Influence of substrate and its temperature on the optical constants of $CuIn_{1-x}Ga_xSe_2$ thin films

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Abstract: We investigate the influence of substrate and its temperature on the optical constants of $CuIn_{1-x}Ga_xSe_2$ (CIGSe) thin films using the Transfer-Matrix (TM) method. The optical constants of a CIGSe layer on top of a TCO layer were calculated considering the realistic optical constants of the TCO (transparent conducting oxide) layer after CIGSe deposition. It was found that TCO substrates could influence the optical constants of CIGSe layers and that the ITO (Sn doped In_2O_3) substrate had a larger impact than IMO (Mo doped In_2O_3) for the CIGSe (x=0.4)

film when comparing to a reference on bare glass substrate. Additionally, the varied substrate temperatures did not impact the optical constants of CGSe (x=1). For CIGSe (x=0.4), the refractive index n stayed relatively independent although at low temperature the grain size was reduced and the Ga/(Ga+In) profile was altered compared to that at high temperature (610 °C). In contrast, the extinction coefficient k at low temperature showed absorption at longer wavelengths because of a lower minimum bandgap ($E_{g,min}$) originating from reduced inter-diffusion of Ga-Se at a low substrate temperature.

1. Introduction

In the last few decades, $CuIn_{1-x}Ga_xSe_2$ (CIGSe) thin films have attracted considerable attention due to their promising application in thin-film solar cells [1, 2]. The CIGSe layer, being the absorber, determines the optoelectronic properties of the solar cell device to a great extent, accurate optical constants (refractive index n, extinction coefficient k) of this layer are hence critical to understand and predict the optical

properties of the entire device. However, great discrepancies are found among the optical constants available in the literature [3-9], which can lead to non-negligible errors in optical simulations for specific samples. It is well known that the experimental parameters can affect the formation and resulting properties of thin films. This is proven to be strongly pronounced for the ternary or quaternary CIGSe compound [10-12]. Although the extraction of optical constants with a high precision is difficult, we can assume that the dominant cause for discrepancies between films arises from physical differences in the film, rather than experimental uncertainties.

Recently, ultra-thin (with absorber less than 500 nm thick) solar cells are emerging because of the potential to further reduce the material consumption and resulting cost [13-15]. However, the high efficiency can't be maintained when the absorber is less than 500 nm thick [13], one of the main underlying reasons is the incomplete absorption of the solar spectrum. If solar cells of this type are directly grown on transparent conducting oxide (TCO) contacts instead of conventional

opaque metallic Mo substrates, it will enable the implementation of light trapping technologies from the rear side, thus helping to better utilize the solar spectrum and maintain the efficiency. Furthermore, the CIGSe solar cells on TCO substrates have applications in tandem and bifacial devices, which have the potential to further improve the efficiency [16-19]. To realize a high efficiency together with the reduction of material consumption, optical simulation thus appears especially important, because it can provide theoretical guidance on how to optimize the structure optically and achieve an optimum use of the solar spectrum [14, 17, 20]. For accurate simulation, realistic and accurate optical constants are needed. Two factors which could significantly affect the optical constants of specific CIGSe films are substrate material and substrate temperature. In addition, CIGSe solar cells deposited at low temperature are also a focus of current research due to the possibility of further cost reduction without worsening the device performance [21]. Furthermore, a low substrate temperature benefits both the performance of a single CIGSe solar cell on TCO

substrate [22] and the stability of the bottom CIGSe cell during the deposition of a top cell in monolithic tandem solar cells [23]. Despite this, to the best of our knowledge, little information has been reported regarding the influence of the substrate and its temperature on the optical constants of CIGSe layers. Therefore, we re-investigated the optical constants of CIGSe layers considering the aforementioned two parameters (TCO substrate and its temperature) in this paper.

