Proc. Estonian Acad. Sci. Phys. Math., 2003, **52**, 3, 299–307 https://doi.org/10.3176/phys.math.2003.3.06

Analysis of Zn(O,S) films for Cu(In,Ga)Se₂ solar cells

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Received 20 January 2003, in revised form 24 March 2003

Abstract. Thin films of Zn(O,S), deposited by atomic layer deposition (ALD), were investigated as buffer layers in Cu(In,Ga)Se₂ solar cells. The oxygen to sulphur ratio of these films was varied by alternating diethylzinc (DEZ)/H₂S and DEZ/H₂O cycles. Solar cell efficiencies of up to 14% were achieved, with the best result obtained for 20% DEZ/H₂S cycles. Properties of films deposited on glass were studied, showing a variation of resistivity, structure, and band gap for varying sulphur content. A coupled X-ray photoelectron spectroscopy/ultraviolet photoelectron spectroscopy–ALD system was used to study band alignment at the Cu(In,Ga)Se₂/Zn(O,S) interface. Conduction and valence band offsets were determined for ZnS and Zn(O,S) deposition with 20% DEZ/H₂S cycles and compared to previously determined values for ZnO deposition.

Key words: atomic layer deposition, solar cells, Cu(In,Ga)Se₂, Zn(O,S) buffer layer.

1. INTRODUCTION

Thin film solar cells based on Cu(In,Ga)Se₂ (CIGS) are one of the most promising alternatives for future low cost solar electricity. In the present highefficiency devices, the overall structure is soda lime glass (SLG)/Mo/CIGS/CdS/ ZnO/Al:ZnO, where the CdS layer is a thin buffer layer deposited by chemical bath deposition. To allow for vacuum processing of the whole device, a dry alternative for this buffer deposition is desirable. For environmental reasons, it is also desirable to find a Cd-free buffer material. The simplest option would be to omit the CdS layer and deposit ZnO directly onto the CIGS layer. However, this approach has generally proven unsuccessful, one possible reason for which is considered to be the damage of the CIGS surface induced by the ZnO sputtering.

In [¹], we investigated the direct deposition of ZnO onto CIGS by atomic layer deposition (ALD). This is a soft deposition method well suited for buffer layer

formation, resulting in conformal layers. Comparisons were made between these direct ZnO devices and their CdS-containing reference cells, and this for absorbers of both CuInSe₂ (CIS) and CIGS with a Ga/(Ga + In) ratio of approximately 30%. We observed that the efficiencies of the CIS/ZnO devices are close to those of their CdS-containing reference cells, whereas the difference between the CIGS/ZnO devices and their reference cells is larger. This difference is mainly due to a loss in open circuit voltage.

In connection with these results, we have determined the conduction band offset (ΔE_c) at the CIGS/ZnO and CIS/ZnO interfaces by ultraviolet photoelectron spectroscopy (UPS) in a coupled X-ray photoelectron spectroscopy (XPS)/UPS–ALD system to -0.2 ± 0.2 eV and 0.1 ± 0.2 eV, respectively. A negative offset is a possible explanation for the observed loss in open circuit voltage of the CIGS/ZnO devices. For CIGS, a different buffer material, with higher conduction band minima relative to CIGS, is needed. In this work, we investigate ZnS and Zn(O,S) films as buffer layers on CIGS and determine their band alignment to CIGS.

2. EXPERIMENTAL

The ZnS and Zn(O,S) films were deposited in a Microchemistry F-120 reactor using the sources H₂O, H₂S, and diethylzinc (DEZ). In most cases, the temperature in the deposition zone was 120 °C. The pulsing sequences were DEZ/N₂ purge/H₂O or H₂S/N₂ purge, with pulsing times of 200/400/200/400 ms. For the Zn(O,S) films, sequences with H₂O and H₂S were alternated. For example, a film with 20% H₂S pulses was obtained by running four sequences with H₂O and one with H₂S repeatedly. Here we will use the notation Zn(O,S)20% for such a film. Solar cell devices were fabricated using the process described in [²], except for the CIGS and buffer layers. The CIGS was deposited by co-evaporation as described in [³], with a substrate temperature of 500 °C. Due to poor calibration of the sources, the Ga/(Ga + In) ratio was only around 20% while our standard value was around 30%, and the film thickness almost twice the normal value of 1.8–2 µm.

