Role of a disperse carbon interlayer on the performances of tandem a-Si solar cells

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1. Introduction

The increasing research on transparent conductive oxides (TCOs) is aiming to exploit their high conductivity and high transparency to visible light, giving rise to a plethora of market opportunities for applications as transparent electrodes in optoelectronic devices such as solar cells [1, 2], organic light emitting diodes [3, 4] and liquid crystal displays [5].

The TCOs used in commercial thin film silicon solar cells as front contact layer are mainly based on indium-tin oxide (ITO) [6, 7], due to its high stability and low resistivity, or the newly commissioned amorphous TCOs such as indium molybdenum oxide and indium zinc oxide, produced at low temperatures [8–12]. Nevertheless, the high demand for indium is leading to a decrease on its supply, and in the near future the increase of prices will limit its use, thus opening a window for the use of alternative oxides such as fluorine-doped tin oxide (FTO) [1, 13, 14], aluminium-doped zinc oxide (AZO) [15–18].

Presently, FTO is commonly applied as front contact in amorphous silicon solar cells due to its thermal resistance, chemical stability and texturized surface, guaranteeing a long lifetime and optimized efficiency of solar cells [13, 14]. However, TCOs based on zinc oxide have received recently considerable attention due to their low cost, resource availability, non-toxicity and high thermal and chemical stability, which are very important properties for application in solar cells [2, 19]. Indeed, it was demonstrated that ZnO films doped with Al, Ga or B can have low resistivity, high transmittance and stability for a broad range of processing
Most of the researchers nowadays use sintered ceramic AZO targets. Such targets are mainly produced by hot pressing or conventional sintering, leading to the formation of microstructural defects and in some cases the appearance of undesired phases, namely the formation of a spinel phase (ZnAl$_2$O$_4$), which is a non-conductive phase [23]. In order to avoid these problems as well as to reduce the costs associated with the target production by more than 50%, an alternative approach is proposed in this work: the use of low-cost non-sintered nanostructured ceramic targets formed by nanoparticles obtained by a new patented process [24] based on the detonation of an emulsion containing both Zn and Al. This process has the advantage of having Al more uniformly distributed in the ZnO matrix when compared to the traditional mechanical grinding method without any post-preparation. This approach, besides reducing the production costs, does not require a sintering step, being thus possible to be extended to multi-dopant target compositions.

In the thin film silicon solar cells studied in this work, TCOs were used at three different positions: as a front contact, at the bottom (between the n-doped layer and the metal contact) [1, 2, 25] of the single junction [26] and as an intermediate reflector of the tandem solar cells [27]. These TCOs should be highly transparent in the range of the solar spectrum, highly conductive, non-toxic, have high carrier mobility and high stability against atomic hydrogen and an appropriate refractive index for coupling of light into the silicon absorber material and high scattering ability. These parameters should be optimized as a function of the type of silicon absorber material and high deposition temperature [19]

Regard the TCO deposition conditions, they were the same for both targets (AZO NST and AZO ST): power density $P = 12.30$ W cm$^{-2}$, distance between the target and substrate, $d = 15$ cm; deposition pressure, $p_d = 2.67 \times 10^{-3}$ mbar. Prior to the depositions, the chamber was evacuated to a base pressure of $10^{-6}$ mbar using a turbo-molecular pump. A shatter between the target and the substrate enabled the protection of the targets from cross contamination. The thickness of the films was measured using a surface profilometer (Ambios XP-Plus 200 Stylus). The crystal structure of the films was confirmed using an x-ray diffractometer (XRD) (PANalytical XPer PRO) in Bragg-Brentano geometry ($\theta/2\theta$ coupled). The surface roughness of the TCO was measured with an Asylum MFP3D atomic force microscope (AFM) in AC mode. The substrate surface and cross section were analysed on a ZEISS Auriga CrossBeam scanning electron microscope (SEM)/focused ion beam setup. To increase the surface sensitivity, SEM images were typically obtained at a low acceleration voltage of 2 kV. The AZO thin films were also deposited on Si wafers and analysed by energy-dispersive x-ray spectroscopy (EDS) integrated in the same Zeiss Auriga platform using an Oxford INCA x-act silicon drift detector and an Oxford INCA microanalysis software. Semi-quantitative analysis were performed using the K peaks of O, Al, Zn and C, being the quantitative optimization performed using the Si peak.

