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Effect of oxide treatment at the microcrystalline tunnel junction of a-Si:H/a-Si:H tandem cells

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Abstract

The electrical transport taking place in the $\mu\text{-Si}$ tunnel recombination junction (TRJ) of a-Si:H/a-Si:H tandem solar cells and the role of CO_2 plasma oxidation performed between microcrystalline layers is investigated in this paper with the computer code AMPS. Oxidized interfaces were modelled as simple highly defective intrinsic $\mu\text{-Si}$ layers. Two different tunnel junction structures are studied in this paper: (a) $(\text{n})\mu\text{-Si}/\text{oxide}/(\text{p})\mu\text{-Si}$ and (b) $(\text{n})\mu\text{-Si}/(\text{i})\mu\text{-Si}/(\text{p})\mu\text{-Si}$. In the last configuration the oxide interface is removed and replaced by a thin defective (i) $\mu\text{-Si}$ layer. Both tunnel junctions have comparable theoretical and experimental tandem solar cell efficiencies which indirectly proves that our modelling assumption for oxidised interfaces is correct. A-Si:H/a-Si:H tandem solar cell efficiencies depend on the thickness of the intrinsic layer introduced in the tunnel junction. The optimisation of this thickness provides a more controlled way of achieving greater efficiencies in a-Si:H/a-Si:H tandem solar cells. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The performance of a-Si:H/a-Si:H tandem cells can be improved by using smaller mobility gap materials at the tunnel or recombination junction (TRJ). The optical absorption of microcrystalline silicon ($\mu\text{-Si}$) makes this material ideal for this purpose. Therefore various research groups have implemented entire $\mu\text{-Si}$ tunnel junctions in their tandem cells [1,2]. Our tandem solar cell structure is as follows: $\text{SnO}_2/\text{F}/\text{p-a-SiC:H}/\text{i-a-Si:H}/\text{n-}\mu\text{-Si:H}/\text{p-}\mu\text{-Si:H}/\text{i-a-Si:H}/\text{n-a-Si:H}/\text{Ag}$. We have achieved efficiencies of $9.89 \pm 0.05\%$ in the annealed state [1]. To reach this figure interface oxidation treat-

ments were needed at two interfaces: i-a-Si:H/n- $\mu\text{-Si:H}$ and n- $\mu\text{-Si:H}/\text{p-}\mu\text{-Si:H}$. The oxide layer at n- $\mu\text{-Si:H}/\text{p-}\mu\text{-Si:H}$ junction is around 3 nm thick [3]. The structural property of this microcrystalline junction was verified by the cross-sectional transmission electron microscopy (XTEM) which confirmed that layers are crystalline [3].

Our first investigations on the electrical transport made with the computer programme AMPS (analysis of microelectronic and photonic devices) showed that the small mobility gap of $\mu\text{-Si}$ increased recombination in the tunnel junction and reduced undesired trapping in a-Si:H absorbers [4]. In a tunnel junction having a simple $(\text{n})\mu\text{-Si}/(\text{p})\mu\text{-Si}$ structure the ‘good’ recombination between electrons and holes, photogenerated in the first and in the second sub-cell respectively, takes place in a region ~ 3.5 nm thick near the n/p interface and mainly located inside the $(\text{p})\mu\text{-Si}$ layer. We found

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that the ‘good’ recombination peak is approximately located where the Fermi level at thermodynamic equilibrium crosses midgap. The larger activation energy of (p) μ -Si moves the Fermi level to the middle of the gap inside of this region. In the rest of the μ -Si layers recombination occurs between electrons and holes coming from the same sub-cell. This type of recombination is hereafter called ‘bad’ recombination and electrical losses.

Our working hypothesis is that the oxide layer increases the defect density near the oxide/ μ -Si interfaces and it can be easily tunnelled through either by electrons or holes. These largely defective and small band-gap regions favour the good recombination. To simplify our approach we modelled in our previous papers [3,4] the presence of this oxide with a thin, undoped, and largely defective layer ($>10^{19}$ cm $^{-3}$) having the μ -Si mobility gap. The oxide layer shifts and pins the quasi-Fermi levels near midgap, moving the good recombination peak towards the n/p interface. In principle, the same effect could be induced by adding an intrinsic μ -Si layer between the doped μ -Si layers. This intrinsic layer will force the Fermi level to cross midgap within the same layer, but a small density of defects ($<5 \times 10^{17}$ cm $^{-3}$) could mitigate the good recombination and could degrade the performance of the tandem cell.

