Wet processing in state-of-the-art Cu(In,Ga)Se₂ thin film solar cells

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Abstract

Interface quality plays a key role in solar cell applications. Interface recombination at the front and rear surfaces, which determine this quality, have significant effects on open circuit voltage and fill factor values. In this work, several surface treatments were applied on Cu(In,Ga)Se₂ (CIGS) surfaces to improve the interface quality. Besides, the passivation layer implementation was investigated to reduce interface recombination between the buffer and absorber layers.

Introduction

Thin film (TF) photovoltaics (PV) have become more appealing recently due to their advantages when compared to Silicon (Si)-based solar cells. TFPV have low material usage and thus have a short energy payback time. They allow for the use of a variety of substrates such as rigid glass, or flexible and light materials like steel, molybdenum foil etc. This makes them suitable for building integrated photovoltaic applications. The two main TF absorber materials are Cadmium telluride (CdTe) and copper indium gallium selenide\sulfide (CIGS). Both have high conversion efficiencies and the world record power conversion efficiencies are 22.1 % and 22.9% for CdTe and CIGS TF, respectively. In addition to these advantages, TF modules have outstanding outdoor performance which means better performance in very hot weather or under cloudy circumstances as compared to Si-based solar cells. Given all these advantages, it should not be surprising to find TF modules on the PV-market.

In thin film solar cell technology, to form a p-n junction, a n-type buffer layer is grown/deposited on a p-type absorber layer. The most commonly used buffer is a CdS layer because it forms a suitable junction with CIGS layer. This buffer layer is deposited by using a chemical bath deposition technique. By using the CdS/CIGS structure, the highest record of power conversion efficiency of 22.9% was achieved. However, this structure suffers from parasitic absorption losses in the near-UV due to the small bandgap energy of CdS (2.4-2.5eV) [1]. Furthermore, cadmium is a toxic material which makes the CdS layer undesirable. Because of both environmental concerns and absorption losses, Cd-free buffer layers such as In₂S₃ and Zn-based (Zn(O,S),Zn(O,S,OH) ZnS) semiconductor material are used as an alternative. Amongst the many alternatives, Zn(O,S) is most widely studied, because of its wider and tunable bandgap energy of 2.6-3.8 eV (by changing the O/S+O ratio). Moreover, it has higher transparency when compared to CdS. Hence due to its wider bandgap energy and higher transparency, the parasitic absorption losses are eliminated. Zn(O,S) buffer layer increases

the short circuit current (Jsc) but it lowers open circuit voltage (Voc) due to its typically improper band alignment with CIGS [2].

To produce high-performance solar cells, the quality of the interface between the absorber and the buffer layer plays a crucial role [3,4]. The main reason for the losses on Voc and fill factor (FF) are attributed to increased interface recombination at the front and rear interface and also reduced electron transport through the interface [5,6]. To improve Voc, a passivation layer can be implemented between absorber/buffer layers. Passivation can take place through two different mechanisms. Through a reduction of the density of interface defects, which is called "chemical passivation", or through the reduction of the charge carrier concentration at the interface, called "field-effect" passivation. So far, several studies have shown that adding a metal oxide layer as a passivation layer $(Al_2O_3, GaO_x,$ etc.) between absorber (CIGS) and buffer (CdS) layer improves the Voc [7,8]. However, a clean surface of CIGS is essential before depositing the buffer layer, because the possible undesirable impurities and secondary phases hinder electrical performance of device. KCN and HCl chemical etching are mostly used to remove secondary phases Cu_xSe and ZnSe respectively. Buffiere et al. have shown that ammonia sulfide (AS) $((NH_4)_2S)$ etching, which is less toxic, can be an alternative for KCN etching proving that the minority carrier lifetime is increased [9]. However, the front surface passivation layer and the effect of surface treatments before buffer layer deposition have not been investigated yet for Zn(O,S)/CIGS interface.