The analysis were performed at 15 keV, with an aperture size of 60$\mu$m, a magnification of 1000$\times$ and an acquisition time of 120 s for each sample. The surface chemical composition of the TCO was examined by x-ray photoelectron spectroscopy (XPS) using a XSAM800 (KRATOS) spectrometer operated in a fixed analyzer transmission mode with a pass energy of 20 eV, a non-monochromatized AlK$_x$ X-radiation ($h\nu = 1486.6$ eV) and a power of 120 W (10 mA $\times$ 12 kV). Samples
were analyzed under a typical pressure of $10^{-9}$ mbar. All sample transfers were made in air and the samples were analyzed at room temperature, at a take-off angle relative to the surface holder (TOA) of 45°. XPS Peak 4.1 (freeware) was used for peak fitting. As a reference for charge accumulation compensation, C 1s binding energy for the lower BE component was set to 285 eV. For quantitative analysis, sensitivity factors were taken as C 1s: 0.25; O 1s: 0.66; Zn 2p$_{3/2}$: 5.39.

The determination of the refractive index ($n$) was carried out using a phase modulated-type spectroscopic Ellipsometer (HORIBA-Jobin Yvon UVISEL) in a spectral range of 0.6–6.5 eV, and the measurements were analysed with DELTAPSI2 Windows™ based software.

The electrical resistivity ($\rho$), free carrier concentration ($N$) and mobility ($\mu$) were inferred by Hall effect using a van der Pauw geometry (Bio Rad HL5500) at a constant magnetic field of 0.5 T. A Kelvin probe system (KP Technology Ambient KP5000) was used to determine the work function ($\phi$) of the films with a gold sample (with $\phi = 5.1$ eV) as reference. The transmission spectra of the TCO films were recorded with a double-beam spectrophotometer (Shimadzu UV/VIS 3100 PC) from which the optical gap ($E_g$) was determined through the Tauc’s plot [25].

The tandem solar cells were fabricated on SnO$_2$:F-coated glass substrates with the following structure: SnO$_2$:F/p-in–pin/TCO or SnO$_2$:F/p-in–pin/Al. Individual doped and intrinsic silicon thin films were deposited by RF plasma-enhanced chemical vapour deposition (RF-PECVD) using a mixture of SiH$_4$ and H$_2$ for the intrinsic layer, while the addition of B(CH$_3$)$_3$ and PH$_3$ was used to obtain p- and n-type layers, respectively. The i$_1$ layer is 85–90 nm thick with 1.81 eV band gap, while the i$_2$ layer is about 410 nm thick with a 1.74 eV band gap. The importance of using absorber layers with different optical gaps, leads to a broader absorption spectrum, and decreased photo-degradation thus obtaining solar cells with higher efficiencies.

After the back contact deposition, the solar cells were annealed at 150°C for 1.5 h, which is the standard procedure for improving the semiconductor/metal interface when Al contacts are used. The $I$–$V$ curves were measured in a calibrated Spire Sun Simulator 240A at AM1.5 (100 mW cm$^{-2}$) light conditions. Spectral response measurements were performed in the wavelength range from 400 to 800 nm using a tungsten halogen lamp and a Cornerstone 260 Newport monochromator. Bias light was provided by two high-power OSRAM Opto Semiconductors light emitting diodes at wavelengths of 470 and 625 nm.

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) patterns (normalized to the film thickness) obtained for the films deposited on glass substrates. As shown in figure 1, both films are crystalline showing the ZnO$_{002}$ peak at 2$\theta$ $\sim$ 34.3° and revealing a hexagonal structure and orientation along the c-axis, perpendicular to the substrate.