The ZnS and Zn(O,S) films deposited on glass were characterized by X-ray diffraction (XRD) and optical transmission and reflectance measurements. The resistivity was measured with a four-point probe set-up, and the growth rate determined by measuring the final film thickness using a profilometer.

The coupled XPS/UPS–ALD system, used to study interface formation and band alignment, is described in [⁴]. Samples measuring $8 \times 20 \text{ mm}^2$ were mounted on a rod enabling transfer between the ALD reactor and the XPS chamber without exposure to air. In the coupled system, the ALD reactor is rebuilt to allow for the sample rod, resulting in an increased reaction volume. The pulse duration was prolonged by a factor 10 compared to the standard ALD recipes to ensure coverage of the precursors in the modified reaction volume. The analyser background pressure was around 2×10^{-9} mbar. The positions of the

core level peaks were determined by fitting Voigt functions and using Shirley backgrounds. The position of the Fermi level was calibrated using the Fermi edge of a sputter cleaned Ag foil. The valence band maxima (VBM) were determined by linear extrapolation of the valence band edge to the background level.

3. RESULTS

3.1. Deposition on glass

First, ZnS and Zn(O,S) films were deposited on glass. A complete study of the process window was not performed. Instead, the process parameters used for ZnO deposition were chosen and only the fraction of H_2O to H_2S pulses varied. This was based on the experience from ZnO deposition, where the ALD process temperature window, established on glass, was not directly applicable to CIGS substrates. In many cases, poor or no growth was observed on CIGS although the growth on a glass substrate, loaded together with the CIGS in the reactor, was normal. It was observed that a lowering of the temperature improved the ZnO film uniformity on CIGS. At the same time the ZnO growth rate on glass decreased slightly from above 2 Å/cycle at 150°C to 1.5–1.7 Å/cycle at 120°C. Zn(O,S) was deposited with 5, 10, 20, 33, and 100% H₂S sequences. The growth rate for all of these films was around 1 Å/cycle.

The resistivity of the films, as measured by four-point probe on films of about 200 nm, increases with an increasing sulphur content. We measured resistivities of $2.5 \times 10^{-2} \Omega cm$ for Zn(O,S)5% and $4.4 \times 10^{-2} \Omega cm$ for Zn(O,S)10%. For films with a higher sulphur content, the resistivity was immeasurably high. Our results are very similar to those reported by Yousfi et al. [⁵] in their study of ALD Zn(O,S) buffer layers for CIGS, deposited in a Microchemistry F-120 reactor. In that work, the sulphur content of the film is reported to be higher than the percentage of H₂S pulses, with, for example, above 90% sulphur for 30% H₂S pulses. This means that the growth does not proceed according to the ideal layer-by-layer model.

The results of the XRD measurements are shown in Fig. 1. A clear variation in crystal plane spacing is seen. For Zn(O,S)20% our XRD data suggest an amorphous or nanocrystalline structure in accordance with [^{5,6}]. For ZnS deposition, the obtained plane spacing of 3.11 Å is close to that of the (0 0 2) or (1 1 1) ZnS plane [⁷]. For Zn(O,S)33%, this peak is shifted to 3.0 Å, whereas for Zn(O,S)5% and Zn(O,S)10% H₂S, two peaks are seen with values close to the (1 0 0) and (1 0 1) plane spacing of hexagonal ZnO [⁸].

Optical transmission (*T*) and reflectance (*R*) measurements were performed on 200 nm thick films deposited on glass. The absorption coefficients (α) were calculated using the relationship $T/(1-R) = e^{-\alpha d}$ [⁹], where *d* is the thickness of the film. The absorption coefficient for direct band gap materials such as ZnO and ZnS is related to the band gap through $\alpha \propto (h\nu - E_g)^{1/2}$ [¹⁰]. A plot of α^2 versus energy is shown in Fig. 2. There is quite a large incertitude in the band



Fig. 1. X-ray diffraction spectra for ZnS and Zn(O,S) films deposited on glass. The obtained plane spacing values are 3.1 Å (100%), 3.0 Å (33%), 2.6 Å and 2.9 Å (10%), and 2.5 Å and 2.8 Å (5%). No peaks are observed outside the shown interval.