In this work, the interface between the buffer (Zn(O,S)) and absorber (CIGS) layer by implementing a passivation layer and surface treatments was investigated. Buffer layers were grown by chemical bath deposition (CBD) and CdS was the reference for comparison. Several etching and cleaning steps using a $(NH_4)_2S$, and two-step treatment aqua reqia $(HCl:NHO_3)$ (AQ) by followed AS were implemented as surface treatment prior to Zn(O,S) and CdS buffer layer deposition, respectively. So far, the TiO_2 material is shown that it is promising material for front surface passivation in kesterite solar cell with point contact opening using KCN process [10]. Also, it is used as an electron selective contact for CIGS solar cell [11]. In light of these performed studies, TiO_2 layer was chosen as a passivation layer to reduce interface recombination. In addition to this, a new process, which is AS etching process to find alternative a KCN etching process, is used to create point contact openings in the TiO_2 passivation. Before the fully finished solar cell characterization, the time resolved photoluminescence (TR-PL) and photoluminescence (PL) measurement is performed. Because both measurements are effective way to take information about interface properties. This work represents a promising starting point for investigation of surface treatments and passivation layer for Zn(O,S)/CIGS interface.

Experimental Section

Surface etching and cleaning with $(NH_4)_2S$: The samples were produced molybdenum (Mo) coated soda-lime (SLG) substrate. The CIGS/Mo/SLG and fully covered TiO_2 layer/CIGS/Mo/SLG samples were dipped into pure ammonia sulfide $((NH_4)_2S)$ solution for 5 or 15 min, and followed by 3 min of rinsing in deionized water. *KCN process:* the fully covered TiO_2 layer/CIGS/Mo/SLG samples were dipped into a 5 wt% solution in H_2O for 2 min. Then samples were rinsed with deionized water and dried with N_2 gun. *Two step surface treatment:* Firstly, the CIGS/Mo/SLG samples were dipped into $HCl:NHO_3$ solution for 20 sec, then the samples directly dipped into pure $(NH_4)_2S$ solution for 5 or 15 min. The samples were rinsed with deionized water for 3 min. After surface treatments, the chemical bath deposition was performed to form the buffer layer on CIGS layer. *TiO_2 surface passivation:* The TiO_2 layers were deposited by spin-coating method with 1000 r/min, 1000 r/min/s^2 for 60 s, two different ethanol-based solution used for desired thickness. KCN and AS treatments were performed on CIGS absorber fully covered by TiO_2 layer. TP-PL and PL measurements were

performed with an excitation wavelength of 532 nm to determine the minority carrier lifetime and defect mechanism.

Results

(NH₄)₂S surface cleaning for CIGS layer

The samples (CIGS/Mo/SLG) were dipped in a pure $(NH_4)_2S$ solution for 5 and 15 min followed by a rinsing deionized water before the Zn(O,S) buffer layer deposition. Figure 1 presents photoluminescence spectra and minority carrier lifetime of Zn(O,S)/CIGS structure for untreated and CIGS surface etched in a pure $(NH_4)_2S$ solution. The untreated sample with the CdS buffer layer is the reference sample for comparison. It can be clearly seen that the untreated sample with Zn(O,S) buffer layer requires the surface treatments to improve interface properties and increase the minority carrier lifetime. The highest lifetime was observed for the 5 min pure $(NH_4)_2S$ surface treated Zn(O,S)/CIGS sample. Post 5 min of etching, the lifetime was observed to decrease. It may occur due to the interface property change for Zn(O,S)/CIGS.

