

Spray-deposited Al-doped ZnO transparent contacts for CdTe solar cells

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ABSTRACT

Transparent and conductive Al-doped ZnO (AZO) thin films were deposited by ultrasonic spray pyrolysis of alcoholic solutions in ambient atmosphere without any post-growth treatment. Spraying parameters, composition and acidity of the sprayed solution, and doping level were systematically investigated in order to obtain AZO films suitable for applications in solar cells. It was confirmed that the amount of aluminum chloride as the dopant and acetic acid as the stabilizing agent are decisive for film morphology and opto-electrical properties. Films of 1.1 μm in thickness deposited under optimized conditions on borosilicate substrates exhibited resistivity of $5 \times 10^{-3} \Omega \text{ cm}$ and an average transmittance of 82% in the wavelength range 400–900 nm. A resistivity of $3 \times 10^{-3} \Omega \text{ cm}$, one of the lowest values reported in literature for sprayed AZO, was obtained for a film thickness of 3 μm maintaining a high optical transmittance of $> 74\%$. The latter film was applied as a transparent electrical contact in a CdTe solar cell and an efficiency of 12.1% without antireflection coating was achieved. The average efficiency value of $> 11\%$ measured for 22 fabricated solar cells demonstrates the feasibility of using spray-pyrolysis technique for the deposition of large area AZO contacts for solar cell applications.

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1. Introduction

Doped zinc oxide is a popular transparent conducting oxide (TCO) widely used in photovoltaic, window and display technologies [1,2]. Although the conductivity and chemical stability of ZnO are not as good as for the indium tin oxide (ITO) standard [3], it exhibits a relatively wide intrinsic direct band gap of $\sim 3.3 \text{ eV}$ [2] ensuring high visible transparency, can be textured during or after thin film deposition, which is critical for the efficient light trapping in thin film solar cells [4], and finally, may offer cost reduction as compared to In-based TCOs. Intrinsic ZnO (i-ZnO) is highly resistive because native point defects such as Zn-on-O antisite (Zn_O), the Zn interstitial (Zn_i) and the O vacancy (V_O) cannot deliver sufficiently high donor concentrations [2]. Substitutional doping of ZnO with Al, In, Ga, B or F does not only lead to high carrier concentrations of 10^{20} – 10^{21} cm^{-3} but also improves the film corrosion resistance [5,6]. Al-doped ZnO (AZO) is one of the most conducting representatives, which is typically deposited by magnetron sputtering at laboratory and industrial scale, with resistivity as low as 1 – $2 \times 10^{-4} \Omega \text{ cm}$ [7,8]. Sputtered AZO/i-ZnO bilayer is commonly employed as the front transparent contact in high efficiency $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin film solar cells [9], although recent studies demonstrate that similar

bilayer structure can also be successfully applied to CdTe thin film solar cells with efficiency of up to 14.0% [10] or 15.6% [11].

The true low-cost potential of ZnO-based TCOs can be fully realized when combined with a low-cost and high throughput deposition method. Chemical spray pyrolysis is a simple non-vacuum technique that can be applied at ambient pressure and can be easily scaled up for large area deposition. There is a considerable amount of literature data on spray deposited ZnO thin films over the last 40 years, e.g. [12–18] and many others. In a typical deposition process, salts of zinc and appropriate dopant are dissolved in water or organic solvents such as methanol, ethanol or isopropyl alcohol, and the solution is sprayed with an inert carrier gas onto a substrate heated to 300–600 °C. A small amount of acetic acid added to the solution was found to be beneficial for the film properties because it increases the solubility of Zn salt, suppresses hydrolysis reactions causing insulating hydroxides $\text{Zn}(\text{OH})_2$, and promotes the formation of zinc acetate complexes [19]. The lowest resistivity was obtained for In-doped ZnO by Major et al. [20], when they reported the value of 8 – $9 \times 10^{-4} \Omega \text{ cm}$ and an average visible transmittance of 85%, the record that still stands today. For AZO, the lowest value of $3 \times 10^{-3} \Omega \text{ cm}$ was reported by Olvera et al. [17], although the same group reported later $1.0 \times 10^{-2} \Omega \text{ cm}$ with a transmittance of about 80% [21]. Annealing in hydrogen [15] or in vacuum [22] helps to improve electrical and optical properties, resulting in resistivity on the order of $10^{-3} \Omega \text{ cm}$. Despite the numerous investigations of sprayed AZO films, only a few groups did actually implement them as transparent contacts in thin film

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solar cells, e.g. [14,23,24], which could be partially accounted to non-optimum film properties or the need for the high-temperature deposition or post-annealing, both being energy- and cost-intensive processes when it comes to possible industrial implementation.

The purpose of this study is to optimize the spray deposition of AZO films without any post-annealing treatment and to apply them as transparent contacts in CdTe solar cells. Spraying parameters, composition and acidity of the sprayed solution, and doping level are systematically investigated in order to obtain AZO films with optical transparency of $> 80\%$ in the 400–900 nm wavelength range corresponding to the spectral response of the CdTe solar cell, maintaining a smooth morphology and an acceptable sheet resistance of below $10 \Omega/\square$, as it is recommended for current solar cell technologies [25]. The influence of deposition parameters on morphology, crystallinity, as well as optical and electrical properties of the AZO thin films is discussed. The solar cells' results obtained with the sprayed AZO contact are finally compared with the AZO reference prepared by magnetron sputtering.