Fig. 2. Squared absorption coefficient versus photon energy for ZnS and Zn(O,S) films on glass.

gap determination from the extrapolated intercept of these data. For amorphous films, the band gap is often extracted from $\alpha \propto (E - E_g)^2 / E^2$ ([¹¹] and references therein). By using this expression for the Zn(O,S)20% film, a band gap value of 3.0 eV was obtained. However, it was again difficult to define a linear region in the plot. For the 10% film, that exhibited weak diffraction peaks, the band gap was as low as 2.4 eV if the expression for amorphous films was

used. Our results follow those in $[^{5,6}]$ with respect to the observation of band gap minima for some intermediate Zn(O,S) composition. However, the absolute values of the band gaps for the intermediate compositions vary substantially.

3.2. Solar cell devices

Solar cell devices with ZnS or Zn(O,S) buffer layers were fabricated and compared to reference cells with a CdS buffer. The number of ALD cycles and the ratio of H₂S/H₂O containing cycles were varied. For higher sulphur contents, the efficiencies of the devices depend largely on thickness, exhibiting optimal values for films deposited with 100-300 cycles. For Zn(O,S)5%, the currentvoltage behaviour resembles that of devices with no sulphur in the buffer layer. Quality devices were obtained for 300 cycles of Zn(O,S)10% or Zn(O,S)20%, with the best result of 14% efficiency for the Zn(O,S)20% film (Fig. 3). The corresponding reference cells also measured around 14% in efficiency. A detailed device analysis is not the scope of this contribution but will be presented in more detail in a forthcoming work. Here, it is only used to get a first indication on how a variation of the sulphur content in Zn(O,S) can influence the solar cell junction. The low Ga content of the CIGS layers in this study is likely to have some impact on the results, and repeated experiments should be performed with the standard Ga content. Nevertheless, on the basis of the present results, we have chosen to concentrate this XPS/UPS interface study on Zn(O,S)20%, and compare this to ZnO and ZnS.



Fig. 3. Illuminated current-voltage characteristics of a device with a Zn(O,S)20% buffer layer compared to its reference cell containing CdS. The solar cell parameters open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and efficiency are also given.

3.3. XPS/UPS study

For the XPS/UPS studies, standard [²] SLG/Mo/CIGS substrates, with a Ga content around 30%, were used. The samples were transferred to the analysing chamber either directly from the CIGS evaporation chamber, with a maximum air exposure time of 30 min, or after intermediate storage in vacuum. Core level and Auger peaks were collected for Cu, In, Ga, Se, Zn, S, Na, O, and C using non-monochromatic Mg and Al K α radiation. Valence band spectra were collected with He I and II lines, respectively. The sample was then introduced into the deposition zone of the ALD reactor and heated to 120 °C. A number of deposition cycles were performed after which the sample was withdrawn into the XPS chamber and cooled down. A new set of spectra was collected and the procedure was repeated until a thick ALD film was obtained. For the ZnS deposition cycles between the XPS analysis numbered 10/10/30/200 and for Zn(O,S)20%, 20/30/200. With an approximate growth rate of 1 Å/cycle, this should yield up to 25 nm thick films.

The valence band offset (ΔE_v) was determined by comparing the VBM-In4d distance on the CIGS surface, the In4d-Zn3d distance for a thin overlayer film, and the Zn3d-VBM distance on the thick film. These spectra are shown in Fig. 4 for the ZnS deposition. The evolution of the XPS core level peaks was studied to separate possible band bending from chemical shifts due to, for example, intermixing. In our case, a shift of 0.05–0.07 eV for all CIGS peaks was observed after ZnS deposition, and concluded to be due to band bending. In the Zn(O,S)



Fig. 4. Valence band spectra collected with He II 40.8 eV radiation of (1) untreated $Cu(In,Ga)Se_2$ (CIGS) surface, (2) CIGS substrate with thin ZnS film, and (3) thick ZnS film. In spectra (2), the position of the Zn 3d peak at around 10 eV coincides with the In 4d satellite from the He II 48.4 eV line, so the peak position was determined after satellite subtraction.

case, a shift of 0.1 eV was observed for all peaks except for the Cu 2p peak that was shifted by 0.2 eV. The reason for this is not clear and intermixing cannot be excluded. The resulting ΔE_v is -1.2 eV for ZnS and -1.3 eV for Zn(O,S)20%, compared to -2.2 eV for CIGS/ZnO as previously determined [¹²]. For the calculation of ΔE_c we used the optical band gaps of 3.45 eV for ZnS and 3.0 eV for the amorphous Zn(O,S)20% presented in Section 3.1 and Fig. 2. This gives a ΔE_c of 1.0 eV for CIGS/ZnS and 0.5 eV for CIGS/Zn(O,S), with an estimated total error in the ΔE_c determination of ± 0.2 eV.

