Window layer development for microcrystalline silicon solar cells in n-i-p configuration

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Abstract

The development of p-type and front ZnO layers, being window layers in n-i-p solar cells, is considered in this work. Electrical and optical properties of these layers were investigated on glass substrates, subject to thickness and doping variations. Subsequently, the effects of p-layer thickness and doping and front ZnO thickness on solar cell performance were studied. The optimal conditions for concerned layers are obtained, and discussed in terms of the built-in voltage, potential barriers and total reflection.

1 Introduction

The development of microcrystalline silicon (μc-Si:H) solar cells prepared in n-i-p (substrate) configuration has been the subject of extensive research [1-3]. Since non-transparent substrates may be used in these solar cells, the properties of p-layer covered with a ZnO film, that serve as window layers, are critical to achieve high performance devices. Here, we present the work focused on the development of these window layers. For the development we start with our standard glass substrates with texture etched ZnO [4], which are also used for p-i-n cell development. This substrate serves as a benign and reproducible standard for the optimization of the layer growth conditions. To obtain a highly reflective back contact the texture etched ZnO is covered with an Ag/ZnO sandwich layer.

2 Experimental

Silicon thin films were deposited by plasma enhanced chemical vapour deposition (PECVD) at a substrate temperature of 180 °C in a multichamber UHV system. P-type and intrinsic layers were grown at very high excitation frequency (VHF) of 94.7 MHz. For the n-layer growth, radio frequency (RF, 13.56 MHz) excitation was used. Silicon films were deposited from a mixture of silane (SiH₄) and hydrogen (H₂). Phosphine (PH₃) and trimethylboron (TMB) were added to the process gas to produce n- and p-type doped layers, respectively. Solar cells were prepared in n-i-p configuration in the following sequence: substrate/μc-Si:H(n)/μc-Si:H(i)/μc-Si:H(p). The cells were illuminated through ZnO:Al front contact, deposited on p-layer and covered with Ag grids. ZnO:Al was produced by RF magnetron sputtering with a power of 250 W at a temperature of 150 °C. The cells were deposited on two types of substrates: glass/ZnO(textured) [4], used as an easy handling and standard substrate for optimisation of layers, and glass/ZnO(textured)/Ag(100 nm)/ZnO(80 nm) for improved light trapping (see Fig. 1). The deposition conditions of n-type (around 20 nm thick) and intrinsic (nominally 1 μm thick) layers were kept constant during this study. The μc-Si:H i-layers were prepared from a mixture of SiH₄ and H₂ gases, at the silane concentration ratio SC = [SiH₄] / ([SiH₄] + [H₂]) of 5.3%.

P-layers, employed in solar cells, were deposited at varied TMB concentration (defined by the ratio of trimethylboron to silane flows, C_{TMB} = [TMB] / [SiH₄]) and thickness. Additionally, a thickness and a doping series of p-layer were deposited on glass substrates to investigate structural and electrical properties. The structural properties of the layers were probed using Raman scattering measurements, with excitation at 488 nm. The ratio of integrated intensities attributed to crystalline and amorphous regions,
ICRS = Ic / (Ic + Ia) was used as semi-quantitative value of the crystalline volume fraction [5]. Conductivity measurements were performed on films equipped with coplanar electrodes 5 mm in length separated by a 0.5 mm gap.

Varied thickness front ZnO:Al layers were used in solar cells and, also, deposited on glass substrates to evaluate optical and electrical properties. The transmission (T) and reflection (R) were measured on a Perkin-Elmer photospectrometer, type lambda 950, within a spectral range from 320 to 2000 nm.

Solar cells were characterised by current–voltage (J-V) measurements under AM 1.5 illumination and quantum efficiency (QE) measurements. Short circuit current density (J_SC) values obtained from QE measurements were also used to verify short-circuit current density (JSC) values, obtained from J-V data, to avoid possible errors related to device area determination.

