit current (J_{sc}) of 31.58 mA/cm², an open circuit voltage (V_{oc}) of 636 mV and a fillfactor of 80.9 % is reached. These results have been certified by the Fraunhofer Institute (ISE

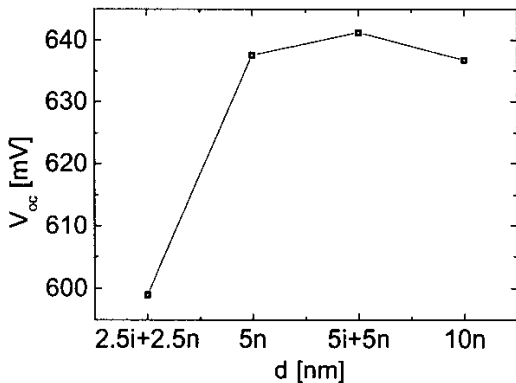


Fig. 3: Open circuit voltage of a-Si:H/c-Si(p) for various emitters. n and i denote a-Si:H(n) and a-Si:H(i), respectively. The number in front of n and i indicate the appropriate nominal layer thickness.

Freiburg). To our knowledge this is the highest efficiency reported for an a-Si:H(n)/c-Si(p) solar cell. In order to enhance the

efficiency we proclaimed to deposit an intrinsic buffer layer as it was done by Sanyo for the inverse structure.

Fig. 3 shows V_{oc} for a-Si:H/c-Si(p) solar cells consisting of emitters with and without intrinsic buffer layers. The emitter has a nominal thickness of 5 and 10 nm, respectively. The solar cell with the 2.5 nm a-Si:H(n) + 2.5 nm a-Si:H(i) has an open circuit voltage of below 600 mV, that is far below the V_{oc} of the other emitter combinations. We believe that this lack in V_{oc} is not due to shunts of these ultra thin layers, but rather due to depletion of the a-Si:H-layers, which cannot dispose enough charge carriers in order to form the n/p-a-Si:H(n)/c-Si(p) heterojunction. This is important for ultra thin emitters and will be investigated in more detail in [8]. The comparison of V_{oc} of the cell with 5 nm a-Si:H(n) + 5 nm a-Si:H(i) emitter with 5 nm and the 10 nm thick a-Si:H(n) emitters indicate an enhancement of V_{oc} by about 5 mV. V_{oc} for the cells with only n-type a-Si:H(n) as emitter is independent on emitter thickness, as long as $d > 5$ nm, see also [3]. Similar results have been reported in [9, 10] for the passivation of n-type silicon wafers, where an enhancement of 4 mV has been reported due to the introduction of an intrinsic buffer layer. The reason for this enhancement may be the further reduction of recombination at the a-Si:H / c-Si interface. This effect can originate from two reasons:

- (a) a-Si:H(i) is able to passivate defect states at the c-Si surface better than a-Si:H(n).
- (b) a-Si:H(i) has a lower density of defect states in comparison to a-Si:H(n) even in these ultra thin films. This would reduce recombination within a tunnel distance of the a-Si:H(i)/c-Si(p) interface.

To further explore this effect, we analysed similar structures with PL and UPS measurements.

3.2 Photoluminescence

In Fig. 4, the PL-spectra for the solar cell with the 5 nm emitter and the 5 nm a-Si:H(i) + 5 nm a-Si:H(n) emitter is shown. The samples have been illuminated with a wavelength of 500 nm. The maximum of these spectra is roughly at 1130 nm. This corresponds to the band-band recombination in c-Si. Therefore the splitting of the quasi Fermi levels are responsible for the intensity of the photoluminescence signal of this heterojunction. It should be noted, that although we used a pulsed laser (1 ns), we will use the concept of quasi Fermi levels. The charge carriers thermalise within the bands in the ps-range. For times longer than this, the concept of quasi Fermi levels can be used. The main PL-signal is observed directly after the excitation of charge carriers by the light pulse. Therefore we argue that the PL-intensity integrated over time mainly reflects the maximum splitting of the quasi Fermi level, after illumination of the sample. In the following we try to calculate the difference in the splitting for the Fermi level for the two samples. The generalised Planck's law for the photon flux j_γ for photons at energy E per unit area, energy and solid angle Ω is given by [11, 12]:

$$j_\gamma(E) = \frac{2c}{(hc)^3} \cdot a(E) \cdot \frac{E^2}{\exp((E - \mu)/kT) - 1} \quad (1)$$

where E is the photon energy, c is the velocity of light, T the temperature of the sample, h and k are the Planck and Boltzmann constants. μ is the chemical potential of the photons

which is equal to the difference of the quasi Fermi levels for

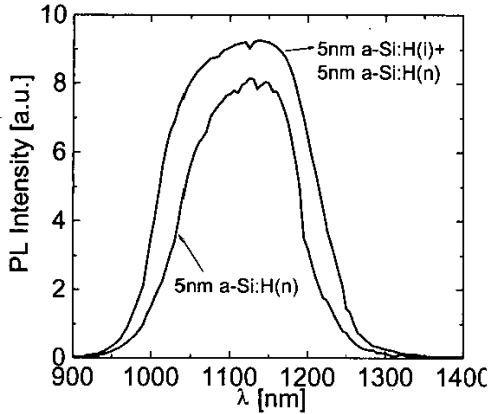


Fig. 4: PL-spectra in the range from 900 – 1200 nm, for a-Si:H/c-Si(p) solar cell consisting of an 5 nm a-Si:H(n) nm a-Si:H(i) emitter and a 5 nm a-Si:H(n) emitter, respectively.