The Transfer-Matrix (TM) method [8, 9, 24, 25] was applied to investigate the optical constants of CIGSe films. The TM method is a 1D simulation method for light propagation inside a layer stack taking multiple reflections into account. At each interface, light will be divided into two parts (reflected and transmitted). The reflected (transmitted) portion of light depends on the optical constants of two media at the interface. This method is widely used in conjunction with the optical measurements of reflectance (*R*) and transmittance (*T*) at normal incidence, which is the same illumination geometry as in the solar cells

[25]. We have previously reported the calculation of optical constants of CIGSe layers directly on glass substrates by applying the TM method [9]. In this paper, we extended the model for the CIGSe layers on TCO substrates. An in-house software package named RefDex based on the TM method was developed using the programming language Matlab™ [26], which enables the calculation of optical constants of an arbitrary layer in the layer-stack structure.

2. Experiments

In this work, $CuIn_{1-x}Ga_xSe_2$ ($0 \leq x \leq 1$) thin films were taken for the investigation of their optical constants. CIGSe films were grown via the standard 3-stage co-evaporation process [27]. In the 1st stage, the Ga-Se and In-Se precursors were deposited seperately with the sequence of the Ga-Se precusor prior to In-Se at the substrate tempertaure T_1=410 °C; during the 2nd stage, the substrate temperature was ramped up to T_2, Cu was evaporated and terminated at Cu/[Ga+In] of 1.06; Ga-Se and In-Se evaporation were carried out again but simutaneously until Cu/[Ga+In] reached around 0.88 in the 3rd stage. The substrate

temperature in the 2nd and 3rd stage keeps the same but higher than that in the 1st stage, the substrate temperature mentioned in this paper denotes the temperature T_2 unless it is specified. IMO (Mo doped In_2O_3) and ITO (Sn doped In_2O_3) were employed as the TCO substrates for their high conductivity and successful application in CIGSe solar cells [22, 28]. The TCO layers were fabricated in a base pressure of 10^{-5} Pa at room temperature by magnetron sputtering. The In/Sn composition of the target is 90:10 wt%. The deposition rate was around 1.1 nm/s and the final thickness of TCO layers was approx. 200 nm. Since transmission measurements for Mo substrates are not possible due to the high absorption of Mo, we used CIGSe films coated on glass substrates (microscope slides, see Figure 1) as a reference for comparing the effect of the TCO substrates. To investigate the influence of substrate temperature on the optical constants of CIGSe, the films were deposited at substrate temperatures of 610 °C and 440 °C on glass substrate. Aqueous Bromine solution was introduced to reduce the effect of surface roughness on the calculation of optical constants of

CIGSe films [9] and to etch the CIGSe films [29] completely for the investigation of optical constants of TCO layers. Optical measurements were carried out using an UV-Vis photospectrometer with an integrating sphere. Scanning Electron Microscopy (SEM) was applied to determine the morphology information of CIGSe films and the thickness of each layer. Energy dispersive X-ray spectroscopy (EDX) was used to investigate the In-Ga inter-diffusion across the CIGSe absorbers.

3. Results and discussion

3.1. Influence of substrate

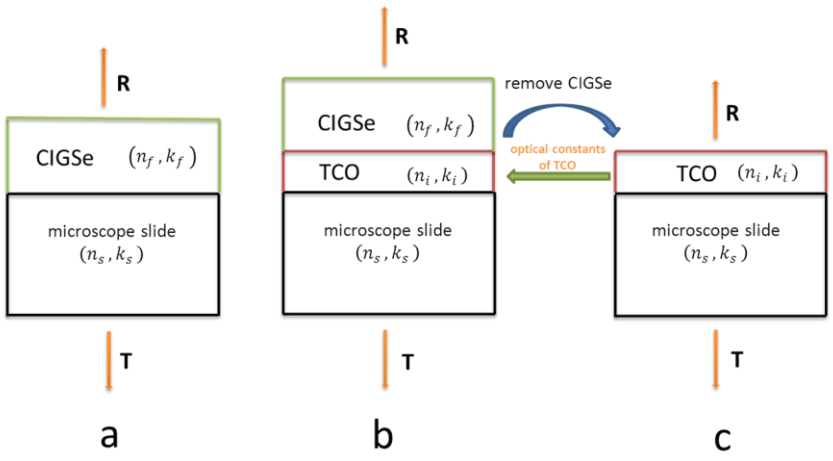

Figure 1. Schematic of the layer-stack structure for the determination of optical constants: (a) air/ CIGSe/microscope slide/air, (b) air/ CIGSe /TCO/microscope slide/air, (c) air/TCO/microscope slide/air

