

# SIMS depth profiling of CdTe-based solar cells grown on sapphire substrates

M. Emziane<sup>a,\*</sup>, K. Durose<sup>a</sup>, D.P. Halliday<sup>a</sup>, N. Romeo<sup>b</sup>, A. Bosio<sup>b</sup>

<sup>a</sup> Department of Physics, University of Durham, South Road, Durham, DH1 3LE, UK

<sup>b</sup> Department of Physics, University of Parma, Viale delle Scienze 7a, 43100 Parma, Italy

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## Abstract

CdTe/CdS/TCO solar cell structures were grown on sapphire substrates especially to investigate the impurity distributions in them. The study was performed using quantitative secondary ion mass spectrometry (SIMS) depth profiling, from the CdTe back surface through to the TCO layer. The species investigated were F, Br, Na, Si, Sn, In, O, Cl, S and Te, and for the purpose of comparison, some of the structures were investigated in their as-grown state. It has been shown that while Si concentration profiles are similar to those for structures grown on glass, Na was more than one order of magnitude lower when sapphire was used as substrate instead of glass. This demonstrates that Na diffused from the glass substrate. Moreover, the overall Na concentration in structures with and without CdCl<sub>2</sub> treatment showed that Na also originated from the CdCl<sub>2</sub>, which is in accordance with our recently reported studies of impurities in CdCl<sub>2</sub>. The concentration of Br was found to be at least 10 times higher in the etched structures compared to the un-etched ones, especially near the CdTe surface where there was a clearly resolved diffusion profile. In the CdTe active layer, the concentration of F was about  $4 \times 10^{15} \text{ cm}^{-3}$  with a relatively flat level but with surface segregation following heat treatment. Finally, the potential diffusion of Sn and In from the sputtered SnO<sub>2</sub>/ITO:F TCO layer into the CdTe active layer was investigated. It was found that there was no measurable diffusion of Sn from the SnO<sub>2</sub> layer into CdTe. Moreover, the SnO<sub>2</sub> layer played an important role in preventing the diffusion of In from the In-containing TCO layer.

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## 1. Introduction

Float glass is widely used as substrate for the deposition of polycrystalline thin film solar cells, and at the same time very little is known about the effect that it has on the potential diffusion of impurity species from the glass into the device structure and particularly into the active and window layers. In recent reports [1,2], we have shown that for CdTe/CdS/TCO solar cell structures grown on glass substrates, there is some evidence of Si, O and Na diffusion into the CdTe active layer from the glass. This was demonstrated using quantitative SIMS depth profiling from the CdTe surface down to the glass substrate. This effect was also confirmed when the samples were depth profiled from the front side, i.e. from the TCO surface down to the CdTe layer after glass substrate removal [3], where it was shown that these species are present in the CdS window layer as well.

On the other hand, F is often introduced during the growth of the TCO and/or the CdS layer, and, prior to the deposition of the back contact, the CdTe-based solar cell structures are subject to a chemical etching that uses either bromine–methanol or nitric–phosphoric solution. Here also, very few data are available in the literature regarding the effect that these processes may have on the concentration and distribution of elements such as Br and F in the structures and, ultimately on the final device. The post-growth treatment of CdTe/CdS solar cell structures in presence of CdCl<sub>2</sub> has recently been the focus of many reports that underline its importance in activating these devices [1–7].

In this study, CdTe/CdS/TCO solar cell structures were grown on sapphire substrates in order to avoid any contamination coming from the constituents of a glass substrate. The samples were depth profiled using quantitative SIMS analysis to reveal the concentration and distribution of the most important impurity elements that have a potential doping effect on both layers of the CdTe/CdS heterojunction. The data were compared with our previous findings from structures grown on glass substrates [1,2]. The SIMS was done from the CdTe side

\* Corresponding author. Tel.: +44 191 334 3812; fax: +44 191 334 5823.

E-mail address: [m.emziane@durham.ac.uk](mailto:m.emziane@durham.ac.uk) (M. Emziane).

of the structures, and to avoid unnecessary contamination, the CdTe surfaces were not polished prior to SIMS profiling.