3. Results

Fig. 2a shows the variations in dark conductivity (σ_d) and crystallinity (ICRS) with the deposition time of p-type films, deposited at C_TMB = 1. The variations in p-layer thickness with deposition time, estimated based on the deposition rate of 0.8 Å/s, are shown by the arrow. It is seen that both σ_d and ICRS increase with deposition time. For the 20 nm thick film, the σ_d is around 10^{-5} S/cm and reaches the value of 3 S/cm for the thickest film studied here (100 nm, 20 minutes deposition time). The effect of p-layer thickness on solar cell performance is presented in Fig 2b. A significant rise in the open circuit voltage VOC (from 400 mV to above 510 mV) is observed when p-layer thickness increases from 20 nm to 60 nm. A subsequent increase in p-layer thickness does not result in the improvement of VOC values. The values of short-circuit current density (J_SC) tend to decrease with p-layer thickness and drop down to 12 mA/cm² for 100 nm thick (20 min. deposition time).

The effect of TMB doping on the properties of p-layers is summarised in Table 1. To improve the thickness measurement accuracy, the p-layers were prepared for a deposition time of 8 minutes, twice thicker than used in solar cells. One can see the deposition rate Rd and dark conductivity (σ_d) increase with C_TMB, while ICRS decreases. The deposition rate is increased twice when the doping changes from C_TMB = 0.5% to C_TMB = 2.5%. Subsequently, the p-layers prepared with varying TMB doping were employed in a series of solar cells. The effect of p-layer doping on the performance of solar cells is shown in Fig. 3. The p-layers were deposited for 4 minutes, at C_TMB varied between 0.5% and 2.5%. A significant increase in VOC (from 350 mV to 525 mV) is observed with an increase in C_TMB from 0.5% up to 1.5%. Subsequent increase in C_TMB above 1.5% does not result in VOC improvement. The fill factor (FF) increases with p-layer doping. The JSC values rise with doping up to C_TMB < 1.5% and decrease for C_TMB > 1.5%. The figure shows that for this series of cells, a maximum in conversion efficiency is obtained when the p-layer is prepared at C_TMB = 1.5%.
Fig. 4a shows the effect of thickness on electrical and optical properties of the front ZnO. Sheet resistance decreases from around 600 to 50 Ω/cm² with increasing ZnO thickness from 30 to 155 nm. The absorption (A) of ZnO, calculated with $A = 1 - T - R$, is presented in Fig. 4b for 30, 70 and 155 nm thick layers. The figure also includes the results of the total reflection measurements for the solar cells fabricated with these ZnO layers as front contacts. It is seen that 70 nm thick front ZnO results in the lowest total reflection, which is near to 1% at the wavelength of 600 nm.

The effect of the front ZnO thickness on solar cell performance is shown in Fig. 5. P-layers of these solar cells were deposited at CTMB = 1.5% for 4 minutes. One can see that $J_{SC}$ values have a maximum when 70 nm thick ZnO is used, reaching the level of 19 mA/cm². Fill factor (FF) values tend to increase (from 68.8% to 72.3%) with front ZnO thickness, while $V_{OC}$ remains almost constant.

Fig. 6 shows the effect of back reflector on solar cell performance. Both J-V curves (Fig. 6a) and corresponding QE curves (Fig. 6b) are shown. Using glass/ZnO/Ag/ZnO substrate, $J_{SC}$ value is improved by around 2 mA/cm² in comparison with the cell deposited on glass/ZnO. The QE data demonstrate the improved cell response in long wavelength region. The overall performance of the cell grown on ZnO/Ag/ZnO back reflector remains encouragingly high, with FF value of around 73% and conversion efficiency of 8.25% for 1 μm thick i-layer.

4 Discussion

The correlation of dark conductivity ($\sigma_d$) and crystallinity ($I_{CRS}$) with p-layer thickness is evident in Figure 2a. The properties of μc-Si films prepared by PECVD are known to be thickness dependent and the microstructure changes significantly with the deposition time [6-8]. The general trend observed in Fig 2a, namely, an increase in $\sigma_d$ and $I_{CRS}$ with film thickness, is largely consistent with previous report [9-10]. Another possibility to vary $\sigma_d$ is to change p-layer doping (see Table 1). One can see that in this case, $\sigma_d$ rises with increasing CTMB, while in contrast to the thickness series results, $I_{CRS}$ decreases, since it is known that an incorporation of boron may suppress the crystallinity [11-12]. We note an increase in deposition rate ($R_d$) with CTMB is observed, in a broad agreement with previous report [12].