Two-step surface cleaning for CIGS layer

In this work, to reduce roughness of the CIGS layer, aqua regia solution was used instead of bromine solution. Because, the lesser toxic aqua regia can be an alternative method to bromine processing because it is known in the literature to reduce the roughness of the surface [10,11]. Before the buffer layer deposition, one-step and two-step surface treatment were applied to CIGS surface. For one-step surface treatment , the samples were dipped in $HCl:NHO_3$ solution with ratio of 1:3. For two-step surface treatment the samples were dipped AQ and followed by pure $(NH_4)_2S$ treatment for 5 min or 15 min. The AS surface treatment was applied after AQ treatment to remove any possible secondary phase (especially $CuSe_2$) and any other impurities [9]. After both surface treatments, the samples were directly dipped in chemical bath for CdS deposition. The sample with deposited CdS buffer layer was used to understand the effects of this surface treatment, before the investigation of Zn(O,S) buffer layer. Figure 2 shows photoluminescence spectra and the minority lifetime of CdS/CIGS structure. The PL intensity increases for both (one and two-step) surface treatments. It can be said that the surface was improved due to the surface passivation or removing the impurities at the interface. The same trend was also observed before the buffer layer deposition but it is not shown here. The result of TR-PL measurement is shown in Figure 2. The aqua regia surface treatment is not enough to improve surface properties, and, thus AS treatments is used to improve lifetime of the samples. Thus, it can be said that two-step surface treatment improves the surface property of CIGS, and it thus can be an alternative for bromine processing.

(NH₄)₂S and KCN surface treatments on passivation layer for openings

For front surface passivation, several dielectric materials can be used. In this work, TiO_2 was selected for investigation of front surface passivation layers for CIGS thin film solar cells. Because the chemical bath deposition contains ammonia and it is known that TiO_2 is resistive to it, unlike the Al_2O_3[10]. Two different thickness of TiO_2 layer (3 and 6nm) implemented between CdS and CIGS layers. Before the buffer layer deposition, PL and TR-PL measurements were performed to determine the effects of the passivation layer. It is observed that the PL intensity increases when the passivation layer is implemented, but there is no lifetime improvement. For that reason, further investigation is ongoing. Nevertheless, the improvements were observed on the lifetime and PL intensity when both surface treatments and buffer layer were applied. Two chemical baths were prepared to compare surface treatments effects for each thickness. Figure 3 and 4 show the PL spectra and lifetime of CdS/3nm TiO_2 layer/CIGS and CdS/6nm TiO_2 layer/CIGS structures, respectively. It can be clearly seen that the PL intensity increases with all surface treatments. For thinner passivation layer, 5 min

AS surface treatment, the highest PL intensity and lifetime improvement was observed. However, for 15min AS treatment, it is clearly seen that the lifetime and PL intensity decreased, like KCN surface treatment. The reason could be that the TiO_2 layer starts to be disappeared after that treatments. For thicker passivation layer, the PL intensity and lifetime show similar trends for all surface treatments. According to the graphs (Figure 4), it can be said that thick passivation layer blocks the electron transport through CdS layer to the CIGS. For that reason, the lifetime of the untreated passivation layer sample has lower as compared to the surface treatments applied samples. The results show that AS treatment could be a promising alternative process to KCN process. Besides, all of the surface treatments present improved PL spectra and lifetime than untreated samples for each thickness. We believe that this could be the evidence for point openings.

Summary: $(NH_4)_2S$ surface treatment was successfully applied between the Zn(O,S) and CIGS layer. This process is effective to increase minority carrier lifetime when Zn(O,S) buffer layer is used. The proposed two alternative wet chemical surface treatments show promising results for solar cell applications. Two-step surface cleaning ($HCl:NHO_3$ etching followed by $(NH_4)_2S$ treatment) and pure $(NH_4)_2S$ etching process show that they can be safe and non-toxic surface treatment alternatives for highly toxic bromine or KCN processing, respectively. It is shown that TiO_2 can be a front surface passivation material in CIGS solar cells, however more advanced characterization is ongoing.