## 2. Experimental

The structures were grown on 1 in.  $\times$  1 in.  $\times$  0.5 mm, *c*-plane oriented and polished sapphire substrates of 5 N purity. A transparent conducting oxide (TCO) film consisting of  $\sim$ 1.2  $\mu$ m fluorine-doped indium tin oxide (ITO:F) followed by  $\sim$ 300 nm SnO<sub>2</sub> (TO) was first deposited by reactive sputtering using Ar+CHF<sub>3</sub>+O<sub>2</sub> and Ar+O<sub>2</sub>, respectively, for ITO:F and TO. A CdS window layer of about 80–90 nm thickness was then deposited by sputtering in Ar+CHF<sub>3</sub> ambient, and for both the TCO and the CdS layers, the total pressure in the chamber was kept at  $5 \times 10^{-3}$  mbar. The CdTe active layer had a thickness in the range of 6–8  $\mu$ m and was deposited for 10 min by close space sublimation (CSS) at temperatures of 750  $^{\circ}$ C and 540  $^{\circ}$ C for the source and the substrate, respectively. The CdTe used as source material was 6 N pure. The CdTe/CdS/SnO<sub>2</sub>/ITO:F/sapphire structures were further processed by thermally depositing a 200–400-nm-thick CdCl<sub>2</sub> layer on top of them and then heat treating them in air at about 400  $^{\circ}$ C. Finally, the structures were chemically etched in bromine–methanol solution for about 5 s. For reference, one of the structures was kept as-grown, i.e. without CdCl<sub>2</sub> treatment or chemical etching.

SIMS depth profiles of Si, In, Cl, Na, O, Sn, S, Te, F and Br were recorded on a Cameca IMS 4f using oxygen and cesium primary ion beams. Except for F and Br, the SIMS calibration was carried out by depth profiling CdTe single crystal implants in order to extract the relative sensitivity factors (RSFs) of the

species considered in this investigation. RSF values for F and Br were extrapolated from HgCdTe SIMS standards. The SIMS depth profiling of both the samples and the implants were performed under similar conditions. Also, all the profiles from the present samples grown on sapphire substrates were obtained using the same SIMS conditions as previously for the samples grown on glass substrates to allow a straightforward comparison.

## 3. Results and discussion

Since RSFs for the CdTe layer were used in this study to calibrate all the profiles recorded, we will therefore limit our discussion of the quantitative SIMS data to the CdTe active layer of the solar cell structures although the data presented allows also a qualitative description of the distribution of impurities in the CdS window layer.

Fig. 1 shows the quantitative SIMS depth profiles of Na, Si and O recorded from CdTe/CdS/SnO<sub>2</sub>/ITO:F/sapphire structures as-grown (i.e. unprocessed) and following processing by CdCl<sub>2</sub> heat treatment and bromine–methanol chemical etching. Na exhibited background levels of  $6 \times 10^{13}$  and  $4 \times 10^{16}$  cm<sup>-3</sup> in the CdTe layer for unprocessed and processed structures, respectively. Na also had a clear declining profile in the as-grown sample versus the processed one, and a similar behaviour was found in as-grown structures as compared to processed ones on glass substrates, where the Na background concentrations were reported to be  $10^{15}$  cm<sup>-3</sup> in unprocessed structures and  $10^{17}$  cm<sup>-3</sup> in processed ones [1]. Overall, the concentration of Na is slightly lower in CdTe when a sapphire substrate is used compared to glass, and this, together with the