Figure 1 schematically illustrates the determination of optical constants of CIGSe samples. The TM method allows the calculation of *R/T* of a multilayer structure as a function of optical constants and thickness of each layer. Inversely, it can extract the optical constants of an arbitrary layer if all other parameters are known, (for a more detailed description, see Ref. 8, 9). Since the thickness of each layer and optical properties (*R/T*) of the whole structure can be measured and optical constants of the microscope slide and air are known, it is possible to calculate the optical constants of a CIGSe film just on a glass substrate directly. This is depicted in Figure 1(a). In Figure 1(b), however optical constants of both the TCO and the CIGSe are unknown. Additionally, the CIGSe deposition could alter the optical constants of the underlying TCO, using optical constants of TCO before the CIGSe deposition could

introduce a large error in the calculation of optical constants of the CIGSe film on TCO substrate. Thus the optical constants of the TCO layer should be obtained after the CIGSe deposition. The steps of calculation are as follows: (1) *T* and *R* are measured for the structure in Figure 1(b); (2) The CIGSe layer is then completely removed by aqueous Br_2 solution (TCO layers do not react with Br_2 solution), the remaining structure is illustrated in Figure 1(c), *R* and *T* are measured for this structure; (3) The structure configuration in Figure 1(c) is the same as that in Figure 1(a). Optical constants of the TCO layer in the structure of Figure 1(c) are then calculated via the TM method as it was done for the CIGSe layer in the structure of Figure 1(a); (4) The optical constants of the TCO layer are now known and they are introduced in the structure of Figure 1(b), finally the optical constants of CIGSe on top of the TCO layer can be obtained by the TM method. The step (2) and (3) should be emphasized during the calculation process, because they enables the most realistic optical constants of the TCO layer underneath the CIGSe layer to be obtained. This determines the

accuracy of the further calculation of optical constants of the CIGSe layer on top in step (4). Figure 2(a) quantitatively compares the optical constants of the ITO layer before and after the CIGSe deposition, a large discrepancy was observed. This validates the necessity to extract the TCO optical constants after the CIGSe deposition. When trying to use the optical constants of the ITO layer before CIGSe deposition in step (4), we could not obtain reasonable optical constants of CIGSe thin films from our calculation (not shown here). The optical constants of the glass substrate were investigated as well both before and after CIGSe deposition, but they were found to be stable.

