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## Preprint

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# Investigation of the Effect of I-ZnO Window Layer on the Device Performance of the Cd-Free CIGS Based Solar Cells

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## ABSTRACT

$Cu(In,Ga)Se_2$ (CIGS) thin films were deposited on Molybdenum coated soda lime glass (SLG/Mo) substrates, using physical vapor deposition (PVD) 3-stage process. The CIGS films were treated by ammonium hydroxide solution before depositing the I-ZnO buffer layer. The I-ZnO layer was deposited using metallorganic chemical vapor deposition (MOCVD) at different substrate temperatures of 200°C, 250°C, and 300°C. The thickness of this buffer layer was varied according to the location of the substrates with respect to the gas flow direction. The CIGS devices were completed by depositing the Al-ZnO window layer by rf magnetron sputtering and applying the Ni/Al front contact grids. The thickness of the I-ZnO buffer layer was measured using a Dek-tak profilometer on sodalime glass substrates used as a reference during the deposition process of I-ZnO buffer layer on CIGS films. Surface depth profiling survey for the elements and their chemical states, as well as their relative concentration was analyzed by X-Ray Photoelectron Spectroscopy (XPS) for as deposited and ammonium hydroxide treated CIGS films. In addition, the performance of the completed CIGS devices was evaluated under standard conditions of 1000 $W/m^2$ and 25°C.

## INTRODUCTION

$Cu(In,Ga)Se_2$ (CIGS) is one of the most promising materials for thin film photovoltaic devices and applications. The current highest CIGS based solar cells efficiency have been achieved by physical vapor deposition technique from elemental sources using a three-stage process [1], deposited on Molybdenum coated soda lime glass (Mo/SLG). Basically, the device structures consisted of ZnO/CdS/CIGS/Mo/SLG, where a buffer layer of CdS is deposited using chemical bath deposition (CBD). During the CBD-CdS process chemical etching and surface modification of the CIGS absorber occur, such as removal of native oxides, etching In, Ga, and Na, and ion exchange between Cu atoms in the CIGS lattice and Cd atoms [2]. In spite of that, it is desirable to find an alternative to Cd material that is less or non-toxic, environmental friendly and feasible for industrial and solar market applications, for example it can be evaporated by continuous evaporation process.

This paper focuses on preparing Cd-free CIGS based solar cells with intrinsic high resistivity ZnO (I-ZnO) films deposited by metal-organic chemical vapor deposition (MOCVD) technique at different deposition substrate temperature and I-ZnO film thickness, and the effect of the prior treatment of CIGS films by ammonium hydroxide ($NH_4OH$) diluted solution on the device performance.

## EXPERIMENTAL

Two series of CIGS films were deposited on SLG/Mo substrates, at constant deposition rates and temperature using the 3-stage deposition process. For the subsequent buffer layer deposition, the surface of the first series of CIGS films was treated by immersing the films in ammonium hydroxide ($NH_4OH$) diluted solution for a period of 20 min at a bath temperature of 60°C.

Then, directly the intrinsic ZnO (I-ZnO) films were deposited by a low-pressure metal-organic chemical vapor deposition (LP-MOCVD). As illustrated in Figure 1, the reaction chamber of the MOCVD system was a cold-wall, rectangular quartz tube. According to this figure, the reactant gases flow direction is represented by the x-axis, and the cross gas flow direction is represented by y-axis, along the substrate surface direction. The reactant gases of ultrahigh-purity diethylzinc (DEZ) and ultrahigh-purity oxygen were used as Zn Precursor and oxidizer, respectively. The DEZ and oxidizer gas were introduced into reaction chamber through two different injectors located at one end of the chamber, then mixed inside the chamber and flowed with the direction of the chamber length (x-axis), and finally pumped out from the other end.