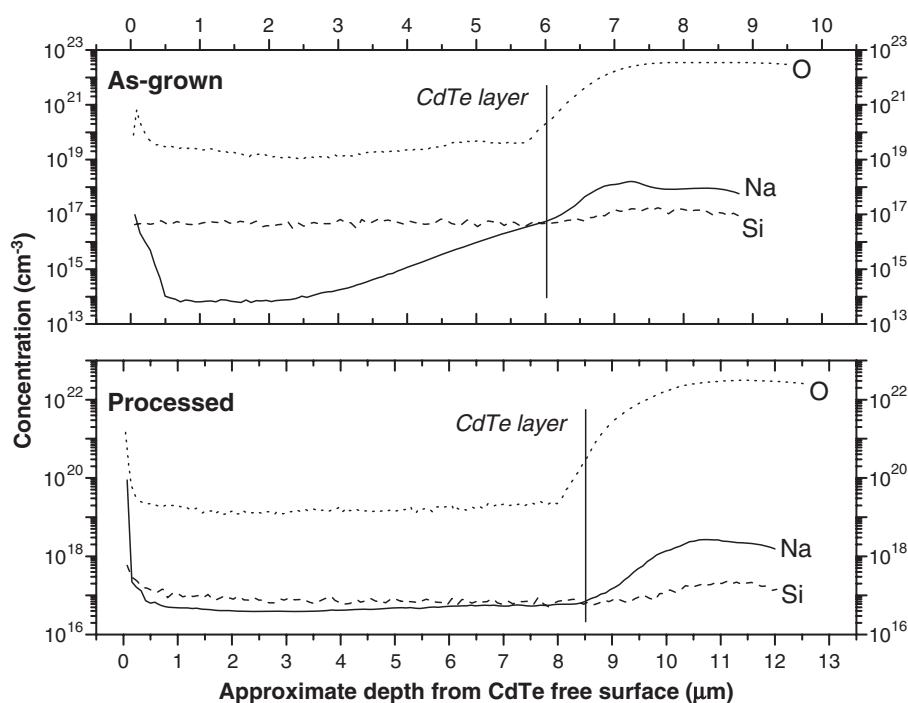


Fig. 1. Quantitative SIMS depth profiles of Na, O and Si in as-grown as well as processed CdTe/CdS/SnO<sub>2</sub>/ITO:F solar cell structures deposited on sapphire substrates. The depth scales are different for the as-grown and processed samples, and the vertical lines show the approximate location of the CdS/CdTe interface in both samples.

diffusion-like profile, confirm that some of the Na present in CdTe was indeed coming from the glass substrate during the CdTe growth. Upon processing, the concentration of Na increases and becomes more homogeneous within CdTe; Na is a known contaminant in CdCl<sub>2</sub> used for processing [2]. Si however had almost the same level ( $\sim 5 \times 10^{16} \text{ cm}^{-3}$ ) and profile shape before and after processing, and this is comparable to the concentration recorded ( $\sim 4 \times 10^{16} \text{ cm}^{-3}$ ) for structures grown on glass substrate [1]. Therefore, the background level of Si does not seem to depend on the nature of the substrate used. O showed a constant background level in CdTe around  $2 \times 10^{19} \text{ cm}^{-3}$  for the unprocessed as well as the processed samples. This is higher than the  $\sim 4 \times 10^{18} \text{ cm}^{-3}$  recorded for O in structures grown on glass [1]. With regard to the effect of the CdCl<sub>2</sub> treatment on the impurity profile within the structures, the concentration trends of Na, Si and O, for unprocessed structures as compared to the processed ones, were in good agreement with our previously reported SIMS data from structures grown on glass substrates [1] and also with our inductively coupled plasma mass spectrometry (ICPMS) data recorded from the CdCl<sub>2</sub> powder used for the heat treatment of the structures [2].

The quantitative SIMS depth profiles of Br, F, Sn and In for CdTe/CdS/SnO<sub>2</sub>/ITO:F structures as-grown on sapphire substrates and following processing are shown in Fig. 2. Br showed a constant concentration of  $4 \times 10^{16} \text{ cm}^{-3}$  in CdTe layer for un-etched structures while for the etched ones the Br concentration in CdTe was at least 10 times higher away from the CdTe surface, and reaches about  $10^{18} \text{ cm}^{-3}$  near the CdTe surface with a clear declining profile. It is therefore clear that

upon etching with bromine–methanol solution, Br is introduced into the CdTe active layer. To the best of our knowledge, this effect has not been investigated before despite the fact that Br behaves as a donor in CdTe and is extensively used as etchant (in solution with methanol) for the chemical etching of the CdTe surface prior to the deposition of the back contact. In the CdTe layer, F had an almost flat background level of about  $4 \times 10^{15} \text{ cm}^{-3}$  regardless of the structure, but F concentration was obviously higher at the CdTe surface and in the first  $\mu\text{m}$  of the CdTe layer for both structures but more particularly for the processed one, as can be seen from Fig. 2. This seems to suggest that F tends to segregate at the CdTe surface, and this segregation appears to be enhanced when the structure undergoes the processing step. It should be pointed out that for the as-grown structure there is a peak of F in the CdS and this results from the CHF<sub>3</sub> used in sputtering the CdS. This appears to anneal out during processing.