In this paper we study two different recombination junction structures: (a) (n) μ -Si/oxide/(p) μ -Si and (b) (n) μ -Si/(i) μ -Si/(p) μ -Si. We include for the first time in our simulations trap assisted multistep tunnelling recombination. We also looked at how our results change when small free carrier effective masses in multistep tunnelling are used and the Poole–Frenkel effect is included in our calculations.

2. Experimental

A-Si:H/a-Si:H tandem solar cells were made by plasma enhanced chemical vapour deposition (PECVD) in an ultra high vacuum multichamber system, PASTA. Cells were grown on SnO $_2$ coated glass (Asahi U-type) in the superstrate configuration SnO $_2$ /p-a-SiC:H/i-a-Si:H/n- μ -Si:H/p- μ -Si:H/i-a-Si:H/n-a-Si:H/Ag and oxide treatment at TRJ

was done by CO $_2$ plasma at a low power (4 W) to reduce damage or etching of the layer. The light current (voltage) ($I(V)$) and spectral responses of these cells were measured at AM1.5 (one sun) illumination. The error in these measurements is within $\pm 3\%$.

3. Results

3.1. Computer simulations: tandem solar cell modelling

We used AMPS to explore the recombination kinetics controlling the electrical transport in the tunnel junction of a-Si:H/a-Si:H tandem solar cells. To gain insight into the electrical transport present in the n-i-p μ -Si tunnel junction we studied the dependence of the tandem cell efficiency on the μ -Si i-layer thickness and the density of midgap states (DMS). The simulations were performed by using two different models: (a) the standard Shockley–Read–Hall recombination [5] and (b) trap assisted multi-step tunnelling as proposed by Hurk et al [5–7]. The second approach has a recombination rate expression that is similar to the one derived by the Shockley–Read–Hall formalism. However in multistep tunnelling the electron and hole cross-sections become field dependent because stronger electric fields increase the tunnelling probability.

Fig. 1 shows the tandem solar cell efficiency vs the (i) μ -Si layer thickness of the n-i-p microcrystalline tunnel junction when we neglect the optical absorption taking place in μ -Si (the μ -Si optical gap or cut-off energy in AMPS was assumed to be 2.3 eV). The μ -Si mobility gap was assumed to be 1.2 eV and uniform. We can see in Fig. 1 that, when we do not include multi-step tunnelling and when we have a smaller DMS in the μ -Si i-layer than in μ -Si doped layers, the best choice is to entirely remove the intrinsic layer. To show this effect the DMS in μ -Si doped layers was intentionally assumed to be 10^{19} cm $^{-3}$. In Fig. 1 we can also see that multistep tunnelling increases the predicted performance of the tandem cell. The maximum cell efficiency is obtained for i-layer thickness within the range 5–10 nm depending

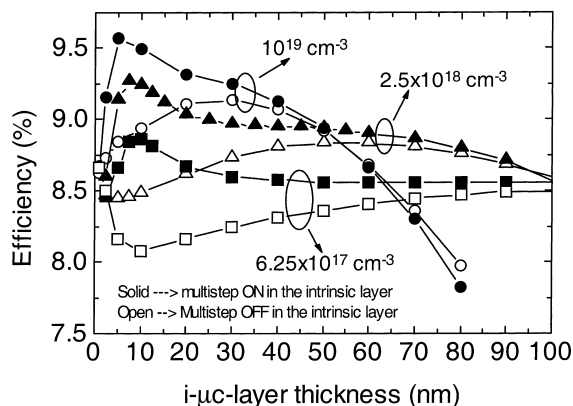


Fig. 1. Computer simulated tandem cell efficiency vs tunnel junction (i)μc-Si:H layer thickness. The μc-Si:H optical gap is assumed equal to 2.3 eV. Lines are drawn as guide for the eye. The errors in efficiency are ±0.05%.

