Depth profiling of a CdS buffer layer on $CuInS_2$ measured with X-ray photoelectron spectroscopy during removal by HCl etching

B. Johnson[*,a,1], J. Klaer[a], Ch.-H. Fischer[a,b], I. Lauermann[a]

[a]Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15 12489 Berlin, Germany

[b]Freie Universität Berlin, Kaiserswerther Str. 16-18 14195 Berlin, Germany

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

[*]Corresponding Author: benjamin.johnson@alumni.tu-berlin.de, Tel: ++49 30 8062 15694, Fax: ++49 30 8062 43199

1. Abstract

A ∼35 nm thick CdS buffer layer has been wet-chemically deposited on a $CuInS_2$ thin layer solar cell absorber and subsequently removed through a stepwise HCl etch process. Sequential etching times of two and three seconds were initially performed to gradually remove the CdS top-layer and leave the $CuInS_2$ surface intact. After each step an investigation of the sample with X-ray photoelectron spectroscopy was used to determine the stoichiometry and elemental binding energies of the sample surface. After the removal of the CdS layer longer etching times were used to study the long-term effects of the HCl. The resulting depth profile revealed Cu diffusion from the $CuInS_2$ into the CdS, although the Cu atoms did not reach the surface of the buffer layer. In addition, a Cd containing layer was left on the sample surface after more than six hours of etching time and is apparently insoluble in HCl, showing that the Cd-S bonds in this layer differ from those in CdS. This method can also be used with other top-layers to create depth profiles.

Keywords: $CuInS_2$, CdS, Diffusion, Interface, HCl, XPS

2. Introduction

The thin layer solar cell with the structure n^+-ZnO/i-ZnO/CdS/Cu(In,Ga)S_2/Mo/glass is a promising technology with efficiencies reaching almost 13%, depending on the method of production [1, 2, 3]. Although this device can deliver an open circuit voltage in excess of 800 meV [4, 5], higher than its Cu(In,Ga)Se_2 counterpart, the achieved V_{oc} falls short of that expected from its 1.6 eV band gap. The same is true for the more simple $CuInS_2$ system with its 1.5 eV band gap and ∼750 meV V_{oc} [3, 4]. As a consequence of this, the overall efficiency of Cu(In,Ga)S_2-based solar cells is well below that of the low band gap selenide system [6, 7].

One of the most likely points in the solar cell stack to be responsible for these losses is the interface between the Cu(In,Ga)S_2 absorber and the CdS buffer layer [8]-[13]. For this reason, the Cu(In,Ga)S_2/CdS junction is the subject of intense research in order to determine the exact role of the buffer layer and the buffer layer/absorber interface in the completed solar cell. It has been well documented in literature that the conduction band line-up at this

junction is not optimal, the conduction band of the $Cu(In,Ga)S_2$ lying energetically further from the Fermi Level than that of the CdS in solar cell quality materials [8]-[10]. The result is increased charge carrier recombination at the interface [13]-[15].

There are, however, apart from the electronic properties of the $Cu(In,Ga)S_2$/CdS interface, also chemical and diffusion processes at work during junction formation which may influence the properties of the completed solar cell [11, 16, 17].

In order to simplify the picture, one must single out specific processes to investigate which are at work during junction formation, in this case those are the behavior of Cu and Cd. Through depth profiling on the completed junction we obtain information about the processes which are active during junction formation and lead to the properties of the final interface. This is not to say that other processes present during junction formation do not also play an important role in the functionality of the completed device, however, these can be the subject of future investigations.