Sn showed flat depth profiles in CdTe with a concentration of about  $10^{14} \text{ cm}^{-3}$  regardless of the structure (i.e. unprocessed versus processed) as shown by Fig. 2. This indicates clearly that, like for the structures on glass substrates [1], Sn concentration and distribution are not influenced by the processing. Furthermore, the constant concentration of Sn had also the same value when In<sub>2</sub>O<sub>3</sub>:F was used as TCO [1] instead of ITO:F/SnO<sub>2</sub>, showing therefore that the main source of Sn in the CdTe is not the TCO. The Sn concentration recorded here is about three orders of magnitude lower than that reported by Godines et al. using SnO<sub>2</sub>:F only as TCO [8]. These authors also reported O concentration around  $6 \times 10^{20} \text{ cm}^{-3}$ , which is again higher than the level we recorded here for

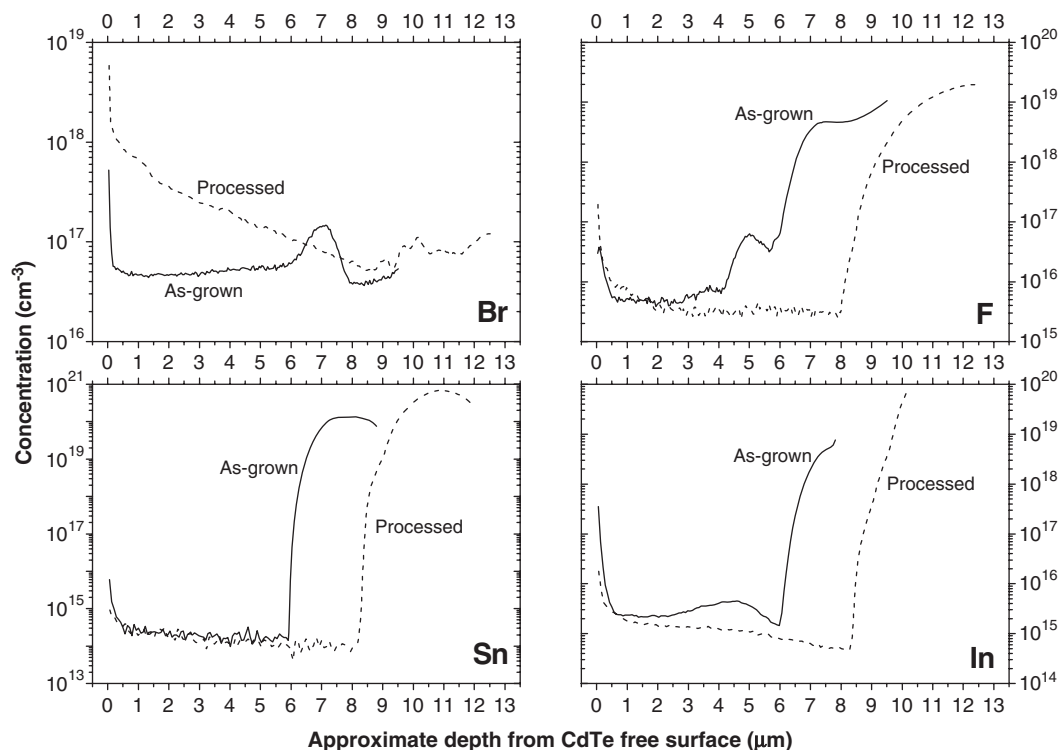


Fig. 2. Quantitative SIMS depth profiles of Br, F, Sn and In for as-grown as well as processed CdTe/CdS/SnO<sub>2</sub>/ITO:F solar cell structures deposited on sapphire substrates. The CdTe/CdS interface is located at a depth of about 6  $\mu\text{m}$  and 8.5  $\mu\text{m}$  for the as-grown and processed samples, respectively.

O ( $\sim 2 \times 10^{19} \text{ cm}^{-3}$ , Fig. 1). These quantitative differences between our data and those published by Godines et al. [8] can be understood in the context that these authors simply used extrapolated CdTe RSFs instead of RSFs extracted from CdTe single crystal implants necessary for an accurate quantification of the SIMS data.