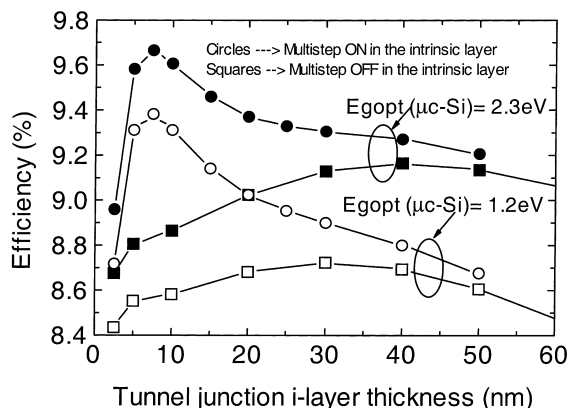


Fig. 2. Computer simulated tandem cell efficiency vs tunnel junction (i)μc-Si:H layer thickness including the optical absorption in μc-Si:H. The density of midgap states in μc-Si:H is equal to $5 \times 10^{18} \text{ cm}^{-3}$.

upon the DMS adopted in the intrinsic layer. The inclusion of multistep tunnelling shifts the greatest cell efficiency to thinner i-layers because thinner i-layers increase the tunnelling probability. The standard Schockley–Read–Hall treatment also predicts thickness dependent efficiencies. Very thin i-layers (>2 nm) cannot hold entirely the good recombination which in n–i–p tunnel junctions spreads over a big portion of the intrinsic layer. Very thick i-layers (>30 nm) favour bad recombination inside the intrinsic layer and efficiencies become similar whether or not, we include multistep tunnelling.

Fig. 2 also shows the dependence of the tandem cell efficiency with respect to the tunnel junction microcrystalline i-layer thickness for two different μc-Si:H optical gaps: (i) 2.3 eV (no light absorption) and (ii) equal to the μc-Si:H mobility gap (1.2 eV). The DMS in all the μc-Si:H layers have been chosen equal to $5 \times 10^{18} \text{ cm}^{-3}$. We see in Fig. 2 that the absorption of light taking place in μc-Si:H is quite significant. Comparing Figs. 1 and 2 we see that larger DMS in the i-layer does not necessarily produce larger efficiencies in a tandem cell. This lack is because large DMS could distort the electric field in the i-layer interior what could reduce the transmission tunnelling probability. We found that in μc-Si:H tunnel junction the recombination is entirely controlled by mid-gap states.

3.2. Experimental tandem cells

Having established the role of the oxide layer with computer modelling, a-Si:H (1.88 eV)/a-Si:H (1.78 eV) tandem cells were also made by using thin (<15 nm) intrinsic microcrystalline silicon as interface layer in the tunnel junction in the configuration n-μc-Si (20 nm)/i-μc-Si (5 nm)/p-μc-Si (20 nm). The properties of this cell were compared with an a-Si:H (1.88 eV)/a-Si:H (1.78 eV) tandem cell using oxidation treatment at the junction n-μc-Si (20 nm)/oxide/p-μc-Si (20 nm). The oxide treatment before the n-μ-Si layer was made in both

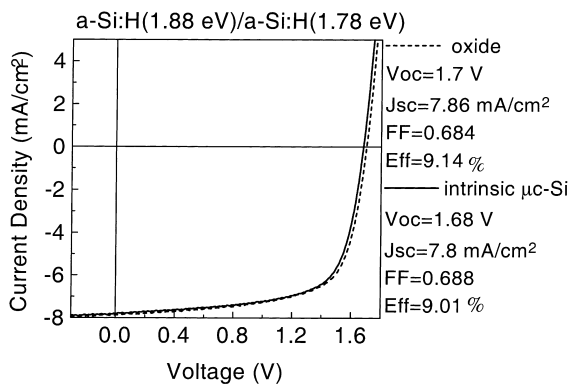


Fig. 3. Experimental I(V) of the tandem cells in the configuration glass/SnO₂:F/p-a-SiC:H/i-a-Si:H/n-μc-Si:H/p-μc-Si:H/i-a-Si:H/n-a-Si:H/Ag. (i) Oxide layer at the tunnel junction, (ii) intrinsic μc-Si:H layer (5 nm) at the tunnel junction.

tandem structures. From Fig. 3, it is clear that for the two cases the $I(V)$ data are similar, with identical V_{oc} , J_{sc} , FF (fill factor), and efficiency. The spectral responses (not shown here) of the top and bottom cells are also similar for the two cases. At present we do not have complete thickness variation of the intrinsic $\mu\text{-Si}$ layer. However preliminary studies on three thicknesses (2.5, 5, and 10 nm) revealed that the efficiency is maximum at 5 nm and this thickness is in conformity with the trend predictions of Fig. 1.

