Combinatorial sputtering of Ga-doped (Zn,Mg)O for contact applications in solar cells

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Abstract

Development of tunable contact materials based on environmentally friendly chemical elements using scalable deposition approaches is necessary for existing and emerging solar energy conversion technologies. In this paper, the properties of ZnO alloyed with magnesium (Mg), and doped with gallium (Ga) are studied using combinatorial thin film experiments. As a result of these studies, the optical band gap of the sputtered $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films was determined to vary from 3.3 to 3.6 eV for a compositional spread of Mg content in the $0.04 < x < 0.17$ range. Depending on whether or not Ga dopants were added, the electron concentrations were on the order of 10^{17} cm^{-3} or 10^{20} cm^{-3} , respectively. Based on these results and on the Kelvin Probe work function measurements, a band diagram was derived using basic semiconductor physics equations. The quantitative determination of how the energy levels of Ga-doped (Zn,Mg)O thin films change as a function of Mg composition presented here, will facilitate their use as optimized contact layers for both $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) and other solar cell absorbers.

Keywords: transparent conductive oxide, electron affinity, high-throughput experiments, electrical contact, photovoltaic, photo-electrochemical

1. Introduction

Development of suitable materials for contact layers is an important research topic in the area of photovoltaic (PV) and photo-electrochemical (PEC) solar cells. Several criteria are used to evaluate the prospects of candidate materials for these solar energy conversion applications. First, the promising candidate contacts must be sufficiently electrically conductive and optically transparent to the solar spectrum, as well as matched well in the energy band positions with the desired absorber layer. Second, it is also desirable to achieve these target properties with non-toxic and earth-abundant materials, which may enable large-scale applications in the future. Third, for PV and PEC absorbers prepared using vacuum-based approaches, the sputter deposition of contacts is beneficial to enable in-line device stack processing for mass production.

One of the most commonly used semiconductors, zinc oxide (ZnO), has been applied in a variety of photovoltaic solar cells, such as Si[1], III-V[2], CdTe[3], OPV[4], perovskites[5], Cu₂O[6], Kesterites [7] and Chalcopyrites [8]. With some tuning, this material can be used in different contact roles, including heterojunction partners (a.k.a. buffer layers [9] or electron selective contacts [10]) for vertical charge transport in immediate contact with absorbers, electrode layers (a.k.a. transparent conductors [11]) for lateral charge transport on top of buffer layers. Besides these contact applications in solar energy conversion, ZnO is a versatile material in its own right, since its wide direct bandgap of $\sim 3.3\text{eV}$ and good electron dopability up to 10^{21}cm^{-3} make it a promising candidate for various optoelectronic applications [12, 13]. Even with such promising attributes, the thin film PV devices made with intrinsic zinc oxide (i-ZnO) as a heterojunction partner are not on par with CdS, the conventional buffer layer that is often prepared by wet process such as chemical bath deposition (CBD). Only 5.2% efficiency is reported with i-ZnO buffer layer for CZTS solar cells, whereas the record efficiency with CdS is $\sim 12\%$ [7]. Also in CIGS, 14% efficiency [8] is reported with i-ZnO buffer layer whereas the record efficiency of CdS/CIGS device is $\sim 21.7\%$ [14].

One of the apparent drawbacks of i-ZnO contacts in CIGS and CZTS solar cells is high carrier recombination at the interface [15], which in principle can result from interface defects, unfavorable band offsets, or both. In the case of sputtering, the first issue is likely to result from the interface damage caused by the energetic deposition of ZnO. This is an interface-specific topic related to sputtering of not only ZnO but also other buffer layers, which has been extensively discussed and addressed in literature [16,17], thus it is beyond the scope of this

paper. The second materials-specific issue can be addressed by tuning the conduction band (CB) minimum of ZnO by alloying it with MgO, CdO and other II-VI materials [18]. This alloying will be beneficial not only for the application as a buffer layer but also for transparent electrode applications of ZnO in thin film PV. The resulting tunability may also be useful for minimizing the band offset with new absorbers, such as SnS [19], Cu₂O [20], CuSbCh₂ (Ch=S,Se)[21,22] for which the CBM position is at a different energy range than for CIGS or CZTS.