A substantial improvement in $V_{OC}$ with both rising p-layer thickness (Fig. 2b) and also increasing TMB doping (Fig. 3) may be attributed to an increased built-in potential in the device, which arises from an increased charge carrier density in the p-layer, as evident in Fig. 2a and Table 1. Since optical absorption in the film increases with its thickness, the $J_{SC}$ values tend to drop noticeably with p-layer deposition time (see Fig 2b). While thicker p-layers function well as doped layers in solar cells, the properties as a window layer are poor in this case. Thus, a short (4 minutes) deposition time was chosen for the series of cells prepared with varied p-layer
doping. The effects of p-layer thickness and doping on $V_{OC}$, concerned above, are consistent with previous report on the properties of p-i-n solar cells [13]. However, the optimal p-layer conditions for p-i-n and n-i-p cells may differ, since in the later case the p-layer does not serve as an immediate substrate for $\mu$-c-Si:H absorber layer growth, and thus, the requirements for the p-layer in terms of crystallinity may be relaxed. Fill factor (FF) values tend to rise with increasing p-layer conductivity, as evident in Fig. 2b and Fig. 3. This may be related, for example, to an improvement in the p/TCO contact, due to a thinner depletion region in p-layer when the Fermi level position ($E_F$) is shifting towards band edge [14, 15]. It is clear from above discussion that an appropriate conductivity and thickness are the key requirements for the p-layer as a window layer in n-i-p solar cells.

As one can see in Fig. 5, front ZnO layer has a strong influence on solar cell performance. The variations in conversion efficiency follow the general trend of $J_{SC}$ changes with ZnO thickness. It is evident in Fig. 4b that 70 nm thick ZnO layer provides improved antireflection conditions. The requirements for antireflection [16] on silicon films given by:

$$n_{AR} = \sqrt{n_0 \cdot n_{Si}}$$  \hspace{1cm} (1)

$$d = \frac{\lambda}{4n_{AR}}$$  \hspace{1cm} (2)

where $n_{AR}$ is the refractive index of the anti-reflection coating, $n_0$ and $n_{Si}$ are the refractive indices of air and silicon, respectively, $d$ is the thickness of the antireflection coating, and $\lambda$ is the wavelength in vacuum. Based on Eq. (1) it is evident that front ZnO layer, having a refractive index of around 2, may provide an antireflection effect, since $n_0$ is close to 4. To obtain the minimum reflectance at the wavelength of 560 nm, the ideal thickness of ZnO is 70 nm calculated by Eq. (2), in excellent agreement with our results, presented in Fig. 4b. The optimal front ZnO thickness found in this work is comparable with those reported by others [17]. While the $V_{OC}$ is found to be nearly independent on ZnO thickness, FF values tend to increase with ZnO thickness that may be due to reduced sheet resistance of front contact (see Fig. 4).

The optimisation of window (p-type and front ZnO) layers in n-i-p solar cells was presented above. These cells were fabricated on glass/ZnO substrates, previously optimised for p-i-n configurations. An improvement in light trapping can be achieved by utilising ZnO (etched)/Ag/ZnO substrate, while $V_{OC}$ is kept almost constant. We note that the trends obtained for the cells grown on ZnO back-reflector are reproducible with those grown on ZnO/Ag/ZnO layers, which indicates that glass/ZnO substrate can serve as a benign and reproducible standard for the optimization of n-i-p solar cells.

5. Conclusions The effects of p-type and ZnO window layers on the performance of n-i-p solar cells with $\mu$-c-Si:H absorber layer have been presented. The results demonstrate that:

- An appropriate p-layer doping and thickness lead to improved $V_{OC}$ and FF.
- The electrical and optical properties of the front ZnO are thickness dependent, and an optimal thickness of 70 nm is obtained, providing the total reflection of the cell is reduced.
- Glass/ZnO substrate can serve as a benign and reproducible standard for the optimization of n-i-p solar cells. When highly reflective glass/ZnO/Ag/ZnO substrates are used, $J_{SC}$ may be improved by around 2 mA/c㎡.

Acknowledgements We would like to thank A. Doumit, M. Hülsbeck and W. Reetz for their contributions here.

References