4. Discussion

The equations derived by Hurk et al. [5] are strictly valid only when the electric field is constant within the region where there is tunnelling. In Fig. 2 the largest efficiency is achieved for a 7.5 nm thick i-layer. The electric field inside of this layer is constant within 12%. The uniformity of the electric field can be better guaranteed for very thin i-layers (<10 nm) or in i-layers having DMS less than the doping densities of the $\mu\text{-Si:H}$ doped layers. For a mobility gap of 1.2 eV, the best fitting of the experimental light $J(V)$ data (not shown in this paper) was achieved when in the (i) $\mu\text{-Si:H}$ layer a DMS $\sim 2 \times 10^{18} \text{ cm}^{-3}$ was adopted.

The sensitivity of the tandem solar cell V_{oc} and efficiency to the semiconductor mobility gap used in the tunnel junction led research groups modelling tandem solar cell having a-Si:H in their tunnel junctions to work with elaborate and complex device approaches. Hou et al. [8] placed the good recombination in a largely defective and small bandgap layer connected to both doped layers by intermediate layers where band edges at the n-layer conduction band and p-layer valence band were graded towards this defective layer. Willemen et al. [7] used trap-assisted multistep tunnelling [5] in conjunction with larger free carrier mobilities within the tunnel junction. As the mobility gap of $\mu\text{-Si}$ is much less than the mobility gap of a-Si:H and is not very well known, an interesting question arises: ‘which is the largest mobility gap that we can use in our n–i–p $\mu\text{-Si}$ tunnel junction and still simulate our experimental results?’ The answer is as follows: even when multi-step tunnelling is in-

cluded, experimental results cannot be matched for mobility gaps greater than 1.25 eV. Larger free carrier mobilities inside the tunnel intrinsic layer also help, but using c-Si mobilities we were not able to fit our experimental results for mobility gaps greater than 1.3 eV. In the calculations with multistep tunnelling shown in this paper electron and hole effective masses were assumed to be one. By decreasing these effective masses, recombination via trap assisted tunnelling can be increased. One more mechanism that can be invoked is Poole–Frenkel [9], which decreases the gap state potential well or free carrier ionisation energy under the affects of an electric field. This decrease is given by $\Delta E = e(qF/\pi\epsilon)^{0.5}$, where ϵ is the dielectric constant and F is the electric field. If the electric field is large enough, this effect could increase thermal emission and capture rates. The electric field within the i-layer of an n–i–p tunnel junction could be $\sim 10^6 \text{ V/cm}$ for which ΔE is $>0.2 \text{ eV}$. Depending on how Poole–Frenkel is treated it could produce an effective mobility gap reduction of ΔE [5] or $2\Delta E$ [9]. By reducing the effective mass to 0.1 in trap assisted multistep tunnelling, by including Poole–Frenkel effect, by increasing the mobilities and by choosing the most appropriate DMS, we could not fit our experimental efficiency for $\mu\text{-Si}$ mobility gaps larger than 1.4 eV.

Our experimental results gave a direct confirmation of our computer simulation and an indirect confirmation to the assumptions made in our modelling for the oxide layer. One achievement of this result is that the thickness and deposition time of the intrinsic $\mu\text{-Si}$ layers can be controlled to achieve consistent results.

5. Conclusion

Both modelling predictions and data confirmed that physical properties of the oxidised microcrystalline interface are similar to the ones of a largely defective intrinsic silicon layer and that efficiencies are comparable by using either one or the other tunnel junction. This study also shows an alternative and more reproducible method to make a tunnel recombination junction, namely by using an intrinsic microcrystalline silicon interface

layer. The experimental tandem solar cell efficiency depends on the intrinsic $\mu\text{-Si:H}$ layer thickness in agreement with the predictions of our modelling when trap assisted multistep tunnelling recombination is included to describe transport inside the tunnel junction. Even by reducing the effective masses, by increasing the carrier mobilities and by taking into account Poole–Frenkel, experimental tandem illuminated $J(V)$ cannot be successfully fitted for $\mu\text{-Si:H}$ mobility gaps larger than 1.4 eV.

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