Alloying ZnO with MgO gives the flexibility to tune the bandgap of the material from that of ZnO (~3.3 eV) toward MgO (~7.7eV) [23,24,25,26]. Although the thermodynamic solid solubility predicted by the ZnO-MgO thermodynamic phase diagram [27] suggests that only about 2% of Mg can be incorporated into ZnO bulk material without segregation, experimentally much higher solubility (up to ~40%) is often achieved kinetically in thin film form [24,25]. A microstructural study of (Zn,Mg)O thin films prepared by pulsed laser deposition (PLD) suggests that the extended solid solubility of Mg in ZnO is substitutional and not micro-segregated [25]. The non-equilibrium nature of sputter deposition can also have a similar effect, leading to higher solid solubility than expected [24]. The resulting ability to vary the bandgap (3.3 - 4.0 eV) and tune the conduction- and valence band positions, while remaining in the wurtzite phase, is a highly desirable quality in a contact material studied for photovoltaic device performance.

Although the bandgap of ZnO can be increased with addition of Mg, there is an undesired reduction in conductivity with the increased Mg content. This is often explained in literature by decrease in crystalline quality of the samples or the changes in quasi bulk properties of the (Zn,Mg)O material [28,29,30]. This undesired decrease in conductivity can be mitigated to some extent by doping (Zn,Mg)O with group-III elements such as Al, Ga or In [31,32]. It is interesting to note that the high conductivity achieved by typical Ga-doped ZnO thin films is due to their highly non-equilibrium as-deposited metastable state (rather than due to classical thermodynamic doping substitution reasons), resulting from growth at relatively low temperature and modest oxygen partial pressure [33]. These deposition conditions are also desirable attributes for depositing ZnO for the purpose of making thin film PV devices [34,35]. In this process, independent control of the bandgap (Mg alloying) and the conductivity (Ga doping) of ZnO are desired to tune the band offset with the absorber without compromising the losses due to series resistance in the solar cell.

In this paper we investigate the materials properties of sputtered Ga-doped (Zn,Mg)O alloys relevant to their use as tunable contact layers for thin film solar cells. Using a high-throughput combinatorial approach, we obtain structural, optical, electrical and surface properties of the resulting Ga:(Zn,Mg)O thin films, pertinent to the application in thin film solar cells. The result shows that although alloying with up to 17% of MgO makes ZnO highly resistive, no phase separation is observed. Doping the (Zn,Mg)O alloys with Ga brings the conductivity to levels higher than 100 S/cm. The Ga:(Zn,Mg)O optical bandgap increases almost linearly from 3.35 to 3.65 eV with increase in Mg content, mostly due to the change in position of the conduction band, and the work function follows this trend. Together, these results are analyzed using semiconductor equations for energy band and charge carriers to determine the band diagram of Ga:(Zn,Mg)O energy level positions as a function of the Mg content. The potential implications for the use of Ga:(Zn,Mg)O in solar cells are discussed.

2. Methods

A systematic analysis of materials properties as a function of a broad parameter space often benefits greatly from the application of high-throughput experimental methods [36,37]. In this paper, we use combinatorial sputtering and spatially resolved characterization to study the properties of Ga:(Zn,Mg)O thin films for contact applications in solar cells. Our current implementation of this thin film approach [38] starts by physical vapor deposition of thin film sample libraries with orthogonal composition and temperature gradients. This combinatorial deposition is followed by spatially resolved characterization of structural, electrical, optical and surface properties of the samples as a function of the position on the library. Finally, the resulting large amounts of experimental data is processed and analyzed by semi-automated custom software routines. More information about each of these three steps of the high-throughput method is provided next.