Tables and Figures

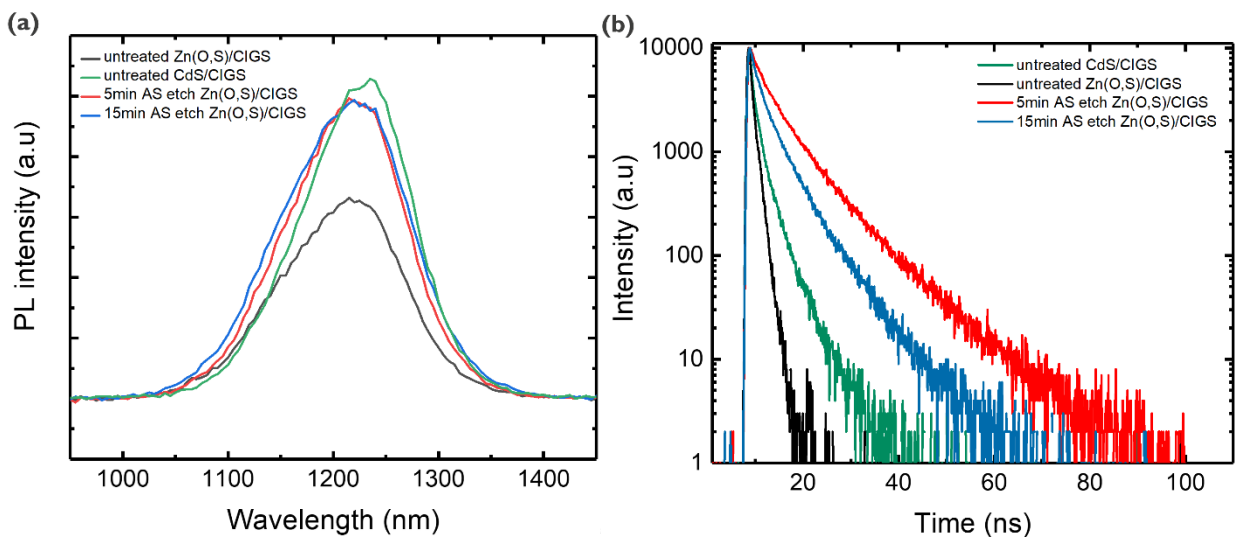
Figure 1: (a) PL spectra, and (b) the lifetime of Zn(O,S)/CIGS structure after pure $(NH_4)_2S$ surface treatment
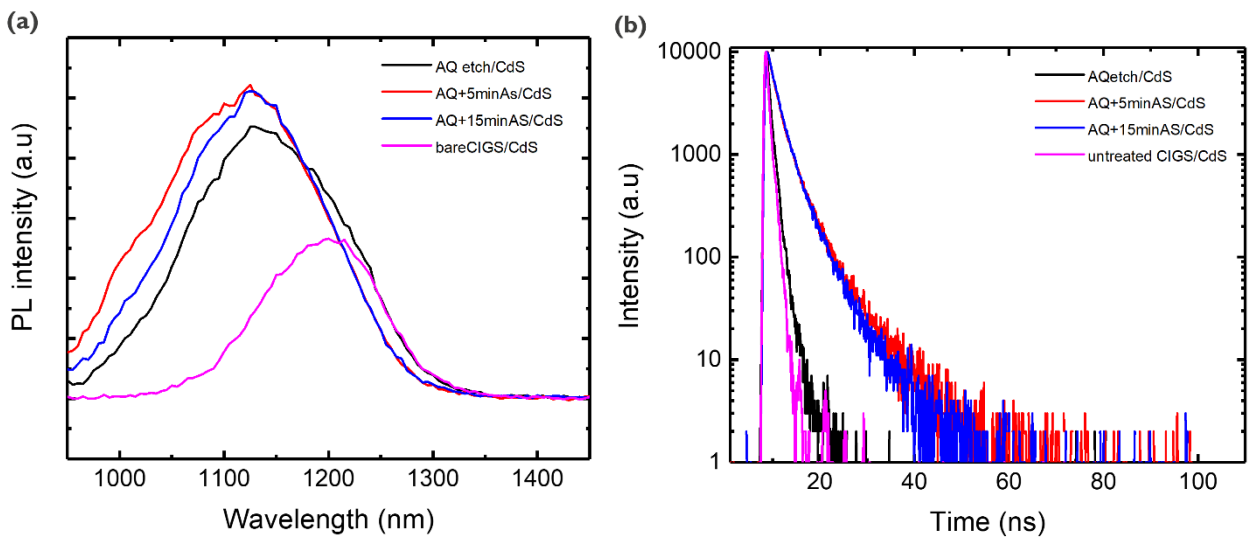
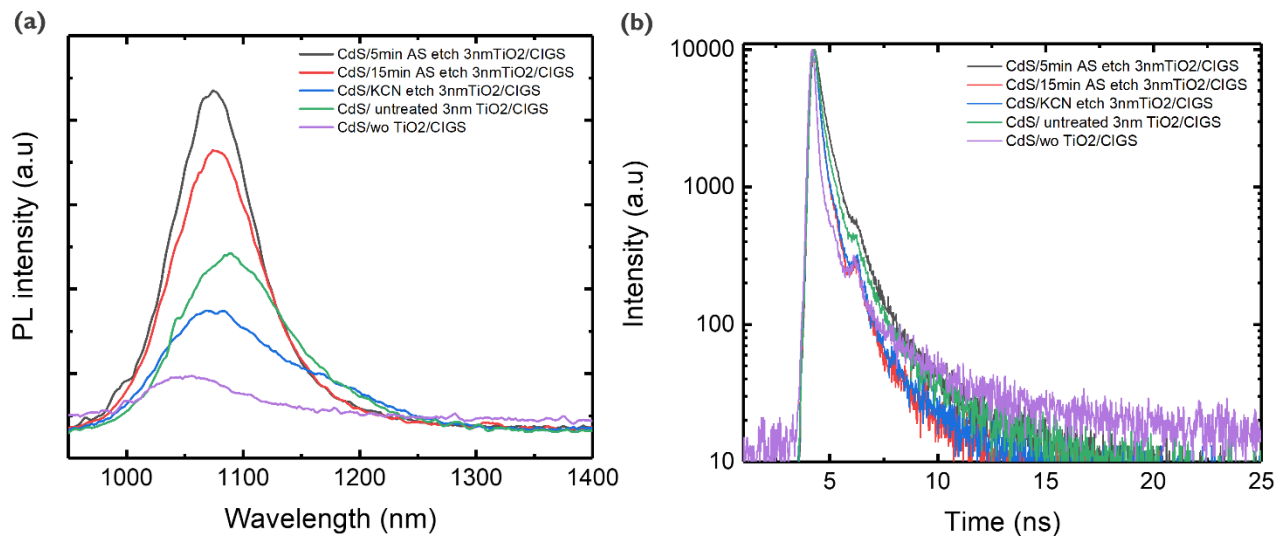Figure 2: After AQ and two-step treatment (a) PL spectra, and (b) liftetime of CdS/CIGS structure