The surface treated CIGS films by ammonium hydroxide were arranged horizontally on a graphite susceptor and heated by five-zone infrared lamps, during the deposition of I-ZnO at different substrate temperatures of 200°C, 250°C, and 300°C. The lamps were independently controlled, along x-axis arranged, and located beneath the reaction chamber. The total gas flow through the chamber during the deposition was between 2000-3000 sccm, while the chamber pressure was maintained at 30 Torr. Due to the chamber geometry, the deposition configuration results in linear combinatorial synthesis and linear variation in thickness of the deposited thin films. This fact was advantageous results in reducing the number of experimental runs that were required at various deposition conditions of substrate temperature and film thickness. Therefore, the thickness of the deposited films of I-ZnO was varied according to the location of the substrates with

respect to the gases injectors' location and gas flow direction within the chamber. The locations of the substrates were identified as No.1, No.2, and No.3 as shown in Fig. 1. Simultaneously, reference soda lime glass substrates were used during the deposition for I-ZnO film thickness, and optical measurements. Hereafter, this series of surface treated CIGS films by ammonium hydroxide with direct I-ZnO buffer layer, after device completion shall be referred to as the "Cd-free CIGS device".

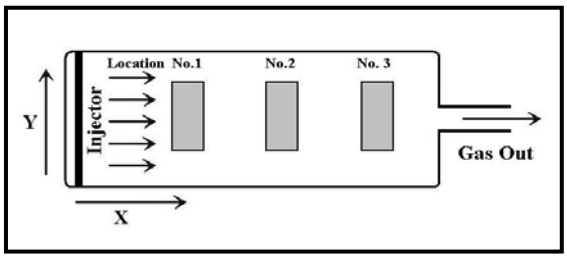


Fig. 1. Schematic top view of MOCVD reactor used to deposit the I-ZnO thin films. Three different locations are identified as No.1, No.2, and No.3 with respect to the gas injector.

For the second series of CIGS films, a standard CdS buffer layer was deposited by immersing the CIGS films in an aqueous solution of $CdSO_4$, $NH_4OH$, and thiourea, for 17 min at bath temperature of 60°C. Subsequently, I-ZnO window layer was deposited using MOCVD at the similar conditions of the direct I-ZnO layer deposited on CIGS/Mo/SLG films, as described above. Hence, this series after device completion will be referred to as "standard CIGS devices".

The CIGS devices were completed for the above both series of direct I-ZnO deposited on CIGS films (Cd-free) and CIGS films with CdS buffer layer, by depositing the conductive Al-ZnO window layer using RF magnetron sputtering, and then by applying the Ni/Al front contact grids using electron beam evaporator. The thickness and the optical properties of the I-ZnO buffer layer were measured using Dek-tak profilometer and the Uv-Vis-Nir spectrometer, respectively, for I-ZnO deposited on soda lime glass reference samples. Furthermore, surface depth profiling survey for the elements and their chemical states, as well as their relative concentration was analyzed by X-Ray Photoelectron Spectroscopy (XPS) for as deposited and ammonium hydroxide surface treated CIGS films. In addition, the Cd-free CIGS devices were characterized and compared to the standard CIGS devices. Such characterization includes quantum efficiency and device performance which was evaluated under standard conditions of 1000 W/m$^2$ and 25$^o$C.

## RESULTS AND DISCUSSION

Using the reference soda lime glass substrates, the I-ZnO layer thickness was measured for Cd-free CIGS devices and standard CGIS devices. Figure 2 shows the thickness of I-ZnO deposited at substrate temperature 200°C and 250°C as a function of the location of the CIGS absorbers with respect to the gas flow direction. It is clear that the deposited I-ZnO layer at location no. 1 (near to the injector) is the thickest whereas the deposited I-ZnO layer at location no. 3 is the thinnest. Furthermore, the overall I-ZnO layer thickness increases with increasing the deposition substrate temperature. For example, for each location, an average increase in I-ZnO layer thickness of about 200Å was measured as the deposition temperature was increased from 200°C to 250°C. On the other hand, an average reduction in the film thickness of about 600Å was measured as the deposition take place away from the injectors at location No.3, for all different deposition temperatures.

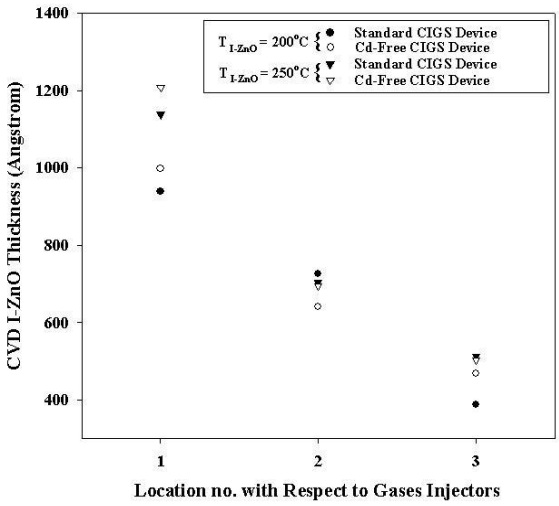


Fig.2. CVD I-ZnO thickness as a function of the substrates location with respect to the gas flow for the I-ZnO deposition temperatures of 200°C and 250°C.