Prior to the thin film depositions, the 50x50 mm Eagle XG glass substrates were cleaned with detergent, sonicated in acetone and isopropanol, and finally exposed to oxygen plasma for 5 min. All the depositions were performed at 12 mTorr partial pressure of argon (99.99%) with a flow rate of 10 sccm in the chamber and a base pressure of 10^{-6} Torr. For the films with uniform substrate temperature, silver paste was used as adhesive between the substrate and the heater, and was baked at 230°C, before the deposition. The substrate temperature gradient was created by the

previously described [39,40] intentional non-uniform thermal contact of the substrate to the heater. The depositions were carried out for 2 hours to achieve (Zn,Mg)O thin films with the thickness range between 175 and 472 nm. The thickness variation is due to the different deposition rate from different target material that gave varying spatial composition, and not due to volatilization of Zn from the substrate heated to the moderate temperature.

Figure 1 shows a schematic of the combinatorial library (4x11 rectangular grid) created for each sample, with superimposed photograph of the film. The experiments were carried out in two stages. In first stage, the (Zn,Mg)O alloy was studied with the compositional gradient on the x-coordinate (with decreasing Zn and increasing Mg towards positive x-axis) and the temperature gradient on the y-coordinate. After finding a suitable range of (Zn,Mg)O compositions and substrate temperatures, in the second stage the gallium composition gradient was introduced (increasing Ga towards more positive y values), keeping the Zn/Mg composition gradient fixed, and the substrate temperature constant at 200°C. The compositional gradients were achieved by radio frequency magnetron co-sputtering of ZnO (99.999% pure), Mg (99.98%pure) and Ga₂O₃ (99.995% pure) targets with 50 mm diameter, positioned at an angle of 45° with respect to the substrate. To achieve the desired compositional range, the power provided to the sputter guns was varied, and was 25, 22 and 18 W for ZnO, Mg and Ga₂O₃ respectively for the libraries presented in this paper.

Figure 1. A photograph of the (Zn,Mg)O sample library with horizontal Mg composition gradient, overlaid with the 4x11 combinatorial grid of points. Stage 1 (left): Substrate

temperature variation study for (Zn,Mg)O films with two curves showing two ranges of temperature gradient. Stage 2 (right): Gallium doping variation study for (Zn,Mg)O films deposited at fixed substrate temperature of 200°C.

After deposition, each sample library was characterized at 44 points (4x11 grid) by spatially resolved X-ray Diffraction (XRD - Bruker D8 Discover) for crystal structure, X-ray Fluorescence Spectroscopy (XRF - Fischerscope XDV-SDD) for chemical composition, UV/Vis/NIR Spectroscopy (custom, with OceanOptics spectrometers) for optical absorption, and four point probe sheet resistance (custom) for electrical properties. In addition, Scanning Kelvin Probe measurements (SKP – KP technology) were used to determine the work function of the films grown for this purpose on Fluorine doped Tin Oxide (FTO) coated glass substrates, with the surface-potential difference measured with respect to a gold reference in air. Since the XRF mapping could not detect the magnesium (Mg) peak, it was used for determining the ratio of zinc (Zn) to gallium (Ga) in the film. The full cation stoichiometry of this film was obtained from the XRF data combined with the Mg to (Zn + Ga) ratio determined from Rutherford Backscattering Spectroscopy (RBS) done in the first and third row of the 4x11 grid, with 8 points per row. To complement the mapping data with more in-depth electrical characterization of the regions of interest, individual small samples were obtained by cutting out $\sim 0.6 \text{ cm}^2$ square sections of a library, resulting in 8 unique samples along the composition gradient. For these samples, Hall effect measurements were taken on a bench top apparatus with the permanent magnet (Accent HL5500) in Van der Pauw geometry. Also, for a few specific samples of interest X-ray photoelectron spectroscopy (XPS, Kratos) measurements were performed to cross-validate the results of the other characterization techniques. Finally, the large amount of data produced as a result of both mapping and single-point measurements was processed and analyzed by custom algorithms implemented in the IgorPro© software package.

