



Direct comparison of atomic layer deposition and sputtering of $\text{In}_2\text{O}_3:\text{H}$ used as transparent conductive oxide layer in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin film solar cells

Jan Keller^{a,*}, Asim Aijaz^a, Fredrik Gustavsson^a, Tomas Kubart^a, Lars Stolt^{a,b}, Marika Edoff^a, Tobias Törndahl^a

^a Ångström Solar Center, Division of Solid State Electronics, Uppsala University, P. O. Box 534, SE-75121 Uppsala, Sweden

^b Solibro Research AB, Vallvägen 5, 75151 Uppsala, Sweden

ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form

15 June 2016

Accepted 11 July 2016

Keywords:

CIGSe

In_2O_3

IOH

TCO

Window layer

ABSTRACT

In this study thin films of hydrogenated In_2O_3 (IOH) were fabricated by physical vapor deposition (PVD) with and without a post-annealing step, and by atomic layer deposition (ALD). The electro-optical properties on glass as well as the performance as a transparent conductive oxide (TCO) layer in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGSe)-based solar cells are compared and related to a $\text{ZnO}:\text{Al}$ (AZO) baseline TCO. Corresponding TCO film thicknesses were adjusted to a resulting sheet resistance of about $R_{sh} = 20 \Omega/\text{sq}$ for all samples. Structural investigations were conducted by X-ray diffraction (XRD) and transmission electron microscopy (TEM), while Hall and optical absorption measurements were performed to analyze the electrical and optical quality of the window layers. It is shown that the fully crystallized IOH layers processed by ALD and PVD show similar microstructural and electro-optical properties, which are superior to the AZO baseline. The finalized solar cells were characterized by current-voltage and reflectance-corrected quantum efficiency measurements. While there is no significant gain in short circuit current density (J_{sc}) for as-deposited PVD In_2O_3 layers, the application of crystalline In_2O_3 TCOs leads to an improvement of more than $2 \text{ mA}/\text{cm}^2$ due to an increase in “optical” band gap energy and less free charge carrier absorption (FCA). The open circuit voltage (V_{oc}) of the best cells is 10–15 mV higher as compared to the AZO reference, independent of the crystallinity and process of the In_2O_3 films. The results indicate that the gain in V_{oc} is due to inherent material properties of the IOH films and does not originate from less sputter damage or an affected i-ZnO/TCO interface. Device simulations show that the higher electron affinity χ of the IOH can explain an increased V_{oc} if the Fermi level (E_F) is pinned at the CIGSe/CdS interface and why it might not be possible to see the gain when alternative buffer layers are applied.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the past decade an increasing interest in hydrogen doped In_2O_3 as a TCO material has emerged. Its high optical band gap energy E_g^{opt} , potentially high mobility (μ) and low resistivity (ρ) allow for negligible parasitic absorption in a broad wavelength region ($\lambda = 350\text{--}1300 \text{ nm}$) at low sheet resistances [1,2]. An extensive material characterization was done by Koida et al. on sputtered IOH layers [1]. The observed high charge carrier densities are achieved by the addition of H_2O during the sputtering process. It is supposed that hydrogen acts as an effective donor in

In_2O_3 by occupying interstitial (H_i^+) or substitutional (H_o^+) sites in the lattice structure [3]. While very small-grained IOH layers were observed for a direct deposition at elevated temperatures of $T \approx 200 \text{ }^\circ\text{C}$ [1], post-annealing of films processed at room temperature resulted in electro-optical properties that are even superior to sputtered tin doped In_2O_3 (ITO) films [1,4].

However, many factors have to be considered when optimizing the sputtering process. The properties of the as-deposited In_2O_3 films depend strongly on the hydrogen and oxygen content during growth. It was shown that too low oxygen flows result in a lower mobility, higher resistivity and higher optical band gap energy [5]. Additionally, the O_2 partial pressure seems to influence which type of elements are accumulated in void-like structures in the In_2O_3 films [5]. For H_2O partial pressures of $5 \times 10^{-5} \text{ Pa} < p_{\text{H}_2\text{O}} < 5 \times 10^{-3} \text{ Pa}$, a completely amorphous grown film is observed, while an undesired crystalline fraction is reported for higher or

* Correspondence to: Uppsala University, Department of Engineering Sciences, Solid State Electronics, Box 534, SE-751 21 Uppsala, Sweden.