electrons and holes. In thermodynamic equilibrium, where μ is equal to zero, eq. 1 reduces to the famous Plank law for the emission of light from bodies with temperature T . $a(E)$ is the samples absorptance, and naturally depends on the energy of the emitted photons via the absorption coefficient α and the reflectivity. $a(E)$ is assumed to be the same for both samples, as the additional 5 nm a-Si:H(i) layer does not influence $a(E)$ at a wavelength of around 1100 nm. As long as we use Fz-wafers, we assume that the Fermi levels are mainly constant throughout the main part of the wafer and thus the difference in the chemical potential is constant and equal to the applied voltage V . As long as $qV < E_g$, an assumption that is easily satisfied for solar cells, eq. (1) can be simplified to:

$$j_Y(E) = \frac{2c}{(hc)^3} \cdot a(E) \cdot E^2 \cdot \exp\left(-\frac{E-V}{kT}\right) \quad (2)$$

Eq. (2) shows that the Intensity at a certain photon energy E is exponentially dependant on the applied voltage. If the solar cell is not electrically contacted V is equal to V_{OC} , for this illumination. While we didn't measure the absolute value of the emitted photons, it is nevertheless easily possible to extract the differences of the open circuit voltage for this illumination of the compared samples:

$$\Delta V_{OC} = kT \ln(j_{Y1} / j_{Y2}) \quad (3)$$

where j_{Y1} j_{Y2} are the photon fluxes at a specific wavelength. At 1130 nm this ratio equals to $9.2/8.1 = 1.13$ which results with eq. 3 in a difference of the measured open circuit voltage of about 3 mV. Taking other wavelengths ΔV_{OC} changes slightly. As the intensity and spectrum is quite different for the pulsed laser and the AM1.5 solar cell simulator it is rather interesting

that the differences in V_{OC} is quite similar. This could be interpreted in a way that the interface recombination is not the main loss mechanisms, as one would expect stronger dependence of ΔV_{OC} on the illumination level. To get more insight into the recombination paths we performed UPS measurements on ultra thin a-Si:H layers deposited on crystalline Silicon wafers with same doping level as used for the preparation of solar cells.

3.3 UPS Measurement

The ultra thin a-Si:H emitter layer has to passivate the c-Si surface states and to form the n/p heterojunction. We determined the position of the Fermi level in reference to the valence band, the slope of the valence band tail states (Urbach energy E_{OV}) and the change in the gap state distribution in dependence on the doping level in order to get an idea about the defect distribution (DOS) in such thin films and thus recombination paths.

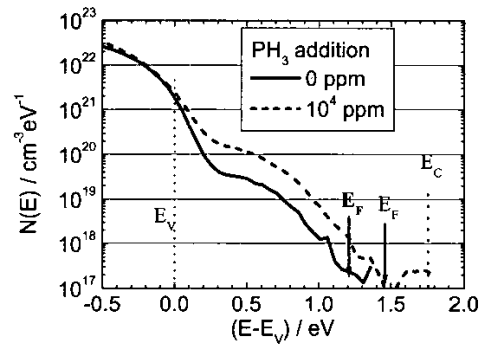


Fig. 5: Comparison of the DOS between an undoped and a phosphorus doped 10 nm thick a-Si:H layer deposited on a c-Si wafer (111).

Figure 5 shows the comparison of the DOS for a nominally undoped (0 ppm) a-Si:H(i) and an a-Si:H(n) layer doped with 10^4 ppm PH_3 / SiH_4 phosphine. Two features can be observed.

- The gap state distribution shows exponential band tail states,
- the DOS in the gap region increases by nearly one order of magnitude and the position of the Fermi level shifts towards the conduction band edge for the phosphorous doped layer.

The valence band edge E_V is determined by a plot of $\sqrt{N(E)}$ vs. E , where the starting point of the linear dependence is set to E_V . Furthermore, we determined the Urbach energy E_{OV} of the exponentially distributed valence band tail states from the slope of a log-linear plot of $N(E)$. The obtained value of E_{OV} reflects the disorder broadening of the valence band. The value of E_{OV} increases with disorder. The Urbach energy is $E_{OV} = 65.2$ meV for the undoped sample and increases to $E_{OV} = 101.3$ meV for the doped sample. Due to higher defect densities in the centre of the band gap and due to higher valence band tail

state energies ultra thin a-Si:H(i) layers on c-Si(p) reduce interface recombination more effectively than a-Si:H(n).

