Influence of sputtering a ZnMgO window layer on the interface and bulk properties of Cu(In,Ga)Se₂ solar cells

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The authors studied the influence of sputtering a ZnMgO window layer for Cu(In,Ga)Se₂ solar cells on bulk and interface electrical properties. Admittance spectroscopy reveals deep levels at the ZnMgO/CdS interface whose activation energy (∼0.4 eV) increases with reverse bias, indicating an unpinned quasi-Fermi level at the interface. The Cu(In,Ga)Se₂ carrier concentration determined by capacitance-voltage measurements decreases to 3 × 10¹⁴ cm⁻³, compared to 1 × 10¹⁶ cm⁻³ in a device with a ZnO window. Scanning Kelvin probe force microscopy verifies the increased depletion region width and indicates that the junction location is unaltered by ZnMgO. Secondary-ion mass spectroscopy shows the presence of Mg near the top and bottom surfaces of the Cu(In,Ga)Se₂ film. They hypothesize that the decrease in carrier concentration is due to compensation doping of the Cu-poor Cu(In,Ga)Se₂ by Mg. Optimizing sputtering conditions to reduce surface damage and Mg migration eliminates the interface states and restores the carrier concentration, resulting in device performance comparable to those with a ZnO window. © 2009 American Vacuum Society. [DOI: 10.1116/1.3256230]

I. INTRODUCTION

The chalcopyrite compound semiconductor represented by Cu(In,Ga)Se₂ (CIGS) is an important and promising material¹,² for thin-film photovoltaic devices. A record efficiency of 19.9% has been demonstrated³ in the laboratory. A typical CIGS device, such as that reported in Ref. 3, consists of a soda-lime-glass substrate, molybdenum back contact, CIGS absorber, CdS buffer, intrinsic ZnO window, and Ni/Al top contact. There has been significant research effort on alternative buffer/window materials⁴,⁵ to substitute for CdS and/or ZnO. The motivations are to increase the collection of current from high-energy photons (for higher short-circuit current density), optimize conduction-band alignment at the interface (for higher open-circuit voltage), and improve environmental friendliness by avoiding Cd. A promising candidate that meets all the above criteria is the ZnMgO alloy. The large bandgap [3.3–3.9 eV (Ref. 4)] and controllable conduction-band offset⁶ allow the possibility of increasing CIGS absorber bandgap and reducing (or eliminating) the CdS buffer with little penalty. Reports of ZnMgO use in CIGS devices⁶–¹² have been emerging rapidly and are generally very encouraging. Compared to their CdS/ZnO-based counterpart, CIGS devices incorporating ZnMgO (sometimes in combination with another layer such as ZnS) demonstrate similar or superior performance, with one work reporting 18.1% efficiency.⁷

The most common methods for depositing ZnMgO on solar cells are sputtering⁶ and atomic layer deposition (ALD),⁷ with the latter showing more success recently. There are reports⁹,¹⁰ that sputtering deposition is susceptible to lower device performance, presumably due to defects introduced at the interface by sputtering damage. Sputtering deposition, however, has a deposition rate that is roughly two orders of magnitude higher than ALD. This advantage, together with the technology maturity, is a critical factor in considering capital equipment and manufacturing cost. Hence, there is a compelling reason to study the effects of sputtering ZnMgO on CIGS materials. In this work, we use magnetron radio-frequency (rf) cosputtering to deposit Zn-MgO from separate ZnO and MgO targets. The cosputtering configuration allows continuous tuning of the Mg composition and conduction band of ZnMgO alloy.¹³