2. Experimental

The AZO thin films were prepared from a 0.1 M solution of zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ (99.99%, Aldrich) in methanol and acetic acid (glacial, Carbo Erba). The proportion of acetic acid was varied between 0 ml and 6 ml per 100 ml of the final solution. Aluminum chloride AlCl_3 (99.999%, Aldrich) was added as the dopant source in variable concentrations from 0 to 0.014 M corresponding to the $\text{Al}/(\text{Al}+\text{Zn})$ ratio from 0 to 0.14.

The layers were deposited on 1 mm thick borosilicate glass substrates of $5 \times 5 \text{ cm}^2$ using an ultrasonic spray pyrolysis (USP) setup. The homogenized solution was sonicated in a 1.7 MHz nebulizer from Solaronix SA. The nitrogen carrier gas flow was kept at a rate of 12 l/min corresponding to an average solution spray rate of 4 ml/min. The corresponding layer growth rate was 50–100 nm/min depending on the solution chemistry, and the deposition duration was 20 min unless specified separately. The droplets were deposited on the substrate through a funnel moving on x - y directions to achieve a good homogeneity. The substrate was heated on a hot plate to 470°C as measured with a thermocouple in the hot plate below the substrate. The spraying was performed under ambient atmosphere without any post-annealing.

The transmittance of the thin films was measured with a Shimadzu UV-3600 spectrophotometer. The presented transmission values always include the glass substrate absorption, i.e. air was taken as reference, in order to obtain real transmittance of the film/glass stack in the 400–900 nm range corresponding to the optimum spectral response of the CdTe solar cell. The film thickness was measured with a profilometer and the sheet resistance with the four-probe method. Carrier concentration

and mobility were estimated from Hall effect measurements at room temperature, which were performed on HMS3000 setup using golden spring-loaded contacts. Scanning electron microscope (SEM) pictures and energy-dispersive X-ray (EDX) spectra were taken with a Jeol JSM-5400 microscope. Microcrystalline structure of the layers was accessed by X-ray diffraction (XRD) on a Siemens 5000 diffractometer with $\text{CuK}\alpha$ radiation. Mean size of the crystalline domains, which may be smaller or equal to the grain size, was calculated from XRD patterns after stripping $\text{CuK}\alpha_2$ lines, using Debye–Scherrer's formula $D=0.9\lambda/\Delta\theta \cos \theta$, where D is the average crystalline domain size, λ is the $\text{CuK}\alpha_1$ wavelength of 0.154056 nm, $\Delta\theta$ is the observed angular full width at half maximum (FWHM) of the (102) reflection in radians, and θ is the diffraction angle.

Glass substrates with optimized AZO layers served as substrates for CdTe solar cells in the “superstrate” configuration [11]. An i-ZnO layer of 50 nm was deposited by radio-frequency (RF) magnetron sputtering on top of the sprayed AZO. CdS and CdTe layers were subsequently grown by thermal evaporation of the compounds. For re-crystallization treatment the layer stack was coated with CdCl_2 and annealed in air. The solar cells were finished with etching in bromine–methanol solution and the deposition of Cu/Au as electrical back contact. No antireflection coating was applied. The details of the solar cell processing have been published elsewhere [11]. The solar cells were characterized by quantum efficiency (QE) and current–voltage (I - V) measurements under standard test conditions (AM 1.5G, 1000 W m^{-2} , 25°C). The reference AZO layer was deposited by radio-frequency magnetron sputtering [26], and the CdTe cell was processed in the same run as described above.

3. Results and discussion

3.1. Effect of solution acidity

Acetic acid, initially added to enhance the solubility of zinc acetate, appeared to have a strong influence on the layer morphology as shown on the SEM images (Fig. 1). Increasing quantities of acetic acid were added to chemical solutions containing nominally 0.03 $\text{Al}/(\text{Al}+\text{Zn})$. Increase of the acetic acid content leads to bigger grain size on SEM images and the formation of faceted AZO layer. This observation is supported by XRD data (not shown), where the average crystallite size increases from 50 nm (0 ml acetic acid) to 110 nm (3 ml acetic acid) and then remains constant. For high acetic acid contents of ≥ 6 ml, the surface faceting results in well-defined grain boundaries and microscopic voids between the grains.

The evolution of layer morphology is accompanied by significant changes in the film resistivity, transparency and thickness, presented in Figs. 2 and 3. The resistivity initially drops between 0 and 2 ml of acetic acid, which can be correlated with the increase of grain size. The lowest resistivity is obtained at the

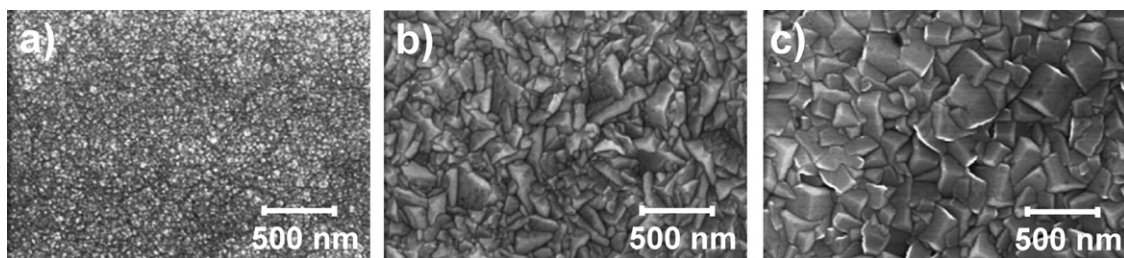


Fig. 1. Top-view SEM images of AZO layers sprayed from solutions containing (a) 0 ml, (b) 3 ml and (c) 6 ml of acetic acid per 100 ml of final solution. Film thickness is 1700 nm (a), 1300 nm (b) and 1100 nm (c) after 20 min deposition. $\text{Al}/(\text{Al}+\text{Zn})$ ratio in the solution is 0.03.

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