4. DISCUSSION

The values of the energy band offsets are based on the assumption that the film composition is equal for films deposited on glass and CIGS as well as for the two reactor designs and for the thin and thick overlayers. To compare the different thick films deposited in the two reactor designs, we compare the Zn Auger parameter, which is the sum of the binding energy of the Zn 2p peak and the kinetic energy of the Zn LMM Auger peak, for these films. By taking this sum, differences due to charging or band bending are eliminated. Our Auger parameters are given in Table 1 together with the atomic concentrations as determined by XPS. In this case, the depositions on CIGS are done in the coupled system, and the depositions on glass in the standard reactor configuration. The change in the Auger parameter closely follows the change in the sulphur to oxygen ratio, indicating how the parameter can be used as a measure of the Zn(O,S) film composition. However, slightly different values are obtained for the Zn(O,S)20% films for the different substrates and the ΔE_c calculation should be corrected for the resulting difference in the band gap. From our optical measurements, we cannot see a clear trend in the band gap versus sulphur content, and a direct measurement of the band gap of the Zn(O,S) film on CIGS would be desirable.

Table 1. Zn Auger parameters and atomic concentrations as determined by X-ray photoelectron spectroscopy of ZnO, ZnS, and Zn(O,S) films. The Zn Auger parameter is the sum of the binding energy of the Zn 2p3/2 peak and the kinetic energy of the Zn LMM peak. The atomic concentrations are determined for Zn, S, and O only, neglecting carbon signals. The films on glass are deposited in the standard reactor configuration, and the films on Cu(In,Ga)Se₂ (CIGS) in the coupled system

	Zn Auger parameter	Reference	Atomic concentrations, %		
			0	Zn	S
ZnO on CIGS	2010.2	2009.8 [¹³]	59	41	_
Zn(O,S)10% on glass	2010.6		36	50	14
Zn(O,S)20% on CIGS	2010.8		27	44	29
Zn(O,S)20% on glass	2011.1		20	44	35
ZnS on CIGS	2011.3	2011.3 [¹³]	9	43	47

Another issue is the composition of the film at the very interface. The untreated CIGS surface has been exposed to air, both during device processing and before the XPS/UPS study. The oxygen, carbon, and sodium contamination layer will therefore be incorporated in some way into the interface region. In previous experiments, we have noticed that the intensity of the O 1s and C 1s peaks diminishes after the standard 30 min heating that precedes deposition, but the peaks are not eliminated. This oxide layer either stays intact during the film deposition, or is incorporated in the growing film. In the latter case, a different sulphur to oxygen ratio could be expected close to the interface for ZnS and Zn(O,S). In the case of thin layers on CIGS, the Zn Auger parameter cannot be determined due to overlap of the Na KLL and Zn LMM peaks.

The difficulties in determination of the true band gap of the Zn(O,S) films on CIGS opens the possibility for several explanations of the obtained high efficiencies with the Zn(O,S)20% film. One could be that there is a large offset, in which case the actual buffer layer thickness must be much thinner than expected to allow for tunnelling, or not completely covering. Another could be that the offset is small enough not to block photoelectrons from the CIGS layer to pass the junction. Further investigations of the Zn(O,S) films on CIGS are required to get a satisfying determination of the ΔE_c .

5. CONCLUSIONS

We have studied ZnS and Zn(O,S) ALD films for buffer layers in CIGS-based solar cells. The devices in this study show improved performance by inclusion of sulphur compared to direct ZnO cells. The best results were obtained for Zn(O,S)10% and Zn(O,S)20%. The properties of the ALD films, studied on glass substrates, show a variation of structure, resistivity, and band gap for a variation in the sulphur content. We have measured the valence band offset -1.2 eV at the CIGS/ZnS interface and -1.3 eV for CIGS/Zn(O,S)20%. However, some questions remain concerning the film composition close to the interface. By using the band gap values determined from optical measurements the conduction band offset was calculated to 1.0 ± 0.2 eV for the ZnS case. For the Zn(O,S) case, where the band gap varies for small oxygen to sulphur ratio variations, the ΔE_c determination is difficult since the films are not equal on glass and CIGS.