3. Experimental Details

In this contribution we look at a $CuInS_2$ (CIS) absorber grown by rapid thermal processing (RTP) [3] after three minutes' etching in 5% potassium cyanide solution (KCN) and the application of a full (∼35 nm) CdS buffer layer by chemical bath deposition. This procedure consisted of a standard chemical bath of 15 mL of 0.0165M Cd acetate dihydrate ($Cd(C_2H_3O_2)_2 \bullet 2H_2O$) in 25% NH_3 solution and 0.372M thiourea (H_2NCSNH_2) in 100 mL water. These were mixed in a double-walled glass container and filled to a volume of 200 mL making the final concentrations 0.0012M for the Cd acetate dihydrate and 0.186M for the thiourea. The CIS substrate was then dipped into the chemical bath and left for 7:00 min at 60°C. Subsequent etching steps in approximately 30 mL of HCl (concentration: 4 weight-% and 8 weight-%, diluted from the manufacturer's delivered 32%) at room temperature removed the CdS incrementally with initial etching times of two or three seconds. The surface was studied after each step with X-ray photoelectron spectroscopy (XPS) to determine the

stoichiometry and binding energies of the surface elements. The XPS analysis used Mg Kα radiation and was quantitative, whereby the measured peak was integrated after background removal and normalized by the appropriate number of scans, ionization cross-section, photoelectron mean free path and the transmission function of the electron analyzer [18].

After the removal of the CdS layer, longer etching times were used in order to study the long-term effects of the HCl and to investigate the properties of any residual Cd left on the CIS surface. This investigation has similarities to the experiments done by Rockett, et al. on CdS deposited on epitaxially grown Cu(In,Ga)Se_2 layers [19].

In Rockett's investigation, the sharp-edged morphology typical of epitaxially grown layers was not rounded by the HCl which was interpreted to mean that the acid did not attack the Cu(In,Ga)Se_2. However, in the case of the RTP-$CuInS_2$ used in this investigation it was found that the HCl indeed dissolved the absorber material. Because this investigation aims to determine whether a Cd-containing layer, insoluble in HCl, remains on the CIS surface after the removal of most of the Cd deposited as CdS, as found in [19], it was vital that the Cd-containing CIS surface not be removed by the etching process. This led to the incremental etching approach.

Also, in order to exclude the possibility that the Cd was temporarily removed by the HCl and then "re-deposited" before the sample was taken out of the acid, the sample was regularly switched to fresh acid baths during the longer etch steps. This also diluted any Cd-containing acid solution remaining on the sample surface from prior baths. During the steps below nine minutes of total etch time, the sample spent no longer than 32 seconds in a single acid bath. Thereafter, up to 18 minutes of total etch time, the sample was moved to a new acid bath after every minute. The last etching step of six hours was completed in only one acid bath.

4. Results and Discussion

Initial experiments involving the HCl etching of CdS on RTP-CIS showed that sufficiently high concentrations of HCl can also dissolve the sulfur-based absorber material. Fig. 1) shows a KCN-etched RTP-CIS absorber layer before and after 1 hour in 32% HCl. The difference between the two images can immediately be seen and has been interpreted as a removal of CIS material, i.e. material dissolved by HCl. Although this concentration is much higher than that used in other experiments described later, the sufficient HCl concentration needed to dissolve the CIS was not determined and the result in fig. 1 led, therefore, to the necessity of the incremental etching. SEM images were also made on CIS layers after shorter etching times in HCl with the same concentrations as those found in the following sections of this paper (4 and 8 weight-%). The results were indistinguishable from CIS etched only in KCN.

Fig. 2 shows the resulting changes in surface elemental ratios and binding energy from the incremental HCl etching of CdS on CIS. The times shown on the x-axis correspond to the actual time the sample was in HCl plus one second for rinsing. Thus, the point at three seconds corresponds to two seconds in HCl, plus one second for rinsing which actually stops the etching process. Also important is that the HCl concentration was 4% until the 24 second mark (the black dotted line in fig. 2). After this, the concentration was raised to 8% to accelerate the etching process.