E-mail address: Jan.Keller@angstrom.uu.se (J. Keller).

lower $p_{\text{H}_2\text{O}}$ [1]. It was shown that a subsequent solid-phase crystallization of amorphous In_2O_3 at elevated temperatures is required in order to achieve a high mobility ($\mu > 100 \text{ cm}^2/\text{Vs}$) [1,6–10]. Here, the increase in mobility from amorphous to crystalline In_2O_3 films is not attributed to less grain boundary scattering. While in as grown, amorphous layers μ is supposed to be limited by scattering from doubly charged oxygen vacancies (V_O^{2+}), it is mainly determined by phonon scattering in annealed, crystalline films [3,7]. The annealing time t depends significantly on the temperature, which should be $> 150^\circ\text{C}$ to ensure a complete crystallization for $t < 2 \text{ h}$ [3]. Furthermore, the ambient condition during annealing affects the properties of the IOH films. A solid-phase crystallization was reported to appear only in vacuum [1,6,7], only in air [10] and in both constellations [9]. It was shown that this behavior depends mainly on the total pressure used during sputtering [9].

In_2O_3 exhibits a high optical band gap energy in the range of $3.4 \text{ eV} < E_g^{\text{opt}} < 3.8 \text{ eV}$ (higher than the fundamental band gap of $E_g \approx 3.0 \text{ eV}$), which is attributed to forbidden optical transitions from the valance band maximum to the conduction band minimum within the dipole approximation [11–14]. A shift to higher “optical” band gap energies for larger degrees of crystallinity after annealing is observed [1,6,15]. This dependency on crystallinity might originate from a higher amount of sub-gap defect states for less ordered films.

Besides sputtering, high quality IOH films have been processed by atomic layer deposition as well. Libera et al. developed an ALD process that uses simultaneous supply of O_2 and H_2O during an ALD precursor pulse [16]. By applying this technique, mobilities of $\mu \approx 110 \text{ cm}^2/\text{Vs}$ were achieved for crystallized IOH films at deposition temperatures $T > 130^\circ\text{C}$ [2,16]. It was shown that the electrical properties of films prepared by this method are mainly isotropic [2]. A different approach was followed by Macco et al., where an amorphous layer was first deposited at low temperature ($T = 100^\circ\text{C}$) followed by a post-annealing in vacuum at elevated temperatures of $T \approx 200^\circ\text{C}$. In this way similar mobilities as compared to the highest values achieved by the 2-step sputter process were reported ($\mu \approx 140 \text{ cm}^2/\text{Vs}$) [15].

There are several attempts to utilize the IOH films as a TCO layer in solar cell devices. An efficiency increase for Si-based solar cells using an IOH TCO was reported already in 2008 [6]. Recently, the its potential in CIGSe solar cells was evaluated as well. The published results on cells that use the standard CdS buffer layer are diverse so far. Only in case of ALD grown In_2O_3 TCOs a significant gain in J_{sc} by a reduced parasitic absorption compared to the commonly used AZO is observed [2]. On the other hand the TCO exchange (from AZO to IOH) led to an increase in V_{oc} of about 10–20 mV for the best cells in several independent studies [2,17,18]. It was suggested that this gain originates from the higher work function of In_2O_3 (compared to AZO) and/or from less sputter damage of the used intrinsic ZnO layer (increasing its conductivity), that in both cases should lead to a more favorable band bending (less interface recombination) [18]. Interestingly, no gain in V_{oc} was detected when applying alternative buffer layers ($\text{Zn}(\text{O}, \text{S})$ [10] and $\text{Zn}, \text{Sn}(\text{O})$ [2,19]), which indicates that the interfaces to the buffer layer might play role as well.