The crystallite average size ($D$) was calculated from XRD patterns using the Scherrer formula [9]

$$D = 0.9\lambda/(\text{FWHM} \times \cos \theta),$$

where 0.9 is the shape factor, $\lambda$ is the wavelength ($\lambda = 1.5406$ Å), FWHM is the full-width at half-maximum of the peak located at 2$\theta$ and $\theta$ is the Bragg angle. For the AZO ST and the AZO NST the values obtained were 31.3 and 27.4 nm, respectively.

The TCO films’ surface and cross section obtained by SEM and the corresponding AFM 3D scan profile are depicted in figure 2.

As observed in the cross-sectional SEM images (figure 2) AZO films are very compact with a preferential growth perpendicular to the substrate, which also agrees with the XRD data (figure 1).

Figure 3 shows the EDS spectrum of AZO thin films deposited from AZO NST and AZO ST targets.

The quantitative analysis (table 1) shows that the sample made from the sintered target (AZO ST) contain less carbon than the AZO NST as expressed by the C/Zn ratios.

In figure 4 the surface chemical composition obtained by XPS of the deposited AZO thin films is presented.
Figure 3. EDS spectrum of AZO thin films deposited from NST and ST targets.

Table 1. EDS atomic composition for AZO NST and AZO ST.

| Element | AZO NST | Error | AZO ST | Error |
|---------|---------|-------|--------|-------|
| C       | 25.8    | ±0.52 | C      | 5.3   | ±0.47 |
| O       | 19.1    | ±0.19 | O      | 25.8  | ±0.21 |
| Al      | 0.2     | ±0.02 | Al     | 0.2   | ±0.02 |
| Si      | 47.4    | ±0.20 | Si     | 55.8  | ±0.21 |
| Zn      | 7.6     | ±0.08 | Zn     | 12.9  | ±0.09 |
| C/Zn    | 3.4     |       | C/Zn   | 0.4   |       |

XPS spectra of the samples display a sharp, narrow Zn 2p_3/2 peak at 1021.2 ± 0.1 and 1021.9 eV corresponding to Zn^{2+} in ZnO and Zn(OH)₂, respectively. The latter may also correspond to a Zn peroxide as suggested by other authors [28]. The O 1s XPS region was fitted with two peaks centred at 530.5 ± 0.1 and 532.2 ± 0.1 eV. The first one is assigned to oxygen bound to metal and the second one to oxygen bound to carbon.

The quantitative analysis (table 2) shows that the sample made from the sintered target (AZO ST) has less carbon than the AZO NST as expressed by the C/Zn ratios.

Given the considerably larger difference of C/Zn ratios between NST and ST films analysed by EDS when compared with the same difference analysed by XPS (see table 2), it may be suggested that the overall NST film (not only its surface) is richer in C than the ST film, given the deeper volume of analysis inherent to the EDS technique (up to 1 μm deep with the experimental conditions used here, against few nm in XPS).

The quantitative analysis reveals a Zn/O atomic ratios of 0.5 (AZO ST) and 0.6 (AZO NST), that should be equal to 1 if pure ZnO was present. A reason for this large deviation could be the existence of a thick contamination layer on the ZnO phase. Zn 2p photoelectrons should be more attenuated than O 1s ones (since kinetic energy of Zn 2p photoelectrons is lower than O 1s kinetic energy) and the XPS ratio should become lower than the real one. However, this hypothesis was discarded by also computing the ratio Zn/O1 from the Zn 3p area (the Zn 3p kinetic energy is larger than O 1s kinetic energy). Within the experimental error, the result was the same as the one obtained from the Zn 2p_3/2. Therefore, the XPS ratio corresponds to the real ratio. This result shows that carbon was mainly present as disperse domains rather than as a continuous film. The stoichiometry found is compatible with zinc hydroxide [29] or zinc peroxide for the AZO ST sample and a mixture of one of these compounds with ZnO for the AZO NST one. Figure 5 shows the smoothed second derivative symmetrical of the XPS Zn 3p region. In this representation, interesting features appear corresponding to loss bands in the high binding energies side of the Zn 3p peak. The ZnO bulk plasmon oscillation is reported in the literature as being in the range 18.1–18.8 eV [30]. At 21.8 eV a feature in the loss spectrum appears that is usually assigned to an interband transition from the O 2s states in the valence band to empty states in the conduction band [28].