The curves (y-values) in the figure show the development of three elemental ratios during increasing etch time in HCl. The red curve shows the [Cu $2p_{3/2}$]/[Cd $3d_{5/2}$] ratio, the blue curve the [Cu $2p_{3/2}$]/[In $3d_{5/2}$] ratio and the green curve the [Cd $3d_{5/2}$]/[S $2p_{3/2}$] ratio. The ratios were determined with quantitative XPS and have an error of $\pm 10\%$, the entirety of which results from fitting the measured peak surface area. The normalization factors contain only systematic errors and influence the curves in fig. 2 through a vertical shift alone leaving the characteristics of the curves intact. The lower, orange curve shows the development of the S $2p_{3/2}$ binding energy and has an error of ± 0.1 eV which also arises from fitting the

measured peak.

Because of the start-stop action of this experiment, any quantitative conclusions made about the duration needed to remove the CdS would be very inaccurate at short etching times because the error associated with the time axis is rather large (±2 sec), but after longer etching times the error becomes much less significant. This graphic is, however, meant to be qualitative. The logarithmic time scale is used to show all data points conveniently and is not meant to indicate a logarithmic time dependence of the etch process. The points at zero etch time are the data from the sample before etching began, i.e. directly after the deposition of CdS.

The most noticeable feature of fig. 2 is the large change in all four curves between 0 and 18 seconds (marked by the gray dotted line). In this temporal region the [Cu]/[Cd] ratio changes from 0 to 3.99 due to the removal of CdS. The [Cu]/[In] ratio changes from 1.27 to 0.42 and corresponds to an initial value not consistent with CIS changing to one between the values for KCN (0.25-0.30) and freshly HCl-etched CIS (0.53-0.62). The [Cd]/[S] ratio changes from 1.22, a value which corresponds to CdS_{1-x} with x $\sim$ 0.2, to 0.04, a value which is no longer consistent with bulk CdS and further supports its removal from the sample surface and the existence of only a thin remaining layer. This apparently large number of S vacancies may be the result of surface contamination, such as CdO, which raises the surface Cd concentration compared to S and masks the true stoichiometry of the CdS. Also, deviations in the experimentally determined transmission function of the electron analyzer from their true values could also lead to abnormally high values of x. Such deviations would, however, leave the shape of the curves in fig. 2 intact.

The [Cu]/[Cd] ratio, combined with the change of phase seen from the binding energy of the S $2p_{3/2}$ peak, shows that the HCl completely removes the CdS quickly as expected and leaves behind a small amount of Cd whose concentration diminishes further with each successive etch step. However, the Cd was never completely removed from the sample surface and was detectable even after six hours of etching time (data point not shown). The

further increase in the [Cu]/[Cd] ratio after longer etch times is probably due to the partial removal of the CIS itself by the HCl, as discussed in the "Experimental" section of this paper, whereby some of the Cd bound to the CIS surface is also removed. This insolubility shows that the remaining Cd is not present as a constituent of CdS because it cannot be dissolved in HCl. The Cd may, however, still be bound to S because it most probably occupies a cationic lattice position in or on the CIS [16, 20]. The point at 539 sec was taken to estimate the amount of Cd left on the sample surface after the CdS had been removed. Within the information depth of the XPS measurement ($\sim$ 3 nm), the sample was found to contain $\sim$ 0.4% Cd which corresponds to a surface coverage of about 0.1 atomic layers. This number is far larger than that which would be expected from the Cd surface layer which would result only from "re-deposited" Cd after successive acid baths. After 539 sec of total etch time, the amount of "re-deposited" Cd on the sample surface would be far below the detection limit of XPS. This Cd-containing layer will often be referred to as the CIS:Cd layer hereafter.

Moving to the [Cu]/[In] ratio, the blue curve in fig. 2 begins with a relatively high Cu concentration and decreases before and during the time in which the CdS layer is actually removed (0 to 18 sec). This is interpreted as a diffusion of Cu into the CdS layer, whereby the In signal increases as the CdS, together with the diffused Cu, are etched away. The missing points prior to six seconds are the result of a lack of both Cu and In signals until this time and show that Cu does not diffuse through the entirety of the CdS layer to its surface. The [Cu]/[In] signal is initially relatively high because Cu has diffused into the CdS and only a small signal comes from the underlying CIS. As the CdS is removed, the Cu signal continues to rise, but because the contribution to the total signal from CIS also increases, the In signal increases more quickly than the Cu signal. The [Cu]/[In] ratio, therefore, approaches a value more consistent with CIS at the point where the CdS is completely removed. This method is, therefore, in contrast to depth profiling techniques such as sputtering, capable of investigating Cu diffusion without disturbing the CIS which is the actual source of the Cu, i.e., there is no additional physical intermixing of the layers.