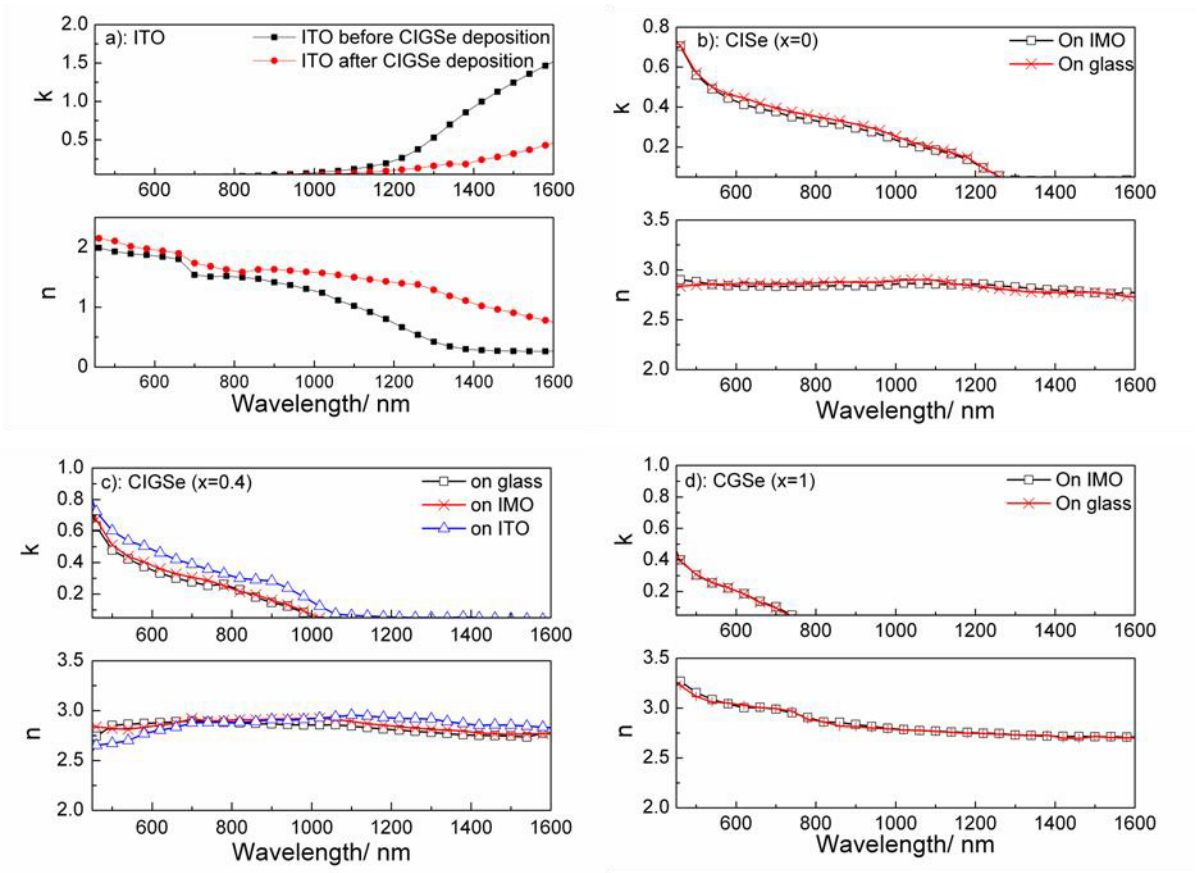

Figure 2. Optical constants of (a) the ITO layer before and after the CIGSe deposition process, (b) CISe, (c) CIGSe and (d) CGSe layers on glass and TCO substrates. To compare the influence of different TCO substrates on the optical constants of CIGSe layers, both ITO and IMO were used as the substrates for the CIGSe (*x*=0.4) layer.

The calculated optical constants of CIGSe layers (*x*=0, 0.4, 1.0) on different substrates are depicted in Figure 2(b), (c) and (d), respectively.

For these three CIGSe samples, we can observe small differences for both refractive index *n* and extinction coefficient *k* between the layers deposited on glass substrates and those on IMO substrates. Despite this, we should stress that the differences are possibly dependent on the TCO layer. To verify this, optical constants of the CIGSe (*x*=0.4) layer on the ITO substrate were also investigated and are illustrated in Figure 2(c). The optical constants on ITO substrate exhibit large differences from those on IMO and on glass substrates. To compare the impact of deviation in optical constants of the CIGSe (*x*=0.4) layer on IMO and ITO substrates, we applied the TM method forward to simulate the *R/T* of the structure air/CIGSe/glass substrate as in Figure 1(a). Since there is no absorption in the glass substrate, the absorbance (*A*) of the CIGSe layer (100%-*R*%-*T*%) could be deduced. The thickness of the CIGSe layer was set to 500 and 2000 nm. From Figure 3, we observe a distinct deviation in absorbance for the two absorbers with different optical constants. The deviation is more pronounced for the 500 nm thick layer. Assuming the complete conversion of absorbed photons to current

under standard AM 1.5 illumination condition, the corresponding deviation of current density J_{sc} can reach 0.8 mA/cm^2 for the 2000 nm thick CIGSe layer and 2.1 mA/cm^2 for 500 nm. This implies the accurate and realistic optical constants are of high necessity to simulate the optical properties of CIGSe solar cells, especially for the thinner absorber. Therefore, for the ultra-thin solar cell, which especially needs theoretical simulations to guide the design of light trapping, realistic and accurate optical constants of CIGSe layers are more significant.