Most of the ZnMgO-based solar cell studies reported to date focus on interface properties.⁵,¹⁰ There have been few study on the CIGS bulk properties as a result of ZnMgO deposition. Change in CIGS bulk property, however, cannot be easily ruled out and will significantly affect device performance if it is indeed present. In this work, we deposit an intrinsic ZnMgO window layer in place of the usual intrinsic ZnO window layer and examine the effects both at the ZnMgO/CdS interface and in the bulk CIGS absorber. Capacitance-voltage (CV) and admittance spectroscopy techniques are employed to investigate the carrier concentration and defect levels in the bulk CIGS and at the ZnMgO/CdS interface. Scanning Kelvin probe force microscopy (SKPFM) is carried out to identify the location of the electrical junction and depletion region. We use secondary-ion mass spectroscopy (SIMS) to study the Mg profile in the CIGS film. The characterization outcome provides guidance to optimizing ZnMgO deposition conditions (such as rf power, Mg composition, and relative timing of ZnO–MgO cosputtering), leading to solar cell performance comparable to devices fabricated using the ZnO window layer.

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Fig. 1. Device structure (not to scale) for the reference device using a ZnO window (a) and ZnMgO sample sets 1 (b), 2 (c), and 3 (d) are shown. The variables in sample sets 1, 2, and 3 are the following: the thickness of ZnMg0.5O layer from 10 to 80 nm, the thickness of an intrinsic ZnO layer from 10 to 40 nm grown prior to the 40-nm-thick ZnMg0.3O, and the Mg composition of the 25-nm-thick ZnMg2O grown at reduced MgO sputtering power from 180 to 60 W after forming a ZnO/Cds interface, in that order.

II. EXPERIMENT

Three sets of CIGS solar cells were fabricated for this study. Their device structures are depicted in Fig. 1, and key performance and characteristics are summarized in Table I. For each set, a series of four samples are fabricated, with one ZnMgO parameter varied, out of small pieces taken from the same large piece of CIGS film. Also, from the same CIGS film, a reference sample is fabricated using the standard process described by Repins et al. with a 100-nm-thick ZnO window layer [Fig. 1(a)]. Typical performance of the reference samples is an efficiency of 14.6%, open-circuit voltage of 630 mV, short-circuit current density of 31 mA/cm², and fill factor of 75%. The layer structure of sample set 1 [Fig. 1(b)] is identical to the reference devices, except that the intrinsic ZnO window layer is replaced by an intrinsic ZnMg0.5O layer with various thicknesses (10, 20, 40, and 80 nm). The Al-doped ZnO remains in place because it is difficult to achieve high conductivity in Al-doped ZnMgO.13 The Zn1−xMg2O films are deposited in an AJA International ATC 2200-V rf magnetron cosputtering system from separate ZnO and MgO targets. The base pressure is 2 × 10⁻⁸ torr and the working pressure is 5 × 10⁻³ torr with argon gas flowing at 40 SCCM (SCCM denotes cubic centimeter per minute at STP). The rF power settings for ZnO and MgO targets are 100 and 240 W, respectively. The diameter of both targets is 75 mm. The distance from the target to the sample is ~150 mm. During the sputtering deposition, the substrate temperature is maintained at 100 °C. The Mg content is determined to be x=0.3 from the calibrated deposition rates of ZnO and MgO. After ZnMgO deposition, the samples go through Al-doped ZnO sputtering deposition and top metal deposition. There is no intentional heating during the steps subsequent to the Zn1−xMgO. The maximum temperature increase in the substrate during these steps is estimated at 10 °C.

Capacitance-voltage and admittance spectroscopy measurements are performed with an Agilent A4294 impedance analyzer. Unless otherwise mentioned, the alternating current (ac) modulation voltage is 35 mV, and the modulation frequency is 10 kHz. The SKPFM technique is based on the noncontact mode of atomic force microscopy. The small tip size (~10 nm), small distance between the tip and sample surface (~10 nm), and the force-sensitive cantilever (~nN/m) ensure high spatial (~30 nm) and energy (~10 mV) resolutions. Details of the technique are described in Refs. 14 and 15. Prior to the SKPFM experiment, the surface of the sample is polished. SIMS measurements of both Mg and Se (whose depth profile is used as a reference to determine the spatial location) were taken by a Cameca IMS-3F at 14.5 keV Cs+ for detection of elements.