It was expected at first that the [Cu]/[In] ratio would approach values between 0.53 and 0.62 for t$\rightarrow \infty$, as found in other experiments after HCl etching of CIS with and without CdS [21]. However, in this case the values of the [Cu]/[In] ratio stabilized around 0.40. A plausible explanation is that after so many etch steps (i.e. extended time in air) the sample surface became contaminated with hydrocarbons or other O and C containing species which masked the true stoichiometry of the surface and reduced the perceived relative Cu concentration and correlates to the O and C peaks seen with XPS. This contamination layer is not, however, the reason for the trends of the [Cu]/[Cd] and [Cu]/[In] ratios seen in fig. 2. In fact, the cover layer would reduce the magnitude of the observed trends, i.e. the changes in concentration ratios: electrons with lower kinetic energies have exponentially lower mean free paths than their higher kinetic energy counterparts and corresponds to an exponentially higher dampening of the signal from the slower electrons. Using Mg Kα radiation the electrons from the Cu $2p_{3/2}$ core level have a kinetic energy of approximately 316 eV while those from the In $3d_{5/2}$ and Cd $3d_{5/2}$ core levels have kinetic energies of 804 eV and 848 eV, respectively.

The final, orange curve in fig. 2 shows the S $2p_{3/2}$ binding energy and has already been briefly discussed. While also displaying a changing value which stabilizes at 18 seconds, this curve has, in contrast to the other curves, a linear slope which is easily seen in a non-logarithmic plot of fig. 2 (not shown). This difference can be explained by the removal of S with the corresponding CdS binding energy and a simple chemical change of the S surface states after contact with HCl which combine to give, in this case, a linear change in the measured S $2p_{3/2}$ binding energy toward $CuInS_2$ values.

The change in the S $2p_{3/2}$ binding energy displayed in the curves, which corresponds to the emergence of a new phase (CIS) on the sample surface after HCl etching, is more important than the absolute value of the binding energy. Binding energy is a band bending-dependent value and, as was observed in many experiments on the CIS/CdS junction, the position of the Fermi Level (band bending) in the CIS and CdS band gaps after CdS deposition was not reproducible.

The Cd $3d_{3/2}$ core level binding energy was also observed. Before HCl etching began the binding energy was 404.39 eV and after the first etch step it shifted to 404.50 eV. Thereafter, the measured binding energy of the Cd $3d_{3/2}$ core level stayed in the range 404.50 eV-404.58 eV for the remainder of the experiment, the total change being less than the experimental error of ± 0.1 eV. One reason why the S $2p_{3/2}$ core level binding energy changed while the Cd $3d_{3/2}$ core level binding energy did not is because the Cd is most likely surrounded by S atoms in both materials while the chemical environment of the S changes from exclusively Cd to Cu and In as next neighbors with the occasional Cd atom. Any real change in the Cd $3d_{3/2}$ binding energy may be well under the resolution of XPS.

The data points from the last measurement after six hours ($t = 23677$ sec) in HCl are not shown in fig. 2. The values of the points are similar to the corresponding points at longer etch times, the most important of which is the non-zero value of the [Cd]/[Cu] ratio.