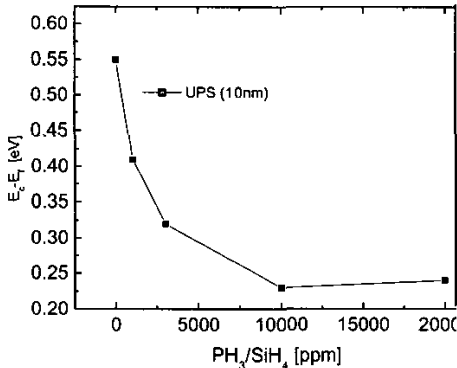


Fig 6: Dependence of the Fermi level position on the phosphine addition for 10 nm thick a-Si:H layers.

An other important point is the position of the Fermi level of these ultra thin a-Si:H layers (Fig. 6). This figure shows ($E_C - E_F$) for various gas-phase concentrations of PH_3 . It is assumed that the energy gap for this thin layers is the same as measured on thick samples, 1.72 eV. For undoped samples ($E_C - E_F$) is 0.56 eV and ($E_C - E_F$) saturates at a value of 0.25 eV at 10000 ppm PH_3 in SiH_4 . The saturation of the Fermi level position is a result of a self limiting process caused by the generation of deep defect levels.

Best results are obtained by combining a-Si:H(n) layers with a-Si:H(i) layers: The a-Si:H(i) layer reduces interface recombination at the interface due to a low defect density in the gap, and the a-Si:H(n) layer further reduces recombination at the interface due to enhanced band bending which leads to an additional field passivation. It should be noted that a thin a-Si:H(i) layer does not reduce J_{SC} [3, 13]: The charge carriers generated in the a-Si:H(i) layer do not recombine, as there is a strong electric field that separates the electrons and holes.

4. CONCLUSION AND OUTLOOK

We have demonstrated the advantages of an 5 nm a-Si:H(i) layer incorporated as buffer layer in a a-Si:H(n)/c-Si(p) heterojunction solar cell. This was investigated by PL and UPS measurement which can be correlated with V_{OC} of this heterostructure. The PL signal is enhanced for solar cells with intrinsic buffer layer and the density of defect states in the amorphous layer is reduced measured by UPS. V_{OC} is enhanced by about 5 mV. It should be mentioned, that we believe that an important loss mechanism in our cells is the rear contact although we used a BSF. Therefore further enhance-

ment in V_{OC} is expected to from the use a-Si:H as a BSF as well [2, 14].

5. ACKNOWLEDGEMENT

The work was partially supported by the Bundesministerium für Forschung und Bildung (BMBF contract # 01SF0016)

REFERENCES

- [1] M. Tanaka, M. Taguchi, T. Matsuyama, T. Sawada, S. Tsuda, S. Nakano, H. Hanafusa, and Y. Kuwano, *Jpn. J. Appl. Phys.* **31**(1992) 3518.
- [2] H. Sakata, T. Nakai, T. Baba, M. Taguchi, S. Tsuge, K. Uchihashi, S. Kiyama, *Proc 20th IEEE PVSEC*, 2000, 7.
- [3] M.L. Scherff, A. Froitzheim, A. Ulyashin, M. Schmidt, W. R. Fahrner, and W. Fuhs, *Proc. PV in Europe, Rome*, (2002), 216.
- [4] D. Borchert, R. Hussein, and W. R. Fahrner, *Proc. of 11th Int. PV Science and Engineering Conf.*, Sapporo, Japan (1999).
- [5] R. Stangl, A. Froitzheim, and W. Fuhs, *Proc. 17th EPVSEC*, Munich, Germany (2002), 1387.
- [6] V. Yu. Timoshenko, A.P. Petrenko, M. N. Stolyarov, Th. Dittrich, W. Füssel, and J. Rappich, *J. Appl. Phys.* **85** (1999), 4174.
- [7] M. Schmidt, O. Milch, Schöppke, Th. Lussy, *Proc. of MRS*, San Francisco, USA (2003), in press.
- [8] R. Stangl, A. Froitzheim, M. Schmidt, L. Elstner, and W. Fuhs, this conference.
- [9] M. Tanaka, M. Taguchi, T. Matsuyama, T. Sawada, S. Tsuda, S. Nakano, H. Hanafusa, and Y. Kuwano, *Jpn. J. Appl. Phys.* **31** (1992), 3518.
- [10] S. Tsuda, T. Takahama, Y. Hishakawa, H. Tarui, H. Nishiwaki, K. Wakisaka, and S. Nakano, *J. Non-Crys. Sol.* **164-166** (1993), 679.
- [11] P. Würfel, *J. Phys. C: Solid State Phys.*, **15** (1982), 3967.
- [12] M. A. Green, J. Zhao, A. Wang, P. J. Reece, and M. Gal, *Nature* **412** (2001), 805.
- [13] D. Borchert, Grabosch, and W. R. Fahrner, *Sol. Eng. Mat.*
- [14] S. Dauwe, J. Schmidt, and R. Hezel, *Proc. of 29th IEEE PVSEC*, New Orleans, USA (2002), 1246.