This indicates that the deposition rate of I-ZnO layer (and its thickness) is influenced by the deposition temperature and the flow direction [3] where the flow rate of the reactant gases increases near to the injector (location No.1) and decrease linearly away from the injector (location No.3). Consequently, the film resistivity is expected to be higher for thin I-ZnO films deposited at low deposition temperature compared to the thick I-ZnO films deposited at high deposition temperature.

The Cd-free CIGS device performance was measured for the as deposited devices and after 4 min annealing at 200°C under standard conditions of 1000 W/m$^2$ and 25$^o$C, as shown in Fig.3. In general, all of the as deposited devices exhibited best performance at the low I-ZnO layer deposition temperature of 200°C. However, after annealing, an overall enhancement in the device performance was observed. For the best Cd-free CIGS device, with I-ZnO deposited layer of 400Å, the device efficiency improved from 10% for as deposited device to 14% after annealing. Although a reduction in the open-circuit voltage ($V_{oc}$) had been observed.

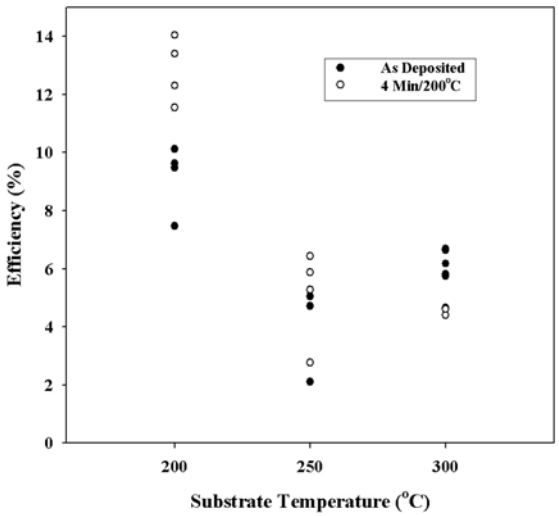


Fig. 3. ZnO/CIGS/Mo/SLG device efficiency (as deposited and annealed for 4 min at 200°C) as a function of I-ZnO deposition temperature.

The decrease in the device performance, as the deposition temperature of I-ZnO increases beyond 200°C, can be explained due to the increase in the relative I-ZnO film thickness above an optimum level, leading to increase the series resistance ($R_s$) of the CIGS devices [4]. Additionally, the deposition of I-ZnO layer directly on CIGS absorber creates a negative conduction band offset (cliff) as illustrated in Fig.4. This type of band offset results in carrier recombination through the defects at the CIGS/ZnO interface, leading to voltage losses. Therefore, in order to avoid device performance degradation for the devices fabricated with direct buffer layer on CIGS absorbers; I-ZnO buffer layer can be alloyed with Mg to increase the band gap and to create a positive conduction band offset and thus prevent the recombination. In fact, the Mg content in ZnO have nearly a linear relationship with the band gap and conduction-band offset [5].

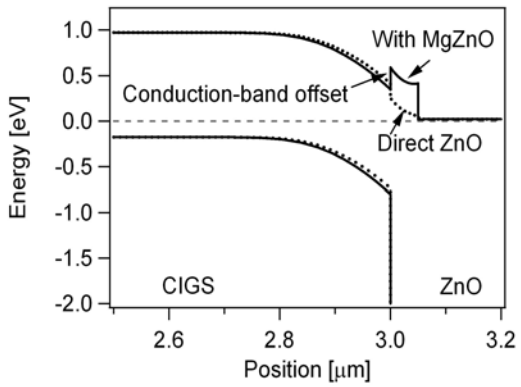


Fig. 4. Band diagrams for direct ZnO layer on CIGS (dotted lines) and with MgZnO buffer layer (solid lines).

