



Improved environmental stability of highly conductive nominally undoped ZnO layers suitable for n-type windows in thin film solar cells



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ABSTRACT

Highly conductive nominally undoped ZnO (b-ZnO), obtained by means of an additional plasma near the substrate during sputter deposition, represent an attractive alternative for ZnO:Al (AZO) commonly employed in transparent windows of thin film solar cells. b-ZnO layers exhibit more than twice higher charge carrier mobility in comparison to AZO layers of the same resistivity ($1 \cdot 10^{-3} \Omega \text{ cm}$). In consequence, a better transparency in near infrared region and an enhanced short circuit current can be achieved for low band gap thin film solar cells. Replacement of AZO for b-ZnO thus enhances their energy output.

In order to allow assessment of suitability of these b-ZnO films for deployment in photovoltaic industry, we examine their stability in various environments, and show pathways to improve it. We demonstrate that the b-ZnO films can exhibit comparable stability to ZnO:Al films in both ambient and heated air over the period of 24 months. However, the examined b-ZnO films degrade faster in accelerated open damp heat (DH) conditions, which we attribute to the lower compactness of columnar microstructure. In order to circumvent this limitation, we introduce a novel multilayered b-ZnO film with an improved environmental stability, as verified by the enhanced optoelectrical performance of DH-treated Cu(InGa)(SSe)₂ solar cells.

1. Introduction

1.1. ZnO layers with high near infrared transparency

Thin film solar cells have a substantially lower carbon footprint compared to the standard wafer technologies [1]. These solar cells rely on the upper-most transparent conductive oxide (TCO) layer which forms an n-type window. One way to improve the energy output of these solar cells is to increase the transparency of this window without compromising its conductivity.

TCO films based on ZnO are affordable alternatives to costly In₂O₃:Sn (ITO). The most common variation is Al-doped ZnO (AZO) that is highly conductive and highly transparent in the visible (VIS) spectral region [2,3]. However, AZO has a major drawback in the pronounced light absorption in the near infrared (NIR) spectral region, owing to the significant free carrier absorption caused by high concentration of free carriers. This is detrimental in those applications where NIR transparency is of importance. For instance, the use of AZO contact layer lowers the amount of light that can be used for effective

energy conversion in thin film solar cells based on Cu(In,Ga)(SSe)₂ and Cu₂ZnSn(SSe)₄ absorbers featuring low band gap, $E_g \leq 1.2 \text{ eV}$.

An alternative to AZO with comparably high conductivity but a better NIR transparency is nominally undoped ZnO [2,4–6] that can exhibit a significantly higher NIR transparency. This is related to a lower density of more mobile charge carriers which in the latter case originate in the variations in zinc/oxygen stoichiometry, or in the background doping by hydrogen [2,4,5].

Moreover, as in the case of AZO films, the highly conductive nominally undoped ZnO can be deposited by planar magnetron sputtering [4–7], which is a popular industrially-used technique that allows large area coating at low deposition temperatures (below 80 °C) required for solar cell stack fabrication.

The nominally undoped ZnO films with resistivities below $1 \cdot 10^{-3} \Omega \text{ cm}$ were recently prepared at ambient temperature by application of an additional plasma ignited by means of low-power RF substrate biasing during nonreactive sputtering from a ceramic ZnO target [6]. These layers, labelled as b-ZnO films (for biased ZnO), exhibit about 2.5 times lower charge carrier density in comparison to

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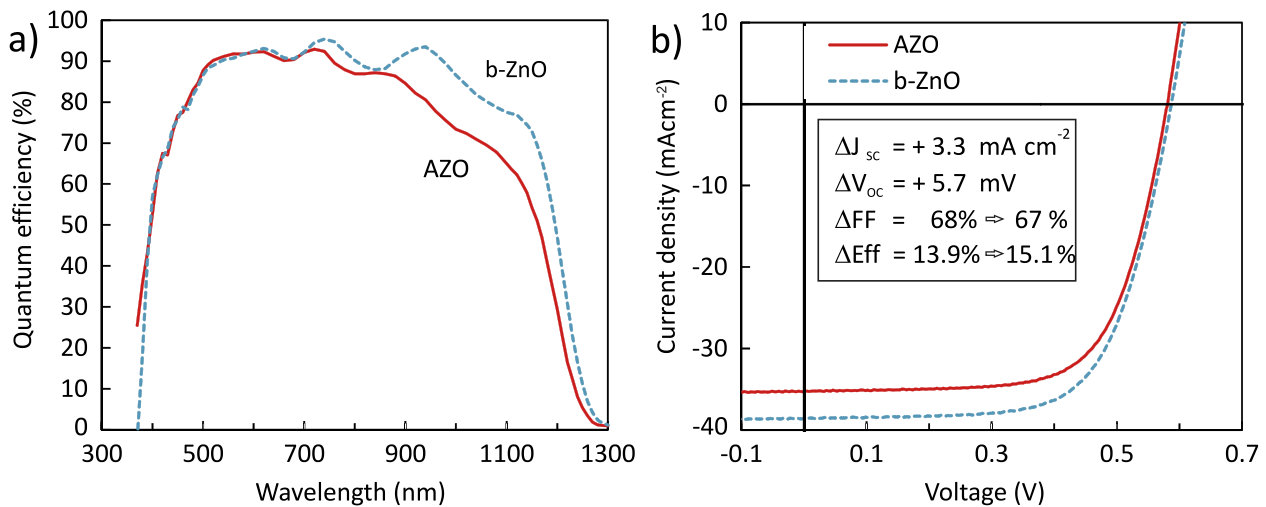