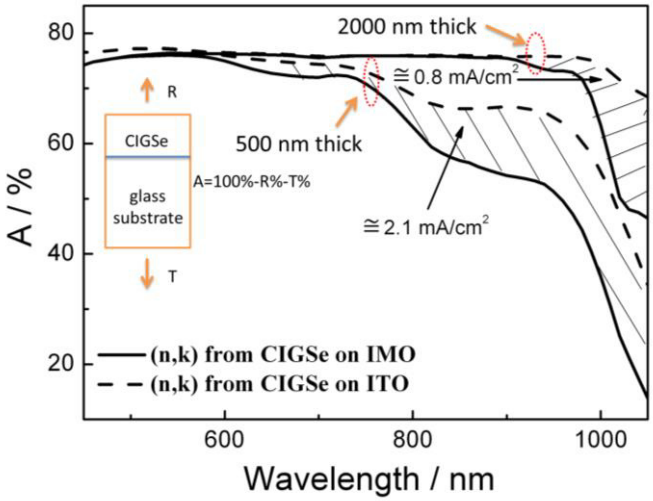

Figure 3. Simulated absorbance *A* of the CIGSe layer in the structure of air/CIGSe/glass substrate for CIGSe thickneses of 500 nm and 2000 nm.

The (*n,k*) of CIGSe are those corresponding to ITO and IMO substrates in Figure 2(c).

However, how the different TCO substrates influence the optical constants of the CIGSe layers is beyond the scope of this paper. Due to the multitude of CIGSe deposition techniques, the variations in recipes even for the same technique, and the further complications of different TCO layers, we here emphasize the proposed model for considering the influence of TCO substrates on the optical constants instead of universal accuracy and applicability of our data compared to those from other literature.

The proposed model can be applied not only to calculate optical constants of the CIGSe layers on the TCO layers, but also possibly to investigate the optical constants of other compact layer in a relatively flat and transparent layer-stack structure, e.g ZnPc on ITO/glass substrate in organic solar cells [30]. The TM method can in principle deal with the forward calculation of *R/T* of a structure with infinite

layers [31], so the number of layers in the structure is not limited to three as in our experimental example (CIGSe/ITO/glass) for the inverse calculation of optical constants. But again the accurate optical constants of the layers other than the one to be investigated should be obtained first taking into account that the deposition of other layers can lead to changes of optical constants of already deposited layers. Additionally, the configuration of our experimental samples consists of optically thin films (CIGSe and TCO layers, coherent propagation of light) on an optically thick film (glass substrate, incoherent propagation of light). It should be noted that the TM method can deal with the case of arbitrary sequential combination of optically thin and thick films.