Depth profiles for In showed a concentration peak ( $\sim 5 \times 10^{15} \text{ cm}^{-3}$ ) in CdTe near the interface with CdS for the as-grown structure. In contrast, the processed structure had a concentration steadily increasing from  $5 \times 10^{14} \text{ cm}^{-3}$  near the CdTe/CdS interface to about  $2 \times 10^{15} \text{ cm}^{-3}$  near the CdTe free surface. This shows that the distribution of In within the CdTe layer is clearly affected by the processing, and that at least some of the In detected in CdTe may well be due to the CdCl<sub>2</sub> treatment as an In level of about  $10^{16} \text{ cm}^{-3}$  was measured by ICPMS in the CdCl<sub>2</sub> powder used [2].

These In levels are low compared with the high In concentrations between  $8 \times 10^{16} \text{ cm}^{-3}$  and  $10^{17} \text{ cm}^{-3}$  recorded in solar cell structures grown using In<sub>2</sub>O<sub>3</sub>:F as TCO without SnO<sub>2</sub> layer, and attributed to an out-diffusion of In into CdTe from the In<sub>2</sub>O<sub>3</sub>:F layer [1,2]. It turned out that, in the present structures, the SnO<sub>2</sub> layer prevented In from diffusing into CdTe from the ITO:F layer.

Fig. 3 shows the quantitative SIMS depth profiles of S and Cl for as-grown as well as processed CdTe/CdS/SnO<sub>2</sub>/ITO:F solar cell structures on sapphire substrates. Cl had a flat profile in CdTe for both the unprocessed and processed samples, while its concentration in CdTe is about 100 times higher ( $\sim 10^{19} \text{ cm}^{-3}$ ) in the processed structures than in the as-grown ones ( $\sim 10^{17} \text{ cm}^{-3}$ ). This comparison also shows that, following processing, a Cl depletion occurs in the region near the CdTe surface as compared to before processing, and this behaviour

was also noticed in the case of solar cell structures deposited on glass [1] and could be due to the chemical etching that follows the CdCl<sub>2</sub> heat treatment. It can therefore be concluded that, quantitatively as well as qualitatively, Cl has a similar trend regardless of the substrate used.

It is interesting to compare S profiles before and after processing. Indeed, S has a background level of about  $2 \times 10^{17} \text{ cm}^{-3}$  before and  $2 \times 10^{18} \text{ cm}^{-3}$  after the structure has undergone the processing. The diffusion of S through the CdS/CdTe interface into the CdTe layer is obvious for both structures, however it is further enhanced following processing as evidenced by the difference in its concentration, and also as the S diffusion profile almost reaches the CdTe free surface in the processed structure compared to the as-grown one. Furthermore, the enhancement of the interdiffusion at the CdS/CdTe interface on processing is corroborated by the more graded Te profile (not shown here) in the processed sample than in the unprocessed one at the CdS/CdTe interface.

As stated above, all the structures reported in this study had their CdTe layers grown using 6 N purity CdTe source material, meaning that the total amount of impurity elements to be anticipated from a starting material of this grade is about  $2 \times 10^{16} \text{ cm}^{-3}$ . However, in the as-grown structures considered in this investigation, the concentrations found for Si ( $5 \times 10^{16} \text{ cm}^{-3}$ ), O ( $2 \times 10^{19} \text{ cm}^{-3}$ ), Br ( $4 \times 10^{16} \text{ cm}^{-3}$ ) and Cl ( $10^{17} \text{ cm}^{-3}$ ) are, as shown in the figures, higher than  $2 \times 10^{16} \text{ cm}^{-3}$ . This finding emphasizes the fact that even before undergoing any processing step, the structures have already some Si, O, Br and Cl coming from impurity sources other than the CdTe starting material. Since these structures were all grown on sapphire (known for its stability at the temperatures used in this study) it is very unlikely that these impurity species are