Fig. 1. External quantum efficiency spectra (a) and IV characteristics under irradiation (b) of the two solar cells with the TCO window formed by either an AZO layer (full line), or a b-ZnO layer (dashed line). These cells are prepared atop an identical Cu(In,Ga)(SSe₂) absorber. The enumerated increase or decrease of the principal solar cell characteristics due to the replacement of the AZO window for the b-ZnO window is summarized in the inset of (b).

the AZO films of identical resistivity. In consequence, their transparency in the NIR spectral region is significantly improved. A replacement of an AZO film by a b-ZnO film as the n-type window of low band gap chalcopyrite and kesterites thin film solar cells thus enhances their short circuit current [6].

The above claim is illustrated in Fig. 1 on the example of the spectral response and optoelectrical characteristics of the two solar cells fabricated from an identical Cu(In,Ga)(SSe₂) (CIGS) absorber ($E_g=1 \text{ eV}$). It can be observed that the external quantum efficiency (EQE) spectra of the solar cell finished with a b-ZnO window shows a substantially higher amplitude in NIR region (i.e., for $\lambda > 750 \text{ nm}$), if compared to its counterpart with an AZO window (Fig. 1a). This results in the rise of the respective short circuit current density, J_{sc} , by $+3.3 \text{ mA cm}^{-2}$, as depicted in Fig. 1b. It is to be noted that the higher J_{sc} is also translated into an improved power conversion efficiency, Eff, from 13.9% to 15.1% (+9%), despite a slightly lowered fill factor, FF (−1%). The open circuit voltage, V_{oc} , is not significantly affected (< +1%).

1.2. Stability issue of ZnO-based layers

An important prerequisite of TCO for its application in thin film solar cell modules is the inherent damp heat (DH) stability. It is known that the sputtered AZO used in commercial CIGS thin film modules protected by encapsulation (with lamination foil, edge sealing and cover glass) does not limit the DH stability of those modules. It is thus of crucial importance that the new TCO material does also not compromise module stability, in order to avoid higher requirements for the encapsulation.

The commonly observed conductivity drop of the ZnO-based layers exposed to DH conditions can be explained on one hand by the inherent instability of ZnO material in the presence of water that is either the source of the degradation process (e.g., hydrolysis reactions) or, at least, a catalyst of the physical or chemical processes [8,9]. On the other hand, the columnar microstructure exhibited by all the polycrystalline ZnO films grown from vapor phase [10,11] features columnar boundaries that represent possible pathways for penetration of water and other reactive agents deep into the film [9,12,13].

It has been also reported that the water in-diffusion within ZnO films is specifically pronounced if these layers are less compact, for instance, as a consequence of their growths at elevated Ar pressures [12] or atop rough substrates (e.g., CIGS absorbers), in which case the microstructure exhibits extended grain boundaries [13]. In fact, the

water vapors can get adsorbed at the exposed film surface and then diffuse within the film through accessible columnar and grain boundaries [8,9,13]. The adsorbed water molecules and their products (e.g., formed hydroxides) are believed to act as electron traps, resulting in the accumulation of trapped electrons at the grain boundaries. This raises the potential barrier that the free electrons have to overcome [14], and thus increases their cross-boundary scattering.

The studies cited above are with no exception related to the environmental stability of extrinsically doped ZnO (mostly AZO), while the stability of the nominally undoped ZnO is rather unexplored; It is commonly reported that nominally undoped ZnO films are prone to degrade faster than AZO films even at relatively low (e.g., ambient) temperatures [2,3,7], specifically if they are prepared by post-deposition treatment (e.g., by H plasma exposure [2] or UV illumination [15]).

In contrary to these reports, recent work indicated that the b-ZnO films made conductive due to RF substrate biasing can possess an excellent stability in ambient air, and only a slightly lower high temperature stability than AZO films [6]. However, it is the resistance of b-ZnO films to harsh conditions (e.g., in damp heat) that can be decisive for their application as the n-type windows in photovoltaic industry.

1.3. Scope of this work

The motivation of the current work is to seek the answers for the following three questions;

1. How the stability of b-ZnO compares to that of AZO?
2. Is the degradation mechanism of b-ZnO films in harsh environments comparable to that of doped ZnO films?
3. What are the means of improving b-ZnO films' stability?

In particular, we investigate the stability of the b-ZnO films tested in various environments. These include ambient air, heated air at 105 °C, as well as the accelerated ageing in DH conditions using 95 °C and 85% humidity. For rigorous assessment of the damp heat stability, both films and completed solar cell stacks are tested in DH with no encapsulation (open DH). Afterwards, we attempt to relate the obtained findings to the crystallographic characteristics of the films under investigation, and suggest pathways for improvements. Finally, we demonstrate a multilayered b-ZnO coating with enhanced DH resistance.

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