3.2. Influence of substrate temperature

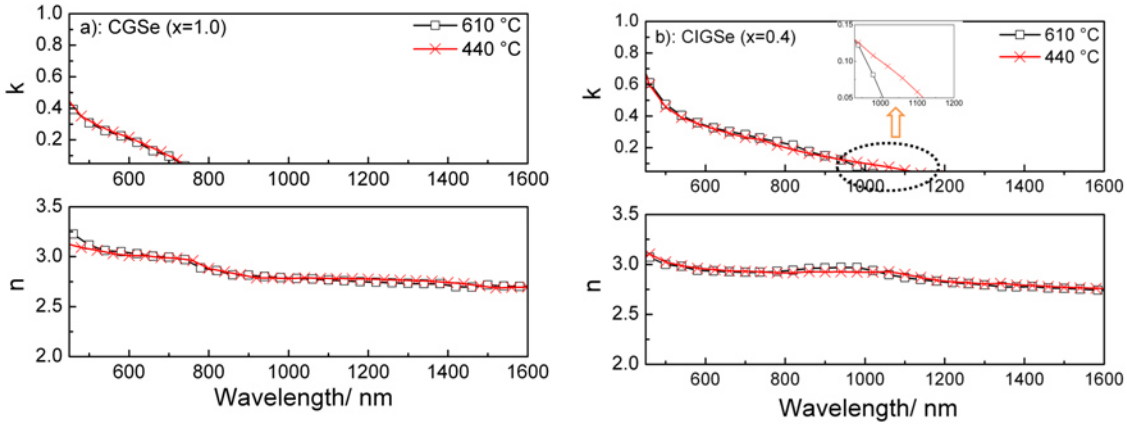

Figure 4. Calculated optical constants of (a) CGSe and (b) CIGSe at two substrate temperatures of 610 °C and 440 °C on glass substrate

Figure 4 compares the optical constants of CIGSe (*x*=0.4) and CGSe (*x*=1.0) at two substrate temperatures of 610 °C and 440 °C on glass substrate. For CGSe both the refractive index *n* and the extinction coefficient *k* remain almost the same. This may be reflected by the similar morphologies shown in Figure 5: both CGSe layers are composed of closely-packed small grains. However, the cross sections of the two CIGSe layers in Figure 5(b) differ in grain size: at the low substrate temperature (440 °C), the CIGSe layer exhibits much smaller grains compared to that at high temperature (610 °C). However, the

grains for both temperatures are closely packed and it is the compactness of the films, which is believed to impact the refractive index values [8, 32]. This can possibly explain the observed fact of the relatively stable refractive indexes for the two CIGSe films. However, the extinction coefficients *k* exhibit differences. The *k* values are comparable in the wavelength range of 450-900 nm for both CIGSe layers, while the *k* values corresponding to a substrate temperature of 440 °C are higher than those corresponding to 610 °C above the wavelength of 900 nm and show absorption in a broader wavelength range. This is related to the changed Ga/(Ga+In) depth profile of the CIGSe layer at different substrate temperatures. Figure 6 shows the EDX line scans across the two CIGSe layers, which indicates a higher Ga/(Ga+In) content at the back side for the CIGSe layer deposited at 440 °C. The EDX results prove that the low substrate temperature (440 °C) can preserve the intentional deposition sequence of Ga-Se prior to In-Se. Owing to the same overall Ga/(Ga+In) ratio for two CIGSe films, lower minimum Ga/(Ga+In) phases at 440 °C are expected.

Because the bandgap is linearly dependent on the Ga/(Ga+In) ratio, the CIGSe layer at 440 °C has a lower minimum bandgap and thus a broader absorption wavelength range. Furthermore, lower Ga/(Ga+In) phases have higher absorption ability, this explains why the absorption ability (*k*) for the CIGSe at 440 °C is higher in long wavelength range (> 900 nm).