We note that several studies of compositional spreads of MgO-ZnO alloys are available in literature. Combinatorial laser MBE (CLMBE) was used to demonstrate the bandgap engineering of this alloy [41]. Similarly, the CVD technique was used to fabricate a compositional spread of 0.5% to 2.5% Mg on a single sample by rotating the substrate holder relative to the flow direction of the metallic precursors [42]. A microstructural study was performed on the compositional spread achieved by PLD from ZnO and MgO ceramic targets with moving

shutters [25]. A similar PLD approach was also utilized to produce a single compact device for simultaneous detection of broadband signals from the entire compositional spread achieved on the substrate [26]. Recently, a two dimensional lateral composition spread of Mg in one direction and Al/Ga in the other direction achieved by PLD, was used to study doping efficiency and the limits of the alloy solubility [43]. Note that most of the aforementioned composition spread studies are based on the intentional composition inhomogeneities in the combinatorial PLD technique,[44] and are performed at constant elevated substrate temperature, which is appropriate for a large number of optoelectronic applications. However, the combinatorial sputtering reported in this paper is better suited for depositing thin films with potential for large area applications, making this paper more directly relevant for solar cells. In addition, the substrate temperature gradients used here at the initial screening stage enable rapid determination of the coupled dependencies of properties on chemical composition and substrate temperature.

3. Results

3.1 Composition and Structure

Combinatorial temperature gradient studies were performed with two sets of temperature profiles in the 100°C - 260°C range (Figure 1) and at room temperature. The results of these studies showed that an elevated substrate temperature yielded more conductive and more crystalline (Zn,Mg)O thin films than the ambient substrate temperature. At higher substrate temperatures (>200°C), although a gradual improvement of conductivity and crystallinity was observed, it was not significant. Thus 200°C was chosen as a constant temperature for further studies as a function of Ga doping concentration. We note that 200°C is also an acceptable post - annealing temperature that is used for thin film CZTS PV devices [45] and CIGS devices reported in literature [46]. Thus the Ga:(Zn,Mg)O material results discussed below should be possible to translate into the PV device results.

Combining the chemical measurement results from XRF and RBS methods gave the compositional information of the whole Ga:(Zn,Mg)O film. Figure 1 shows the concentration distribution of Zn, Mg and Ga elements across the 50 mm square sample library. The results presented in Figure 1 indicate that there are orthogonal and linear gradients of distribution of these chemical elements in the sample library. In this representative sample library, the atomic concentration for Mg varies in the range of 4 - 17%, and for Ga it was in the range of 0.6 - 2.9%.

The chemical content of oxygen was not possible to determine from these measurements, but it is assumed to be nearly stoichiometric, since no metallic secondary phases were observed in XRD, as described next.

Figure 2. (a) X-ray diffraction of (Zn,Mg)O 0002 peak with increasing concentration of Mg from top to bottom. Inset: X-ray diffraction of (Zn,Mg)O:Ga 0002 peak with increasing concentration of Ga from bottom to top. (b) X-ray diffraction of 0002 peak intensity and 0002 peak position with respect to variation in Mg concentration, showing two distinct slopes separated by about 8 at% Mg (see text for more details)

The $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films deposited in the composition range of $x = 0.04 - 0.17$ remained in wurtzite phase with preferential orientation along (0002) direction, indicating that the orientation of the grains had a c-axis perpendicular to the substrates surface. No peaks related to MgO or Ga_2O_3 secondary phases were observed in this composition range. The absence of the MgO peaks suggests substitutional solubility of Mg into cationic sites of ZnO. Previous microstructural study of (Zn,Mg)O film using TEM showed up to 40% of Mg incorporation in ZnO lattice with solid solubility, thus supporting our case [25]. Figure 2 shows the trend of the (0002) wurtzite XRD peaks with increasing Mg content (11 points in x-direction). As expected, with the addition of smaller Mg-atoms (Mg^{2+} ionic radii = 57pm compared to Zn^{2+} ionic radii = 60pm [47]) the peak is shifted to the right, and the crystallinity is also degraded. The inset in Figure 2a shows an improvement of the grain size with an increase in gallium concentration, which has also been reported in other literature [48]. Figure 2b clearly shows how the peak

position increases and the peak intensity decreases almost linearly with the increase in Mg concentration, with the change in the slope at 8-10% Mg composition. Crystallite size calculated using Debye-Scherrer formula (see Figure S2 in supporting information) showed a similar trend, varying between 25.8 nm and 20.6 nm over the studied range of Mg concentration. However, we note that the XRD peak broadening may be also related to alloy inhomogeneities, structural defects and many other effects intrinsic to (Zn,Mg)O thin films