In this study IOH layers were processed by sputtering and ALD on glass and included as a window layer in CIGSe solar cells. A direct comparison of the resulting device characteristics allows for separation between effects of the preparation method (e.g. sputter damage) and inherent material properties of In_2O_3 . The absorber material was cut out from the same region of a large area CIGSe substrate with uniform composition and the CdS buffer layer was grown in the same chemical bath for all solar cell samples. In this way a direct comparison of the different TCOs is ensured, which

helps to further understand the changes in device characteristics when going from an AZO to an IOH TCO layer.

2. Materials and methods

2.1. Sample fabrication

The CIGSe solar cells investigated in this study were manufactured as a stack of soda lime glass (SLG)/Mo/CIGSe/CdS/TCO (IOH or ZnO:Al). Here, the CIGSe absorber was deposited by an inline co-evaporation process at Solibro Research AB, exhibiting an overall composition of $[\text{Ga}]/([\text{Ga}] + [\text{In}]) = 0.43$ and $[\text{Cu}]/([\text{Ga}] + [\text{In}]) = 0.83$ determined by XRF. The molybdenum back contact and AZO front contact were sputtered and the buffer layer ($d = 70 \text{ nm}$) was deposited in a chemical bath. Intrinsic ZnO was not included to rule out any effect of this layer. The In_2O_3 TCO films were processed either by sputtering or ALD, which is described below.

2.1.1. Sputter deposition of IOH

Hydrogen doped indium oxide films were deposited using RF magnetron sputtering by employing a planar compound In_2O_3 target in a custom built sputtering system. The chamber was evacuated to base pressures in the order of 10^{-5} Pa . Argon and oxygen, both of 99.9995% purity, were introduced into the chamber at flow rates ϕ_{Ar} and ϕ_{O_2} respectively, set by mass-flow controllers. An argon flow rate of $\phi_{\text{Ar}} = 100 \text{ sccm}$ and an oxygen fraction of $\Theta \sim 0.1\%$ ($\Theta \equiv \phi_{\text{O}_2}/(\phi_{\text{Ar}} + \phi_{\text{O}_2})$) was used here. Hydrogen doping was achieved by introducing deionized water vapor in the deposition system at a flow rate of $\phi_{\text{H}_2\text{O}} = 0.25 \text{ sccm}$. The working pressure was adjusted via a throttle valve, and the total pressure was kept constant at 1.33 Pa. The target power density was $2.5 \text{ W}/\text{cm}^2$. Films were deposited on SLG and CIGSe solar cells mounted on a target-facing and stationary substrate holder with a target-to-substrate distance of 8 cm. No external heating was supplied during the film growth. After first characterization of the resulting (as grown) IOH layers on glass and on CIGSe, they were annealed in vacuum at $T = 200^\circ\text{C}$ for 1 h to increase the mobility values and characterized again.

2.1.2. Atomic layer deposition of IOH

IOH window layers were also grown in a Microchemistry F-120 ALD-reactor at $T = 145^\circ\text{C}$. As suggested by Libera et al. [16] the films were grown from cyclopentadienylindium(I) $[\text{In}(\text{C}_5\text{H}_5)]$ and a mixture of deionized water and oxygen gas. This procedure resulted in a hydrogen incorporation of about 2 at%. The total cycle number was 2100 and a growth rate of $1.3 \text{ \AA}/\text{cycle}$ was achieved. Further details of the ALD process can be found in an earlier publication [2].

2.2. Characterization methods

Electrical, optical and structural characterization was conducted on the different TCO layers deposited on SLG substrates. Absorption spectra were obtained by R- and T-measurements using a Perkin Elmer Lambda 900 spectrometer with an integrating sphere. Hall measurements were performed at magnetic field of $B = 0.5 \text{ T}$. Film crystallinity and structure were investigated using a Philips X’Pert diffractometer operating in grazing incidence x-ray diffraction (GIXRD) configuration at an angle of incidence of 1 degree.

Transmission electron microscopy analyses of TCO cross-sections in the solar cell device were performed in a FEI Tecnai F30 ST TEM, using an acceleration voltage of 300 kV. Electron transparent cross-sections were prepared in a FEI Strata DB235 Focused Ion Beam, using the in situ lift-out technique.

Download English Version:

<https://daneshyari.com/en/article/6534659>

Download Persian Version:

<https://daneshyari.com/article/6534659>

[Daneshyari.com](https://daneshyari.com)