Another feature, very intense in the AZO NST sample (where we identify the presence of a larger amount of dispersed carbon), appears around an energy loss of 13.1 ± 0.1 eV. It is not a loss peak but rather a photoelectron peak (Si 2p), which appears at a binding energy of 88.8 ± 13.1 = 101.9 eV.

Concerning the feature in the range 18.1–18.8 eV, it is a less prominent feature in the loss spectrum as it should be in the pure ZnO. However, its relative importance is larger in the AZO NST sample than in the AZO ST confirming that the AZO ST film is further away from pure ZnO than the AZO NST film.

Note that as C is a light element with multiple sources (besides the sample itself), the concentrations shown for this element may be affected of some error. Still, what is relevant to emphasize is that the trend to show considerably higher C content for films processed using non-sintered AZO targets is observed with multiple samples using both EDS and XPS.

Figure 6(a) shows the transmittance spectra of the TCOs measured in the wavelength range of 300–2500 nm. The average transmittance in the visible range (400–700 nm) of the NST and ST AZO samples was, therefore, calculated. The average transmittance was found to be 82 and 77%. In the near-infrared region we observed a decrease in the...
Figure 4. XPS spectra of AZO ST and AZO NST films, with detailed regions of all the layers: (a) O 1s and (b) Zn 2p$_{3/2}$ and (c) C 1s core-level spectra.

Figure 5. Smoothed second derivative symmetrical of the Zn 3p region corresponding to escaping electrons energy losses. Energy scale zero was chosen as the Zn 3p$_{3/2}$ binding energy at the peak maximum.

transmittance coming from the increase of reflectance due to the plasma resonance of electron gas in the conduction band [31]. Figure 6(b) shows the evolution of the refractive index ($n$) with the wavelength in the region 300–1200 nm. The refractive index values decreases with the increasing of the wavelength and is close to 2.0 in the visible region. The estimated optical band gaps of the deposited AZO films are presented in table 3. The direct allowed band gap can be estimated to be about $E_g \sim 3.6$ eV (typical of wide band gap semiconductors) for both films.

The electrical properties are summarized in table 3. The resistivity around $10^{-3}$ $\Omega$ cm and carrier concentration of the order of $10^{20}$ cm$^{-3}$ is similar on both samples, while mobility values are 14.0 and 12.8 cm$^2$ V$^{-1}$ s$^{-1}$ for AZO ST and AZO NST, respectively.

It may be noteworthy that the work functions of TCO thin films, such as ITO, are in the range of 4.3–5.1 eV, depending on the stoichiometry, organic contamination and oxidation type and that in the present study, the AZO films have values in the range of 4.7–5.0 eV.

In order to investigate the influence of the back contact structure on the thin film solar cell performances, we have replaced a common Al back contact by a TCO prepared by sputtering from AZO ST or AZO NST targets. The solar cells used in this study were from the same batch and cut from the same solar panel, fabricated without back contact. By doing so, we guarantee that no possible changes in the performance of the solar cell are influencing the results.
Table 3. Electro-optical properties of the TCOs. $d$ is the thickness, $\rho$ is the bulk resistivity, $\mu$ is the Hall mobility, $N$ is the carrier concentration, $AVT$ is the visible average transmittance, $n$ is the refractive index and $E_g$ is the band gap.

| Sample TCO | $d$ (nm) | $\rho$ ($\Omega \cdot cm$) | $\mu$ ($cm^2 V^{-1} s^{-1}$) | $N$ ($cm^{-3}$) | $AVT$ (%) | $n$ (400–700 nm) | $E_g$ (eV) | Work function $\phi$ (eV) |
|------------|---------|-----------------|-----------------|---------------|--------|-----------------|--------|------------------|
| AZO ST     | 400     | $9.9 \times 10^{-4}$ | 14.0             | $4.5 \times 10^{20}$ | 77     | 1.9             | 3.6    | 4.8              |
| AZO NST    | 400     | $1.0 \times 10^{-5}$ | 12.8             | $4.8 \times 10^{20}$ | 82     | 1.9             | 3.6    | 5.0              |

Figure 6. Optical transmittance (a) and refractive index spectra (b) of AZO films with an average thickness of 400 nm.