3.2 Optoelectronic properties

The (Zn,Mg)O optical band gap as a function of Mg composition in the film was extracted from the Tauc plots following the ZnO literature, and is shown in the inset in Figure 3 along with an intrinsic ZnO ($E_g = 3.2$ eV) grown in the same deposition system. The optical bandgap of the $(\text{Zn}_{1-x}\text{Mg}_x)\text{O}$ is observed to change from 3.3 – 3.6 eV with Mg concentration changing in the $x = 0.04$ -0.18 range. This change happens almost linearly, but two distinct slopes below and above 8-10% Mg composition can be observed. The corresponding $d(E_g)/dx$ slope values are 0.022 and 0.017 eV/%Mg respectively. Interestingly, the critical point of 8-10% Mg where the slopes change are very similar to that seen on the Figure 2b for both variations of XRD peak intensity and position with the Mg composition, even though these samples are coming from the same combinatorial library. Similar sets of slopes from Figure 3 and Figure 2b suggest a good correlation between the structural properties of the thin film to its optical properties. The Urbach tail was calculated and its trend with increasing Mg content is shown in Figure S1 in Supplementary Information. The Urbach energy increases from 66 meV to 122 meV with increasing Mg content, which further supports our XRD conclusion that the imperfection of the ZnO lattice increases with addition of Mg.

Figure 3. Optical bandgap of $\text{Zn}_{(1-x)}\text{Mg}_x\text{O}$ at different Mg atomic concentration x . Inset shows Tauc plot for $\text{Zn}_{(1-x)}\text{Mg}_x\text{O}$ ($0.04 < x < 0.17$) at 11 points of the sample library and for the intrinsic ZnO sample. The error bars were determined by performing the Tauc plot analysis at different spectral regions, and plotting the resulting standard deviation of the results.

From the four-point probe sheet resistance measurements, in combination with the thickness of the film determined from X-ray fluorescence model, a conductivity map of the entire 44 point library can be determined. Figure 4 shows the Ga:(Zn,Mg)O electrical conductivity achieved for different levels of Mg alloying and Ga doping. For the undoped (Zn,Mg)O thin films, the conductivity of the ZnO decreases with increasing concentration of Mg, and this result agrees with that of other authors [28, 29, 30]. The observed change is quite linear with the change in the Mg content. With Ga doping, the conductivity of (Zn,Mg)O alloys is improved by more than 10^4 times. In the studied range of Ga doping (0.6 – 2.9%), the Ga:(Zn,Mg)O thin films also showed improvement in electrical conductivity with the increase in Ga, but this trend was weak compared to the variation of conductivity with the changing Mg content. Note that the scattering of the data points in Fig. 4 is more significant in regions around the edge of the substrate, which can be related to temperature variations or differences in oxygen ion bombardment. The highest sputtered Ga:(Zn,Mg)O conductivity reported here (in the 100-1000 S/cm range) is lower than for the record Ga:ZnO conductivities achieved for the films prepared by pulsed laser deposition on crystalline substrates (1,000-10,000 S/cm range) [49]. However, the processing temperature (200C), substrate (glass), and methods (sputtering) used in this study are scalable to large area deposition on temperature-sensitive polycrystalline solar cells.

Figure 4. Conductivity of (Zn,Mg)O and (Zn,Mg)O:Ga sample libraries as a function of Mg composition. The Ga concentration is shown as a color scale.

Carrier densities and Hall mobilities are calculated from Hall effect measurements for Ga:(Zn,Mg)O thin films, and are shown in Figure 5. Both the concentration and mobility of electrons are improved with Ga doping. This data further supports the role of Ga as an n-type dopant (donor) in (Zn,Mg)O. The effect of Mg alloying on the concentration and mobility of electrons seen in the Ga:(Zn,Mg)O samples is weak, as desired for practical applications of these materials as contacts in solar cells. However, both the carrier density and the mobility decrease slightly with increasing Mg content (Figure 5), factoring into the small drop in conductivity observed in Figure 4. In the case of undoped (Zn,Mg)O samples, the decrease in conductivity with increasing Mg content is much more dramatic (Figure 4). As for the measurements done on undoped films, their resistivities lie at the boundary of Hall-effect measurement instrument, which makes it difficult to draw any conclusion regarding the conductivity trend with Mg content.