Devices in sample set 1 exhibit lower efficiencies (see Table I) mostly due to lower open-circuit voltage and fill factor, which is contrary to the expectation of benefits from better conduction-band alignment.16 As seen in the current-voltage plot (Fig. 2), the series resistance of the device increases with ZnMgO thickness while the shunt resistance decreases with ZnMgO thickness. Together, they lead to a reduced fill factor. To determine the impact of the ZnMgO

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>ZnO reference</th>
<th>ZnMgO sample set 1</th>
<th>ZnMgO sample set 2</th>
<th>ZnMgO sample set 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnMgO (nm)</td>
<td>0</td>
<td>10, 20, 40, 80</td>
<td>10, 20, 30, 40</td>
<td>10, 20, 80</td>
</tr>
<tr>
<td>ZnO (nm)</td>
<td>100</td>
<td>NA</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Relative VOC</td>
<td>100%</td>
<td>70%–85%</td>
<td>95%</td>
<td>100%</td>
</tr>
<tr>
<td>Relative ISC</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Relative fill factor</td>
<td>100%</td>
<td>35%–80%</td>
<td>40%–85%</td>
<td>100%–105%</td>
</tr>
<tr>
<td>Relative efficiency</td>
<td>100%</td>
<td>10%–60%</td>
<td>40%–80%</td>
<td>100%–105%</td>
</tr>
<tr>
<td>Interface states at ~400 mV</td>
<td>Absent</td>
<td>Present</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>W at 0 V (µm)</td>
<td>0.28</td>
<td>1–1.4</td>
<td>0.5–0.8</td>
<td>0.2–0.35</td>
</tr>
<tr>
<td>N_d at 0 V (cm⁻³)</td>
<td>1 × 10¹⁶</td>
<td>(2.6–3.0) × 10¹⁴</td>
<td>(0.7–2.3) × 10¹⁵</td>
<td>(5.0–10) × 10¹⁵</td>
</tr>
</tbody>
</table>
layer on the electrical property of the devices, we further performed an admittance spectroscopy experiment conducted over a range of frequency, temperature, and reverse bias, as shown in Fig. 3. The activation energies of the deep levels are obtained from the Arrhenius plot (not shown) of frequency versus temperature at which the \( \frac{fdC}{df} \) spectrum peaks. The admittance spectroscopy results from the devices in sample set 1 all show that ZnMgO introduces a deep level at \( \sim 400 \text{ meV} \). As seen in Fig. 4, the peak temperature corresponding to this deep level increases with reverse bias, indicating an increase in activation energy with reverse bias. Taking the sample with 40 nm ZnMgO as an example, the deep-level activation energy increases from 414 ± 36 meV at zero bias to 514 ± 44 meV at 0.2 V reverse bias. This is a telltale sign of spatially localized, but energetically continuous, interface states whose activation energy changes with the band bending as a result of electric bias. Admittance spectroscopy on otherwise identical samples with ZnO/CdS interface (discussed in later text) does not show the presence of these deep levels. We conclude that these interface states are associated with the ZnMgO/CdS interface. Only those interface states with energy near the quasi-Fermi level contribute to the \( \frac{fdC}{df} \) signal. The quasi-Fermi level near the ZnMgO/CdS interface is not pinned and moves lower with increase reverse bias, which effectively results in sampling of interface states deeper in the bandgap, and hence, larger activation energy. The above results confirm observations from other publications\(^9,10\) that interface recombination may be introduced by sputtering damage. We also observe two (sometimes one) deep levels with smaller activation energies that do not exhibit such bias dependence. These states are more frequently reported and they are attributed to either bulk CIGS defects or states at the CdS/CIGS interface where the Fermi level is presumably pinned. The ideal candidate for admittance spectroscopy study is a one-sided junction where the applied voltage affects only the bulk CIGS. However, the devices in this work may exhibit a bias effect in ZnMgO and CdS because the high resistivity of ZnMgO causes it to be partially depleted and the CdS is possibly damaged by the ZnMgO sputtering. The alternative physical picture is Fermi level unpinning at the CdS/CIGS interface, which is easier to explain and has been reported by other researchers. We opt to present the former because (a) it does not makes sense that ZnMgO sputtering damage removes the Fermi level pinning at the CdS/CIGS interface by reducing the interface states; (b) the trap level exhibiting bias dependence is only observed in ZnMgO/CdS devices, not in the ZnO/CdS (reference sample set) or ZnMgO/ZnO/CdS devices (sample sets 2 and 3). The natural questions are then: how much of the depletion could be in ZnMgO or CdS, and why is a clear shift of junction location not seen in SKPFM? We think it is possible...
to have a narrow depletion region in ZnMgO/CdS layers, which is neither proved nor disproved by our experiment, but is supported by the SCAPS simulation below.