5. Conclusion

The incremental etching of a $\sim$35 nm CdS buffer layer on $CuInS_2$ with HCl was used to remove the top-layer while studying the surface with photoelectron spectroscopy after every etch step. The resulting depth profile showed a diffusion of Cu from the CIS absorber into the CdS buffer layer with no additional intermixing of the layers during the removal of material. On the etched CIS surface a Cd-containing layer was observed after even more than six hours of etching time. This layer was not CdS, as this is soluble in HCl, and means that the Cd-S bonds in CdS and in the CIS:Cd layer are different. It was also found that CIS was soluble in concentrated HCl. Furthermore, we believe this method can be applied to other top-layers deposited on substrates sensitive to the chosen solvent in order to produce depth-profiles of, for example, other buffer layers such as ZnS or Zn(S,O).

6. Acknowledgements

Financial support was provided by the German Bundesminesterium für Umwelt, support code 0327589B (KD-CIS). Also thanks to A. Rockett for the discussion and ideas about etching CdS with HCl.

References

[1] S. Merdes, B. Johnson, R. Sáez-Araoz, A. Ennaoui, J. Klaer, I. Lauermann, R. Mainz, A. Meeder, R. Klenk, Current Transport in Cu(In,Ga)S_2 based solar cells with high open circuit voltage-bulk vs. inerface, Mater. Res. Soc. Symp. Proc. 1165-M05-15 (2009)

[2] I. Riedel, J. Riediger, J. Ohland, J. Keller, M. Knipper, J. Parisi, R. Mainz, S. Merdes, Solar Energy Materials & Solar Cells, **95**, 270-273 (2011)

[3] S. Siemer, J. Klaer, I. Luck, J. Bruns, R. Klenk, D. Bräunig, Solar Energy Materials and Solar Cells **67**, 159-166 (2001)

[4] R. Klenk, S. Bakehe, R. Kaigawa, A. Neisser, J. Reiß, M.Ch. Lux-Steiner, Thin Solid Films **451-452**, 424-429 (2004)

[5] S. Merdes, R. Mainz, J. Klaer, A. Meeder, H. Rodriguez-Alvarez, H.W. Schock, M.Ch. Lux-Steiner, R. Klenk, Solar Energy Materials & Solar Cells **95**, 864-869 (2010)

[6] C.A. Kaufmann, T. Unold, D. Abou-Ras, J. Bundesmann, A. Neisser, R. Klenk, R. Scheer, K. Sakurai, H.-W. Schock, Thin Solid Films, **515**, 6217-6221 (2007)

[7] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, Prog. Photovoltaics: Res. and App. **19**, 84-92 (2011)

[8] R. Scheer, Trends in Vacuum Science and Technology **2**, 77-112 (1997)

[9] A. Klein, T. Löher, Y. Tomm, C. Pettenkoffer, W. Jaegermann, Appl. Phys. Lett. **70**, 1299-1301 (1997)

[10] B. Johnson, L. Korte, T. Lußky, J. Klaer, I. Lauermann, J. Appl. Phys. **106**, 073712 (2009)

[11] D. Abou-Ras, G. Kostorz, A. Romeo, D. Rudmann, A. N. Tiwari, Thin Solid Films **480-481**, 118-123 (2005)

[12] M. Turcu, U. Rau, Thin Solid Films, **431**, 158-162 (2003)

[13] I. Konovalov, Thin Solid Films **451**, 413-419 (2004)

[14] R. Klenk, Thin Solid Films **387**, 135-140 (2001)

[15] A. Niemegeers, M. Burgelman, A. De Vos, Appl. Phys. Lett. **67**, 843-845, (1995)

[16] T. Nakada, Thin Solid Films **361-362**, 346-352 (2000)

[17] T. Wada, S. Hayashi, Y. Hashimoto, S. Nishiwaki, T. Sato, T. Negami, M. Nishitani, 2^{nd} World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, 403-408 (1998)

[18] Practical Surface Analysis, D. Briggs, M. P. Seah, Ed., John Wiley & Sons, New York, New York, USA (1983)

[19] A. Rockett, D. Liao, J. T. Heath, J. D. Cohen, Y. M. Strzhemechny, L. J. Brillson, K. Ramanathan, W. N. Shafarman, Thin Solid Films **431-432**, 301-306 (2003)

[20] T. Yamamoto, I. Luck, R. Scheer, App. Surf. Sci. **159**, 350-354 (2000)

[21] These results are not shown here and will be presented in a forthcoming contribution.