Figure 5. Hall effect mobility and concentration of electrons in 2.7% Ga-doped (Zn,Mg)O decreases with the increase in Mg content, with small variations due to Hall effect measurement uncertainty. The error bars were calculated by performing 3 Hall-effect measurements per each sample. Reliable Hall effect data from undoped samples was not possible to obtain, and hence it is not shown in the graph

3.3 Surface Properties

The work function was measured using the Kelvin probe technique to investigate the surface properties of the Ga:(Zn,Mg)O samples (Figure 6). For this measurement, the sample libraries were grown on glass substrates coated with electrically conductive fluorine doped tin oxide (FTO), because of the high resistivity of the Ga:(Zn,Mg)O films at high-Mg and Ga-free conditions. For the Ga-doped (Zn,Mg)O samples we observed a ~ 0.2 eV decrease in work function (i.e. increase in the Fermi level position) with increasing Mg content from 4 to 18% and increase in Ga from 1 to 3%. This indicates that on the absolute energy scale the Fermi level moves up closer to the vacuum level. These results also suggest the expected increase in the CB position with addition of Mg due to relatively constant conductivity of the Ga:(Zn,Mg)O thin films.

In case of Ga-free (Zn,Mg)O samples, however, we observed a lower value of the work function compared to the Ga-doped (Zn,Mg)O samples. This decrease is somewhat surprising, since there should be a lower concentration of electrons in the (Zn,Mg)O, and hence lower position of the Fermi level on the absolute energy scale. These considerations suggest that there is a very different and quite strong contribution of the surface dipoles to the measured work function in the case of (Zn,Mg)O, as compared to (Zn,Mg)O:Ga. This is not entirely unexpected, given the known surface reactivity of (Zn,Mg)O and the Kelvin probe data being sensitive to the adsorption of water or hydroxyl ions on the surface of a film. The Ga doping in (Zn,Mg)O is perhaps mitigating these effects.

Figure 6. Work function of (Zn,Mg)O and (Zn,Mg)O:Ga thin films with change in Mg and Ga concentrations

4. Discussion

4.1 Band diagram

The results of the chemical, structural, optical, electrical and surface measurements of the Ga:(Zn,Mg)O samples reported here, are useful for initial assessment of this material as a candidate contact layer for applications in PV and PEC solar cells. However, for the actual integration of these or any other potential contacts with the absorber layers, a band diagram is desired, showing the positions of the energy bands and the Fermi level of the contact with respect to the absorber energy levels. Such kinds of band diagrams are often quite complicated and time-consuming to generate using e.g. surface-sensitive photoelectron spectroscopy methods, especially when several possible absorbers are considered. An alternative and simpler approach here, is to use the measured bulk and surface properties to construct the band diagram of the contact layer with respect to the vacuum level. From such band diagram of the contact material, the band offsets with the absorber can be evaluated for PV solar cell applications, since the vacuum level should be approximately similar for the absorber (so called Anderson's rule [50]). In a similar way, the energy level alignment with the redox potentials can be evaluated for PEC solar cells, taking into account the dipole layers that form at the solid/liquid interface (~0.5 eV in the case of water splitting reaction). [51]