Figure 7. (a) Cross-sectional SEM micrographs of the solar cell without metal contact deposited on glass; and (b) proposed schematic view of the thin film solar cell structure with AZO NST contact.

For the electrical characterization of the fabricated cells, an external Al metal contact is placed in contact with the TCO. This external Al contact comes from the measurement setup and has the same area as the cell ($A = 0.039 \text{cm}^2$). The cross-sectional view of the a-Si:H tandem solar without the back metal contact is shown in figure 7(a), while in figure 7(b) we show a schematic view of the silicon thin film solar cell structure with a disperse carbon interlayer. From figure 7(a) we observe that the structure is highly compact and that the thin films are following the highly textured SnO$_2$:F front contact.

Figure 8 shows the $I$–$V$ characteristics of the solar cells with both TCO thin films and external Al as back contact. These experiments were performed in more than ten samples where the films were always grown under the same process conditions. The photovoltaic parameters obtained from figure 8 are listed in table 4.

The solar cell characteristics obtained from the $I$–$V$ measurements under AM1.5 illumination (figure 8) of the solar cells with AZO ST as the intermediate of the back contact structure before the external metal contact are lower than the one of the solar cell using only Al as back contact. This is mainly due to an FF deterioration by about 16% that can be attributed to losses associated mainly to contact series resistance, once the TCO resistivity is more than two orders of magnitude larger than that of Al.
The role of the carbon layer in enhancing the overall build-in electric field. 

Enhancement of solar cell efficiency due to the presence of a disperse carbon interlayer leads to an enhancement in the carriers generated, in line with our above assumptions concerning the role of the thin carbon interlayer role. Indeed, an increase of the short-circuit current ($J_{SC}$) is observed from 9.8 to 10.8 mA cm$^{-2}$ (10% enhancement).

The use of equivalent circuits is a common way to describe the electrical behaviour of electronic devices [42–44]. A proposed equivalent electric circuit of the tandem solar cell when a disperse carbon interlayer is incorporated at the solar cell–AZO interface is presented in figure 11.

$R_{sh1}$ and $R_{sh2}$ are the shunt resistances associated, respectively, to the front and back cells; $R_{tj}$ and $R_{o2}$ are the series resistances associated to each sub-cell from which external contacts are taken; $R_{b}$ is the series resistance of the tunnel junction between front and back cells; and $R_{carbon}$ is the resistance of the carbon interlayer which contributes to enhance the light scattering both in the near field (for light concentration) and far field (for path length enhancement). From this model we can extract that the $V_{oc}$ is higher when the AZO NST interlayer is used as shown in table 4:

$V_{OC} = V_{O1} + V_{O2} + \Phi_C$, \hspace{1cm} (2)

where $V_{O1}$ and $V_{O2}$ are the open-circuit voltages of cells 1 and 2, respectively, and $\Phi_C$ is the potential barrier built-up due to the disperse carbon interlayer.