Figure 3: (a) PL spectra, and (b) lifetime of CdS/3nmTiO$_2$/CIGS structure
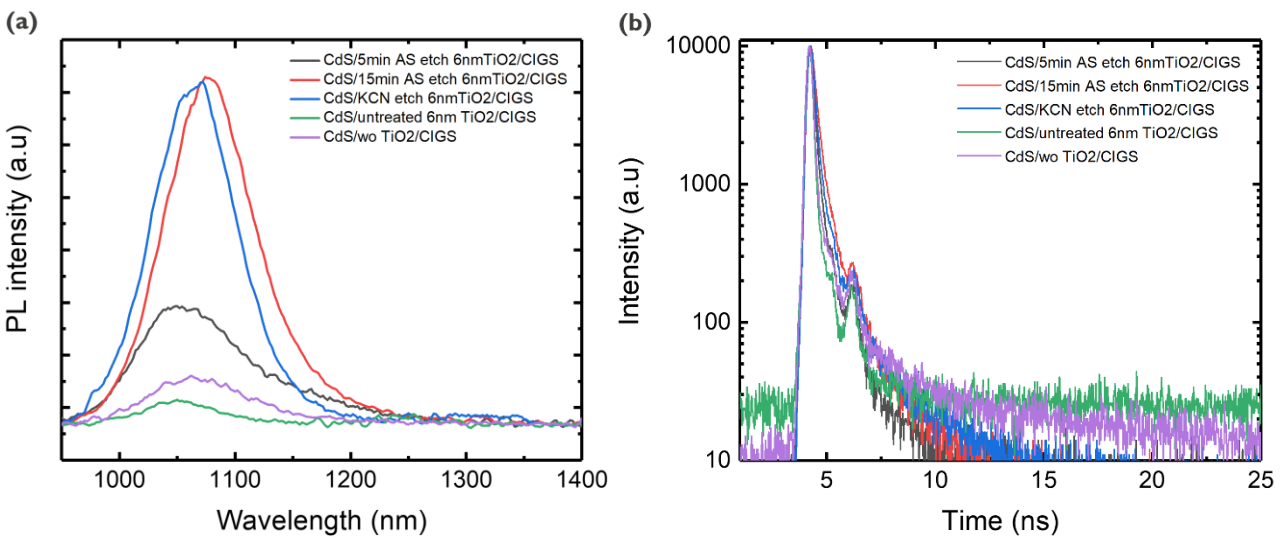