The band diagram of Ga:(Zn,Mg)O with respect to the vacuum level and as a function of Mg content was constructed in three steps. First, the Fermi level was determined directly from the work function measurement (Figure 6) taking the vacuum level as zero reference energy ($WF = E_{vac} - E_f$). Second, measured electron concentrations (Figure 5) were used to calculate the energy of the Conduction Band Minimum (CBM) with respect to the Fermi level from the expression:

$$n_0 = N_c \times \exp\left(-\frac{E_c - E_f}{kT}\right) \quad (1)$$

$$\frac{E_f - E_c}{kT} \cong \ln\left(\frac{n}{N_c}\right) + \frac{1}{\sqrt{8}} \frac{n}{N_c} - \left(\frac{3}{16} - \frac{\sqrt{3}}{9}\right) \left(\frac{n}{N_c}\right)^2 + \dots \quad (2)$$

$$N_c = 2 \times \left(\frac{2 \times \pi \times m^* \times kT}{h^2}\right)^{(3/2)} \quad (3)$$

where, n_0 is the electron concentration, k is Boltzmann constant, T is absolute temperature, and N_c is the effective density of states in the conduction band given by Equation 3. Since the Ga:(Zn,Mg)O were found to be highly doped, an approximation for degenerate semiconductor was used as seen in Equation 2 to calculate CBM. [52]

The effective mass m^*/m_e of ZnO was taken as 0.39 and that of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ for different x was derived using linear variation (d/dx) of Mg composition (x) obtained from other literature [53] as shown in following equations

$$\frac{d}{dx}\left(\frac{m^*}{m_e}\right) = 0.22 \quad (4)$$

$$\left(\frac{m^*}{m_e}\right)_{\text{Zn}_{(1-x)}\text{Mg}_x\text{O}} = 0.39 + 0.22x \quad (5)$$

Third, the corresponding valance band minimum (VBM) energy was calculated by subtracting the Burstein-Moss (BM) parabolic band filling correction from the optical band gaps obtained from the Tauc plot (Figure 3):

$$\Delta E^{BM} = \frac{h^2}{8\pi^2 m^*} (3\pi^2 n)^{2/3} \quad (6)$$

Then, the resulting electronic bandgap (E_g) was subtracted from the CBM energy to obtain the VBM energy. The VBM energy with respect to the Fermi level was also determined by XPS to be > 3 eV. This result is consistent with the VBM value obtained from the combination of the measurements of work function (Kelvin probe), carrier concentration (Hall-effect) and band gap (optical absorption) as described above.

The resulting experimental energy band diagram for Ga doped (Zn,Mg)O with respect to vacuum level as reference is shown in Figure 7, where it is also compared with the theoretical one based on the data in Ref. 53 matched at VBM of 4% Mg. With the increase in Mg concentration up to ~10%, the CBM energy goes up by ~0.5eV (theory : 0.2 eV), VBM energy goes down by ~0.14eV (theory : 0.11eV) and Fermi level goes up by ~0.14eV (not considered by theory). The experimental trends remain similar but become less pronounced in the 6 - 18% Mg range, which may be related to the change in the structural (Figure 2) and optical (Figure 3) properties of the Ga:(Zn,Mg)O thin films also observed close to 8% Mg composition.

The difference between the experimental and theoretical CBM position at lower Mg concentration (Fig. 7) may be related to the very high doping of the material. First, non-parabolicity of the conduction band at the degenerate doping levels may violate the BM shift effective mass assumptions (Eq.6). Second, the high electron concentration may also lead to the band-gap narrowing due to the many body effects (band gap renormalization) [54, 55]. Besides these two physical effects, the CB difference (Fig. 7) could also be caused by the fact that experimental energy band diagram was derived from multiple characterization techniques, each

prone to its own measurement errors. This can also lead to the difference between the absolute conduction band positions determined here (< -5 eV) and that often used in ZnO literature (~ -4.5 eV), which would require further investigations. Regardless, the analysis of our experimental result (Fig. 7) indicates that the electron affinity is decreasing with the addition of the Mg where the ionization potential remains more or less flat. Such tuning of the CBM position (electron affinity) provides excellent optimization opportunities for thin film photovoltaic devices, and other kinds of solar cells.