Furthermore, as shown in Fig.5 obtained by SCAPS-1D simulation software developed by University of Gent, Belgium, the optimal values of the device efficiency can be obtained, when the conduction-band offsets have values between 0.1 eV and 0.4 eV, which correspond to Mg content between 10% and 20%, respectively. It was found that higher content of Mg than 20% creates a high barrier for the light-generated carriers, and thus the device experiences current losses.

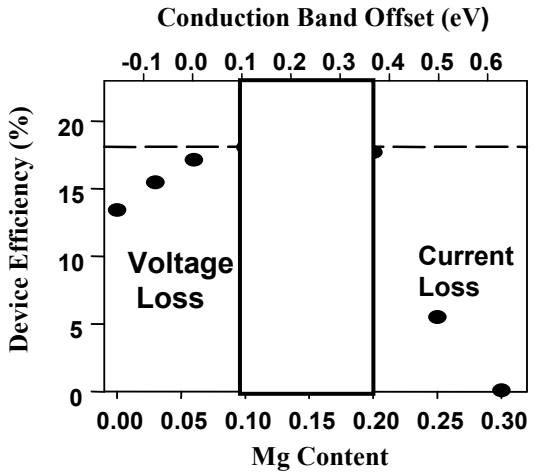


Fig. 5. Conversion efficiency as a function of Mg content.

Figure 6 shows XPS data for as-grown and $NH_4OH$-treated CIGS. Treatments were performed in a glove-box directly attached to the XPS system as described previously in [6]. As it had been reported in [7,8], $NH_4OH$ exposure removes metal oxides, sodium compounds, and $Se^{4+}$ compounds in as grown CIGS films. $Na_yCu_{1-y}(In,Ga)Se_2$ and $Na(In,Ga)Se_2$ segregated phases were observed at the CIGS film grain boundaries and grain surfaces. Both phases are strongly influenced by the amount of the Na out-diffused from the SLG substrate [9,10]. The removal of these surface segregated phases by $NH_4OH$ diluted solution leads to recombination centers passivation near the surface of the CIGS thin film absorber [4]. The XPS data also showed that the Cu/(In+Ga) ratio in the $NH_4OH$-treated samples increases relative to the samples with the native oxide. This is consistent with previous observations by [7,8,11] During MOCVD deposition of I-ZnO, Zn ions substitute the surface In and Ga vacancies. This doping situation was found in good agreement with Fons *et al* [12], where they noticed Cd ions to substitute In and Ga vacancies instead of Cu vacancies available at the surface of CIGS thin films.

## SUMMARY

Cd-free CIGS devices, with direct buffer layer of I-ZnO deposited by MOCVD showed improvement in device performance with device efficiency of 14% after

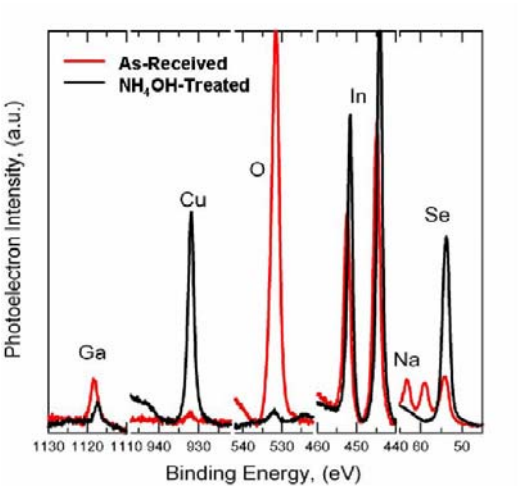


Fig. 6. XPS data for as-grown and $NH_4OH$-treated CIGS films.

annealing. Prior to I-ZnO layer deposition, the surface of CIGS absorbers was treated by $NH_4OH$ diluted solution which cause removing the surface $Na_yCu_{1-y}(In,Ga)Se_2$ and $Na(In,Ga)Se_2$ secondary segregated phases, and enhancing the ion-exchange reaction between Zn Ions and In and Ga vacancies available at the surface of CIGS thin films. The above results indicated that the removal of Sodium segregated phases by $NH_4OH$ treatment passivates the surface recombination center of the CIGS absorber and enhances the device performance. Furthermore, Zn ion substitution of the surface In and Ga vacancies have a doping effect. The device performance can be improved by alloying ZnO with Mg to form a positive conduction band offset which prevent the carrier recombination at the ZnO/CIGS interface.

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