Figure 4: (a) PL spectra, and (b) lifetime of CdS/6nmTiO$_2$/CIGS structure

References

[1] N. Naghavi, D. Abou-Ras, N. Allsop, N. Barreau, S. Bucheler, A. Ennaoui, C. –H. Füscher, C. Guillen, D. Harikos, J. Herrero, R. Klenk, K. Kushiya, D. Lincot, R. Menner, T. Nakada, C. Platzer-Björkman, S. Spiering, A. N. Tiwari and T.Törndahl : Prog. Photovolt Res Appl. **18** (2010), p.411-433

[2] W. Witte, D. Harikos, M. Powalla : Thin Solid Films **519** (2011), p.7549-7552

[3] T. Minemoto, Y. Hashimoto, T. Satoh, T. Negami, H. Takakura, and Y. Hamakawa : J. Appl. Phys. **89** (2001), p. 8327-8330

[4] C. Platzer-Björkman, T. Törndahl, D. Abou-Ras, J. Malmström, J. Kessler, and L. Stolt : J. Appl. Phys. **100** (2006), p.044506

[5] S. Siebentritt : Sol. Energy Mater. Sol. Cells **95** (2011), p. 1471-1476

[6] A. Hultqvist, J. V. Li, D. Kuciauskas, P. Dippo, M. A. Contreras, D. H. Levi and S. F. Bent : Appl. Phys. Lett. **107** (2015), p. 0333906

[7] W.-W. Hsu, J. Y. Chen, T.-H. Cheng, S. C. Lu, W.-S. Ho, Y.-Y. Chen, Y.-J. Chien, and C. W. Liu : Appl. Phys. Lett. **100** (2012), p. 023508

[8] S. Garud, N. Gampa, T.G. Allen, R. Kotipalli, D. Flandre, M. Batuk, J. Hadermann, M. Meuris, J. Poortmans, A. Smets, and B. Vermang : (2018) Phys. Status Solidi A, Early View DOI: 10.1002/pssa.201700826

[9] M. Buffiere, A. A. El Mel, N. Lenaers, G. Brammertz, A. E. Zaghi, M. Meuris and J. Poortmans : Adv. Energy Mater. **1401589** (2014), p. 1-7

[10] S. Ranjabar, A. Hadipour, B. Vermang, M. Batuk, S. Garud, S. Sylvester, M. Meuris, G. Brammertz, A. F. da Cunha, and J. Poortmans : IEEE J. Photovolt. (2017) DOI: 10.1109/JPHOTOV.2017.2692208

[11] W. Hsu, C. M. Sutter-Fella, M. Hettick, L. Cheng, S. Chan, Y. Chen, Y. Zeng, M. Zheng, H. P. Wang, C. C. Chiang and A. Javey : Sci. Rep. **5** (2015), p.16028

[12] A. Slobodskyy, T. Slobodskyy, T. Ulyanenkova, S. Doyle, M. Powalla, T. Baumbach, and U. Lemmer : Appl. Phys. Lett. **97** (2010), p. 251011

[13] V. Depredurand, T. Bertram, M. Thevenin, N. Valle, J. N. Audinot, and S. Siebentritt : Mat. Res. Soc. Symp. Pro. **1771** (2015), p.163-168