Table 4. Comparison of solar cell external parameters as a function of the back contact. $R_s$ is the series resistance, $V_{oc}$ is the open-circuit voltage, $J_{sc}$ is the short-circuit current, FF is the filling factor and $\eta$ is the efficiency.

| Back contact | $R_s$ (Ω) | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | $\eta$ (%) |
|--------------|-----------|--------------|-------------------------|--------|-----------|
| AZO ST/Al    | 69.6      | 1.37         | 9.6                     | 48     | 6.3       |
| AZO NST/Al   | 40.2      | 1.62         | 10.8                    | 63     | 11.0      |
| Al           | 56.8      | 1.55         | 9.8                     | 57     | 8.7       |

In order to confirm the better collection efficiency of the photo-carriers in the presence of the AZO NST back contact, spectral response measurements were carried out. Figure 10 presents the external quantum efficiency (EQE) of the tandem silicon solar cells, deposited with metal and AZO NST/back metal contact. Compared to the standard cell with Al back contact, the solar cell prepared with AZO NST exhibits enhanced EQE in the entire wavelength range, indicating an enhancement in the carriers generated, in line with our above assumptions concerning the role of the thin carbon interlayer role. Indeed, an increase of the short-circuit current ($J_{SC}$) is observed from 9.8 to 10.8 mA cm$^{-2}$ (10% enhancement).

On the other hand, solar cells with AZO NST as the intermediate layer of the back contact structure have higher efficiency than the cells with AI and AZO ST/Al back contacts, mainly owing to an improvement in the series resistance, $V_{oc}$, FF and current density. The $V_{oc}$ enhancement (from 1.55 to 1.62 V) can be associated with the increase of built-in electric field [32–34] due to the presence of the very thin highly transparent carbon associated to the AZO NST as revealed by the XPS data. Besides improving the built-in potential of the solar cell, the very thin carbon interlayer seems to lead to an enhancement on current collection. This last effect can be attributed to back reflected effects promoted by the disperse carbon interlayer due to highly different refractive index of the carbon (≈2.45), n-type silicon (≈4.63) [35] and AZO (≈1.90) [36] layers that also lead to a lens-like effect, as it has been proposed by several authors [37–39]. All these contributions lead to an overall enhancement of solar cell efficiency [40, 41]. In figure 9 we show a sketch of the energy band diagram of the tandem solar cell without and with a disperse carbon interlayer, where the role of the carbon layer in enhancing the overall build-in potential is highlighted.
Figure 9. The energy band diagram of a typical tandem solar cell (a) and a tandem cell with a carbon interlayer (b) under illumination at the short-circuit condition. The symbols CB and VB represent the conduction and valence bands, respectively, and $E_{F0}$, the thermodynamic equilibrium Fermi level. The light enters through the $P$ layer, which is in contact with the TCO.

Figure 10. EQE of the set of solar cells showed in figure 7 where an enhancement of the quantum efficiency for the solar cell with AZO NST/back metal contact is noticed.

4. Conclusions

In this paper it was demonstrated that AZO layers can be deposited by RF magnetron sputtering at room temperature as a back contact on tandem solar cells, from sintered and non-sintered targets. The electro-optical properties of the TCOs are similar: n-type conductivity, resistivity in the range of $1 \times 10^{-3} \Omega \text{cm}$ and average transmittance in the visible range $\sim 80\%$. XRD analysis indicated that AZO NST and ST films were oriented along the c-axis, perpendicular to the substrate surface.

Figure 11. Equivalent electric circuit of the solar cell structure without and with a carbon interlayer modelled in PSpice [45].
We have demonstrated that the use of a structured TCO back contact layer on standard glass/SnO$_2$:F/pin–pin/n TCO/metal amorphous silicon solar cell can improve the overall device performance, when a disperse interlayer of carbon is formed. This carbon disperse interlayer is related to the use of non-sintered AZO targets to fabricate TCOs by RF magnetron sputtering. Carbon was incorporated into the NST AZO film as revealed by x-ray photoelectron spectroscopy and energy-dispersive x-ray analysis and sputtered during the growth process of the TCO. Indeed, the solar cells with AZO NST as back contact have enhanced electrical performances under AM 1.5 conditions, namely current density ($J_{SC} = 11\ mA\ cm^{-2}$), short-circuit voltage ($V_{OC} = 1.6\ V$), fill factor (FF = 63%) and initial efficiency of 11%. Compared to the standard solar cell this improvement leads to a 10% increase in $J_{SC}$ and 20% in efficiency of the solar cell and also in the EQE.

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