The carrier concentration profiles in bulk CIGS absorber layers determined by the capacitance-voltage measurements are plotted in Fig. 5. Compared to the reference solar cell with a ZnO window layer, the carrier concentration is lower in sample set 1 (this alone, without added recombination as speculated in the paragraph above, could reduce short-circuit voltage and fill factor). Consistent with the reduction in carrier concentration, the depletion width for the same voltage bias (e.g., zero bias) is larger. Unlike the interface recombination enhancement due to ZnMgO deposition, the reduction in the carrier concentration in the bulk of CIGS is rather unexpected. The classical CV interpretation assumes a one-sided asymmetrical junction. This is reasonable when the junction is formed predominantly by the degenerate Al-doped ZnO layer and the lightly p-doped CIGS layer (with lightly n-doped CdS and intrinsic ZnO in between). Because the intrinsic ZnO layer is changed, it is necessary to verify that the one-sided asymmetrical junction interpretation is still valid. For the carrier concentration profiles to be comparable, the n-type side of the junction should remain heavily doped for all the samples. We use SKPFM to inspect the location of the electrical junction and extent of the depletion region in the bulk of CIGS.

As seen in Fig. 6, the electrical potential profile starts to drop near the CdS/CIGS interface. This is the expected location of the main junction. The depletion region starts from the point where the electrical potential starts to drop and ends at the point where the potential levels off. The SKPFM cannot provide a precise quantitative determination for the depletion width, as we discussed in Ref. 18, because the long-range Coulomb force between the tip and a sample makes the potential profile broader than the actual depletion width. A qualitative comparison of the potential profiles taken on the device with a ZnMgO window and the device with a ZnO window layer shows that the potential profile on the device with a ZnMgO window is dramatically broader (\(\sim 2\ \mu m\)) than on the device with a ZnO window (\(\sim 200\ nm\)). The sample used in Ref. 19 was grown under nominally the same condition as the samples studied in this work except that it was grown on a GaAs substrate. Prior to the SKPFM experiment, the sample was cleaved and the cross section not polished. However, the devices used for the studies in this work are grown on glass substrate. The cross-sectional surface after cleaving is rough for the SKPFM measurement. Therefore, we mechanically polished the cross sections prior to the measurements. Although we cannot at present exclude that the possible reason of the wide depletion region of the ZnMgO-replaced device is due to the polishing procedure, we are reasonably confident that the values of the depletion region measured by both SKPFM and CV technique are consistent.