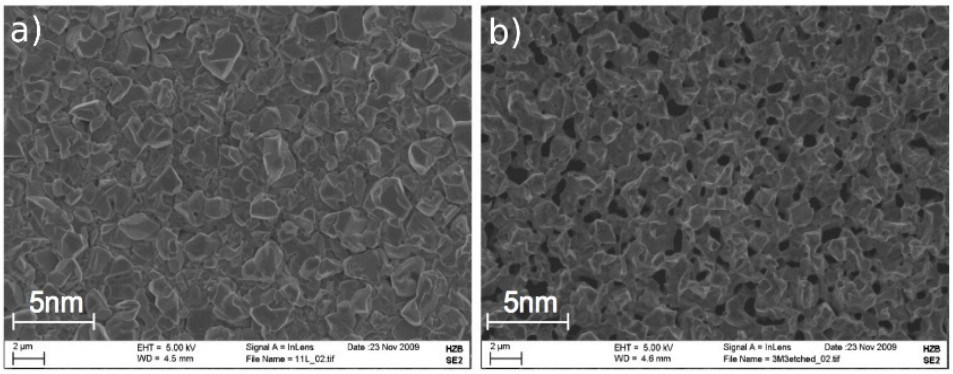

FIGURE 1. Scanning Electron Micrographs (SEM) showing a) the surface of KCN-etched CIS and b) the KCN-etched surface after one hour in 32% HCl. The difference between the two images has been interpreted as a removal of material.

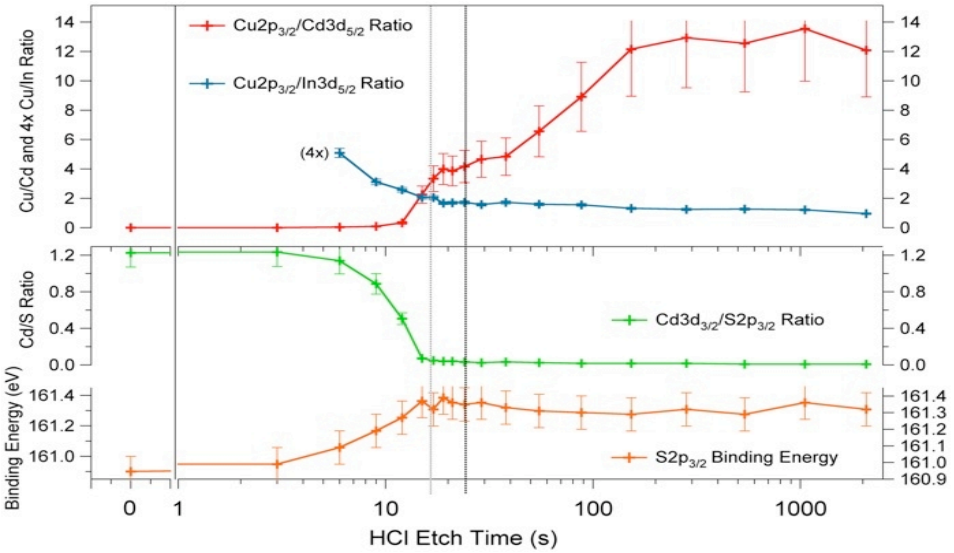

FIGURE 2. The incremental HCl-etching of a ∼35 nm thick CdS layer on a CIS absorber. The changes in the [Cu]/[Cd] ratio (red), [Cu]/[In] ratio (blue) and [Cd]/[S] ratio (green) are displayed along with the change in the S binding energy (orange). Cd remains on the CIS surface ([Cd]/[Cu]>0) after the complete removal of CdS and Cu diffuses into the CdS layer during CdS deposition (high [Cu]/[In] ratio prior to 18 sec). The ratios were calculated using the denoted peak areas and were properly normalized for quantitative XPS analysis as discussed in the text.