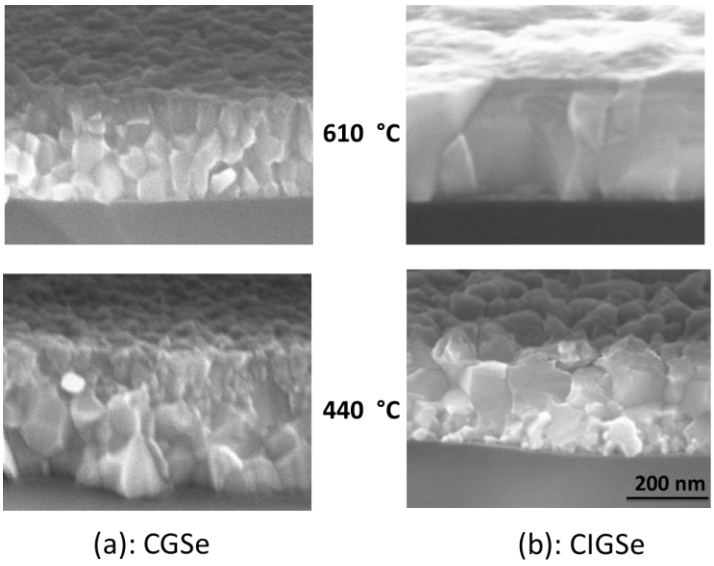

Figure 5. SEM cross sections of (a) CIGSe and (b) CGSe at two substrate temperatures of 610 °C and 440 °C on glass substrate

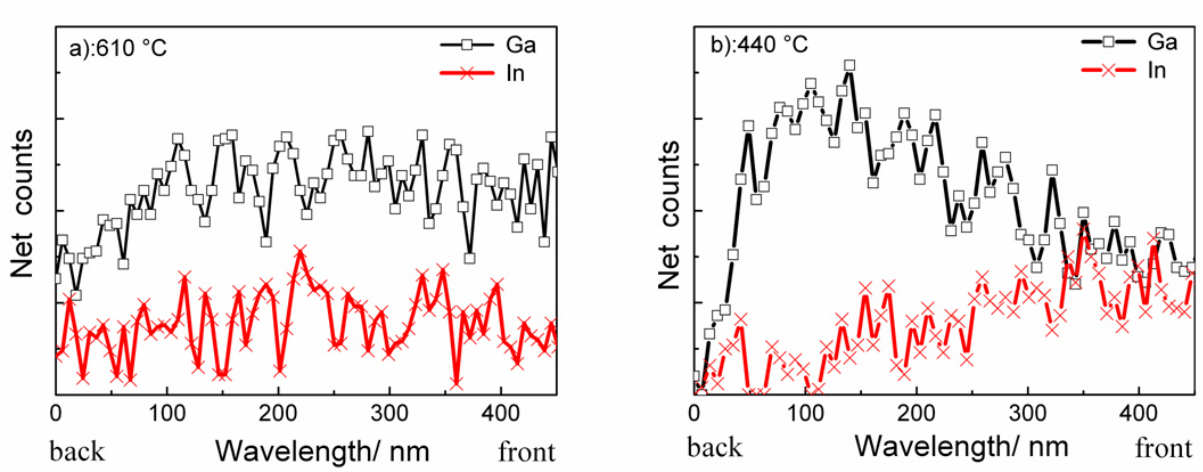

Figure 6. EDX line scan signal (Ga and In) of the CIGSe layer at the substrate temperatures of (a) 610 °C and (b) 440 °C.

4. Conclusion

In this work the optical constants of CIGSe thin films were investigated taking the influences of the TCO layers and substrate temperatures into account. A model was successfully introduced to consider the realistic TCO layers in the calculation of the optical constants of CIGSe thin films based on the Transfer-Matrix method. It was discovered that the TCO layers could influence the optical constants of CIGSe layers and the ITO substrate had a larger impact than IMO compared to the glass substrate. Besides, this model can be applied universally to the layer-

stack structure for the investigation of optical constants. Regarding the influence of substrate temperature, in the case of CGSe, both refractive index and extinction coefficient were little affected by the substrate temperature. For CIGSe (x=0.4), we found that different temperatures have little influence on the refractive index, even though the low temperature changed the morphology (smaller grain size) and the Ga/(Ga+In) depth profile. However, extinction coefficients for the low temperature CIGSe increased in the long wavelength range, which was attributed to the reduced In-Ga inter-diffusion and a resulting lower minimum bandgap.

Acknowledgements

The authors would like to thank C. Kelch for KCN etching, M. Kirsch for IMO and ITO sputtering, J. Albert for technical support. The authors acknowledge the funding from the Helmholtz-Association for Young Investigator groups within the Initiative and Networking fund (VH-NG-

928) and G. Yin specially acknowledges the support of funding from China Scholarship Council.

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