With the assistance of SCAPS simulation software, we further examined the influence of the interface states and the lightly doped ZnMgO window layer. The parameters used in the baseline model are taken from Ref. 21 except for the carrier concentration in CIGS (\(1 \times 10^{16} \text{ cm}^{-3}\)), carrier concentration in Al–ZnO (\(1 \times 10^{20} \text{ cm}^{-3}\)), defect density in CdS (\(1 \times 10^{17} \text{ cm}^{-3}\)), and conduction-band offset between ZnMgO/CdS (0 eV), and the bandgap of ZnMgO (3.6 eV). Interface states at both the CdS/CIGS and ZnMgO/CdS interfaces, assumed to be of donor type and Gaussian distribution (with a distribution broadening of 0.1 eV), may become positively charged and thus skew the capacitance-voltage curve. SCAPS simulation results indicate that the apparent hole concentration at zero bias changes less than 50% as the density of interface states varies from \(1 \times 10^{12}\) to \(1 \times 10^{14} \text{ cm}^{-2}\) and their energetic position varies from midgap to 0.4 eV below the conduction band edge (of the material with the smaller bandgap). The other factor that could affect the CV measurement is the doping in the ZnMgO layer. The undoped ZnMgO exhibits resistivity so much larger than the undoped ZnO layer that it exceeds the measurement range of the Hall measurement. It is possible that the residual n-type doping in ZnMgO is one to two orders of magnitude lower than that of ZnO \(\sim 10^{18} \text{ cm}^{-3}\). At a donor concentration...
lower than $10^{17}$ cm$^{-3}$, the ZnMgO layer is likely depleted at zero bias. The width of the depletion region measured by CV thus includes the contribution from the ZnMgO layer. This contribution, which has an upper limit of the thickness of the ZnMgO layer, is much smaller than the observed increase in depletion width. The application of reverse bias, however, introduces further depletion only in CIGS because the Al-doped ZnO is degenerately doped. Therefore, the apparent hole concentration measured by CV at small reverse bias is not significantly affected by a lightly doped ZnMgO layer. SIMS simulation results indicate that the apparent hole concentration at zero bias changes by a factor of less than 3 when the doping in ZnMgO varies from $1 \times 10^{17}$ to $1 \times 10^{19}$ cm$^{-3}$. Therefore, it appears that neither the presence of positive interface charges nor the reduced donor concentration in the ZnMgO layer is significant enough to reduce the apparent hole concentration by CV experiment to below low $10^{15}$ cm$^{-3}$. The CV results thus point us to the more obvious mechanism—reduction in carrier concentration in CIGS due to sputtering of ZnMgO.

What then causes the reduction in the CIGS carrier concentration in samples with ZnMgO? Clearly, Mg may play a part. Prior studies have indicated that Mg, similar to Zn and Cd, can function as a donor in CIGS. We use SIMS to measure the atomic concentration profile of Mg. The SIMS profile (data not shown) of the reference sample with a ZnO window layer shows that Mg content is above the detection limit (low $10^{16}$ cm$^{-3}$) up to depth of $0.6 \mu$m. The Zn signal qualitatively parallels the Mg signal, indicating the drive-in effect. However, the drive-in distance as judged by the Se, Cu, and In signals at the rear of CIGS is much shorter ($<0.2 \mu$m). We do not know how to compare the drive-in distance in Mo and that in CIGS, so we refrain from drawing a conclusion here. Further SIMS experiments to reveal the quantitative Mg profile with better experiment design and detection limit are to be conducted in the future.

A theoretical study indicates that Mg, being a group-II cation, can act as either a donor or acceptor, depending on the lattice sites it occupies. When Mg occupies the Cu site in both CuInSe$_2$ and CuGaSe$_2$, it behaves as a donor. When Mg occupies the Ga or In sites, it behaves as an acceptor. Experimental results also confirm that Mg acts as a donor in both CuInSe$_2$ (Ref. 23) and CuGaSe$_2$. Near the surface, the CIGS absorber material grown in our group is known to be Cu deficient. In such case, Mg atoms are more prone to taking the Cu sites than those of group-III atoms. Therefore, Mg atoms act as donors near the CIGS surface, which, in turn, compensates the native $p$-type doping and leads to reduced apparent hole concentration. Similar to the case of Zn and Cd, the $n$-type doping capability of Mg can be potentially useful in inducing type inversion and forming buried homojunction something for which the chemical-bath-deposited CdS is thought to be responsible. Of course, such potential can be fully realized only if the doping and migration characteristics of Mg become better understood and controllable.