ACKNOWLEDGEMENTS

The authors thank all members of our research team for technical support, as well as scientific input. This work was carried out at the Ångström Solar Center and financially supported by the Foundation for Strategic Environmental Research and the Swedish Energy Agency.

REFERENCES

- Platzer-Björkman, C., Lu, J., Kessler, J. and Stolt, L. Interface study of CuInSe₂/ZnO and Cu(In,Ga)Se₂/ZnO devices using ALD ZnO buffer layers. *Thin Solid Films*, 2003, 431–432, 321–325.
- Kessler, J., Bodegård, M., Hedström, J. and Stolt, L. Baseline Cu(In,Ga)Se₂ device production: control and statistical significance. *Sol. Energy Mater. Sol. Cells*, 2001, 67, 67–76.
- Kessler, J., Chityuttakan, C., Schöldström, J. and Stolt, L. Growth of Cu(In,Ga)Se₂ films using a Cu-poor/rich/poor sequence: substrate temperature effects. *Thin Solid Films*, 2003, 431– 432, 1–5.
- Sterner, J., Kessler, J. and Stolt, L. XPS instrument coupled with ALCVD reactor for investigation of film growth. J. Vac. Sci. Technol. A, 2002, 20, 278–284.
- Yousfi, E., Asikainen, T., Pietu, V., Cowache, P., Powalla, M. and Lincot, D. Cadmium-free buffer layers deposited by atomic layer epitaxy for copper indium diselenide solar cells. *Thin Solid Films*, 2000, 361–362, 183–186.
- Sanders, B. and Kitai, A. Zinc oxysulfide thin films grown by atomic layer deposition. *Chem. Mater.*, 1992, 4, 1005–1011.
- McMurdie, H. F., Morris, M. C., Evans, E. H., Paretzkin, B. and Wong-Ng, W. New X-ray diffraction powder patterns from the JCPDS associateship. *Powder Diffr.*, 1986, 1, 77 (JCPDS file 36-1450).
- Schulz, H. and Thiemann, K. H. Structure parameters and polarity of the wurtzite type compounds Sic–2H and ZnO. *Solid State Commun.*, 1979, **32**, 783–785 (JCPDS file 89-1397).
- 9. Hong, W. Extraction of extinction coefficient of weak absorbing thin films from special absorption. J. Phys. D: Appl. Phys., 1989, 22, 1384–1385.
- 10. Pankove, J. Optical Processes in Semiconductors. Dover Publications, New York, 1971.
- Jellison, G. E. and Modine, F. A. Parameterization of the optical functions of amorphous materials in the interband region. *Appl. Phys. Lett.*, 1996, 69, 371–373.
- Sterner, J., Platzer-Björkman, C. and Stolt, L. XPS/UPS monitoring of ALCVD ZnO growth on Cu(In,Ga)Se₂ absorbers. In *Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich, 22–26 October, 2001* (McNelis, B., Palz, W., Ossenbrink, H. A. and Helm, P., eds.). WIP-Munich/ETA-Florence, 2001, 1118–1121.
- 13. Briggs, D. and Seah, M. P. Practical Surface Analysis, 2 edn., Vol. 1. John Wiley & Sons, Guildford, 1990.

Cu(In,Ga)Se₂ päikesepatareide Zn(O,S) kilede analüüs

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Aatomkihtsadestatud Zn(O,S) kilesid uuriti kui puhverkihte Cu(In,Ga)Se₂ päikesepatareides. Hapniku ja väävli suhet kiledes muudeti dietüültsink (DET)/H₂S ja DET/H₂O tsüklite vaheldumisega. Päikesepatarei kõrgeim kasutegur 14% saavutati juhul, kui 20% sadestustsüklitest olid DET/H₂S pulsid. Aatomkihtsadestussüsteemiga ühendatud röntgenfotoelektronspektroskoopia ja ultraviolett-fotoemissioonspektroskoopia aparatuuriga vaadeldi energiatsoonide sobitumist Cu(In,Ga)Se₂ ja Zn(O,S) piirpinnal. Määrati juhtivus- ja valentstsooni nihked ZNS ja 20% DET/H₂S sadestustsükli abil valmistatud Zn(O,S) puhverkihtide puhul ning võrreldi andmeid varasemate tulemustega, mis olid saadud siis, kui päikesepatarei puhverkihiks oli ZnO.