Figure 7. Experimentally determined energy band diagram for Ga (2.7%) doped (Zn,Mg)O thin films with respect to vacuum level, with solid green line and green shade representing results from theoretical calculation [53]

4.2 Solar cell applications

The moderate deposition temperature (200°C), the scalable fabrication technique (sputtering) and inexpensive substrates (glass) used in this paper provide an advantage for the application of the studied Ga:(Zn,Mg)O thin films in a thin film photovoltaic and photo-electrochemical solar cell devices. From the applications point of view, the relatively narrow range of conductivity and the substantial variation of the band positions achieved in the Ga-doped (Zn,Mg)O are suitable for experimenting with band alignment for different p-n heterojunction devices, without the influence of the changes in contact resistance. So if the conductivity is desired to be constant but the band positions are required to change, the Ga doped (Zn,Mg)O can be used for device engineering experiments. On the other hand if the application requires variable conductivity,

undoped (Zn,Mg)O can be used. While the Ga:(Zn,Mg)O conductivity is more than sufficient for possible use as a buffer layer, it needs to be further improved for use as a transparent electrode, where conductivity of greater than 1000 S/cm is typically needed. In part, this can be mitigated by growing thicker Ga:(Zn,Mg)O films, so that the overall conductance is higher.

Beyond the simple experimental band diagram presented in this work (Figure 7), more detailed interface studies would be needed to integrate Ga:(Zn,Mg)O films into solar cells. Prior reports on experimental band alignment studies of Mg-free ZnO thin films as buffer layers showed that their conduction band edges are closely matched to the CZTSSe (within ± 0.1 eV [56, 57]) and to the CIGS (within ± 0.2 eV [58]). Additionally, a prior theoretical modeling study of the CIGS/(Zn,Mg)O interface showed that the optimum solar cell results are in the range where the conduction band edge of the buffer layer is 0-0.4 eV higher than that of CIGS [59, 60]. The tunability range of the energy level positions achieved in this study for the Ga:(Zn,Mg)O thin films is thus suitable for the future experimental band alignment studies with thin film absorber layers, and for the subsequent solar cell device integration efforts.

Also in organic photovoltaics (OPVs), the Ga:(Zn,Mg)O material discussed in this work can be used as an electron transport layer (ETL). For the variety of organic material with hybrid structures, one has to find a suitable contact material, requiring tunability of the energy band positions. With its tunable energy band position, (Zn,Mg)O has already been shown to achieve the highest open circuit voltage (V_{oc}) in the P3HT-based OPV device.[61] The tunability helped to increase the V_{oc} from 500 to 900 mV with no loss in short circuit current (J_{sc}), by decreasing the band offset between the lowest unoccupied molecular orbital (LUMO) of the polymer donor and the conduction band of the metal oxide material. More than 8% power conversion efficiency for bulk heterojunction solar cell based on PTB7:PC71 has also been reported after tuning the interface properties by alloying ZnO with Mg [62]. Besides the OPV devices, the Ga:(Zn,Mg)O contact layers might also be suitable for hybrid organic-inorganic perovskite solar cell applications [63].

5. Conclusions

Undoped and Ga-doped (Zn,Mg)O thin films were grown using combinatorial sputtering at moderate 200°C substrate temperature. In a single 50 x 50 mm sample library a compositional spread of Mg was obtained from 4% to 17%, and the Ga concentration was in the 0.5% - 3%

range. In this entire composition range, Mg ions substituted the cationic sites maintaining the crystal structure of ZnO (wurtzite), with linear shifts in the XRD peak positions, and without any diffraction peaks from MgO. From this compositional spread, an optical bandgap variation of 3.3 to 3.6 eV was obtained, compared to 3.2 eV for pure ZnO. The films showed good correlation between the structural properties and the optical properties, as a function of Mg content. Electrically, the undoped (Zn,Mg)O samples showed a carrier concentration in the order of 10^{17} cm⁻³ and the Ga-doped (Zn,Mg)O thin films had concentration of free electrons in the 10^{20} cm⁻³ range. Within the relatively narrow range of electronic transport properties of Ga:(Zn,Mg)O, the change in Mg composition resulted in a corresponding change in the work function and in the energy band positions, as quantified by the band diagram derived from experimental results and semiconductor equations. Overall, these results lead to the conclusion that the sputtered Ga:(Zn,Mg)O thin films constitute an interesting material system to explore how the band-alignment of contacts with different absorber materials influences the photovoltaic and photo-electrochemical solar cell performance.

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Combinatorial Sputtering

Ga(Zn, Mg)O - Band Diagram