The question then arises as to how Mg migrates into CIGS. One obvious mechanism is the segregation of Mg from ZnMgO. Various reports put the phase segregation of Mg in a wide composition range of 30%–50%. Because the nominal Mg content in the ZnMgO used in sample set 1 is quite high (30%), it is probable that some Mg ions leave ZnMgO and diffuse into CdS and further into CIGS. Because the samples were only subject to moderately heated processes after the ZnMgO deposition, we believe that the Mg migration primarily occurs during the sputtering process. In a ZnO–MgO cosputtering process, the MgO sputtering product is likely active and mobile prior to forming the ZnMgO alloy at the target surface. The kinetic energy of the Mg-containing particles is partially responsible for driving Mg into the CIGS film. We therefore focus our next efforts on optimizing the ZnMgO sputtering process to reduce the adverse effects at the interface and CIGS bulk due to the sputtering damage and Mg migration into CIGS.

In sample set 2 [Fig. 1(b)], 40 nm of ZnMgO (Mg composition is unchanged at 30%) is grown after a layer of intrinsic ZnO whose thickness varies from 10, 20, 30, to 40 nm. The intrinsic ZnO layer recovers the interface to CdS and functions as a barrier layer to Mg migration. In this sample set, the $\sim 400$ meV interface states are not seen. The hole concentration is in the low $10^{15}$ cm$^{-3}$, which is better than the first sample set, but still lower than the reference devices with a ZnO window. The devices in the ZnMgO sample set 2 exhibit progressively better performance as the thickness of the ZnO window is increased. Overall, sample set 2 performs better than sample set 1, but it is still significantly inferior to the reference device. Because the MgO sputtering power (hence, the Mg composition) is still quite high for sample set 2, significant surface damage and Mg migration may still occur.

In sample set 3, the rf power of the MgO target is varied from 240 W to 180, 120, and 60 W. The lower MgO sputtering power obviously reduces the surface damage. The lower MgO sputtering power also directly lowers the Mg composition in the ZnMgO alloy, which reduces Mg segregation. Furthermore, the ZnO sputtering is intentionally started about 5 min earlier than the MgO sputtering, to introduce a thin ZnO layer ($<1$ nm). For practical considerations, this thin ZnO layer is thought to provide no more than a ZnO/CdS interface, but it is apparently effective in reducing surface damage and Mg migration due to MgO sputtering, as well. In this sample set, the $\sim 400$ meV interface states are again absent. The hole concentration is high $10^{15}$ cm$^{-3}$, which is closer to that of the reference device with a ZnO window and explainable by the extra depletion due to the lightly doped ZnMgO layer according to SCAPS simulation discussed above. The device performance improves progressively with reducing MgO sputtering power, with those sputtered at 60 W outperforming the reference devices with a ZnO window layer.

III. CONCLUSIONS

Using capacitive techniques, we show that cosputtering-deposited ZnMgO induces observable interface states at
ZnMgO/CdS and reduces apparent hole concentration in the CIGS bulk material. The bias-dependent activation energy of interface states signifies that the quasi-Fermi level is not pinned at the ZnMgO/CdS interface. The reduction in carrier concentration is partially due to—but cannot be fully accounted for by—the influence of positive charges at the interfaces and the extra depletion because of the more intrinsic ZnMgO window layer. The compensation doping effect of Mg in Cu-poor CIGS material leads to the reduction in the apparent \( p \)-type doping in CIGS, and it is thought to be the most likely cause. SKFPM and SIMS experiments indirectly support this hypothesis. Based on the above understanding, we optimize the sputtering conditions in terms of Mg composition, MgO sputtering time with respect to MgO sputtering time. By implementing a ZnO presputtering scheme to form a ZnO/CdS interface layer less than 1 nm thick, we achieve solar cells with ZnMgO window layers whose performance are comparable to reference devices with a ZnO window layer. The ZnMgO window is deposited at reduced MgO sputtering power, and thus, at reduced Mg composition.

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