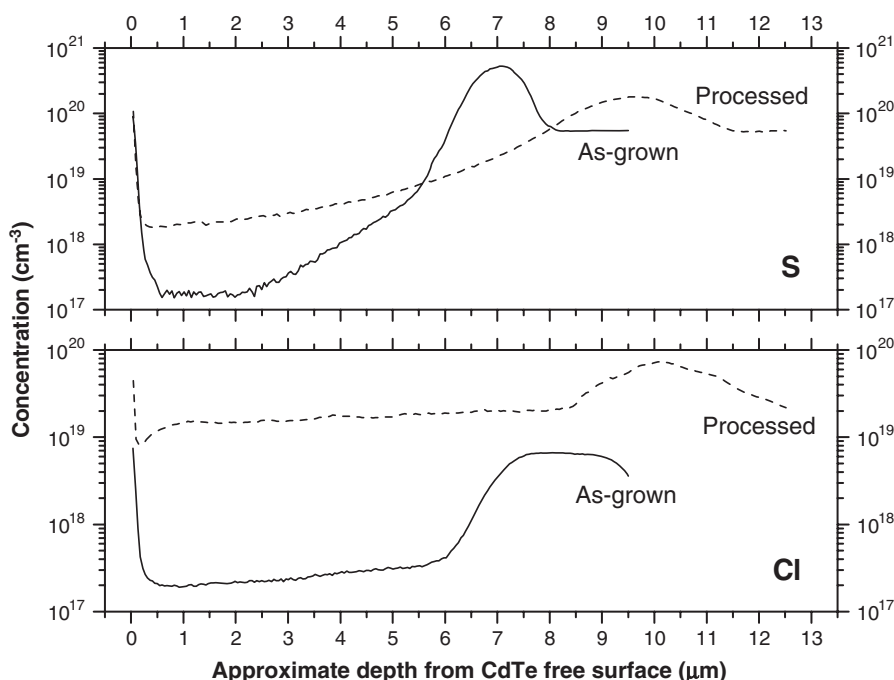


Fig. 3. Quantitative SIMS depth profiles of S and Cl for as-grown as well as processed CdTe/CdS/SnO<sub>2</sub>/ITO:F solar cell structures deposited on sapphire substrates. The approximate location of the CdTe/CdS interface is at a depth of about 6  $\mu\text{m}$  and 8.5  $\mu\text{m}$  for the as-grown and processed samples, respectively.

originating from the sapphire substrates. Therefore, the potential contamination sources are the growth chambers and environments used for the sputtering, and the CSS deposition of the structure layers, together with the diffusion into the CdTe layer of elements from the other layers of the structure.

Most of the profiles recorded show a surface transient with regard to the concentration values, and this is a well-known effect occurring at the beginning of the SIMS depth profiling. It appears from the profiles shown that, while the nominal layer thicknesses were roughly identical for all the structures investigated, the as-grown structure has its CdTe layer thinner than the one of the processed structure. On the other hand, S, F, Br and Na profiles show a well-resolved CdS layer and seem to suggest that the latter is also thinner for the as-grown sample as compared to the processed one. Moreover, compared to its nominal thickness of 80–90 nm for all the structures studied, the CdS layer appears broad as this is due, originally, to a rough CdTe surface. This initial roughening is also known to increase with increased erosion of the CdTe layer during the depth profiling, and may also change substantially when passing the CdS/CdTe and CdS/TCO interfaces. The sputter rate also changes by passing the interfaces, resulting in a less accurate quantification of the depth profiles, i.e. a seriously limited depth resolution. In this investigation, the layer depth scales were calibrated according to the sputter rate measured in CdTe and known to be higher compared to CdS sputter rate, which also explains why the CdS layer appears much thicker than expected.

Finally, when quantitatively discussing the distribution of impurity elements within the CdTe active layer, one has to bear in mind that SIMS analysis on its own is not able to confirm whether the impurities recorded have any electrical activity in the CdTe layer with a direct impact on the performance of the final devices based on these structures.

#### 4. Conclusions and summary

CdTe/CdS solar cell structures were grown on sapphire substrates using ITO:F/SnO<sub>2</sub> as TCO, and quantitatively studied by SIMS depth profiling measurements. The concentration and distribution of Si, In, Cl, Na, O, Sn, S, Te, F and Br impurity elements were determined throughout the un-contacted structures in their as-grown and processed states. This investigation allowed a comparison of the behaviour of impurities when sapphire is used as substrate instead of the

usual glass. It led also to the clarification of the role that the SnO<sub>2</sub> layer plays within the structure as well as the effect of the post-deposition CdCl<sub>2</sub> heat treatment on the impurity profiles. Furthermore, this study brought about an understanding of the distribution of Br following the bromine–methanol etching commonly used for CdTe-based solar cells, the profile of F that is introduced during the growth of ITO and CdS layers and, finally, the interdiffusion of Te and S at the CdTe/CdS interface before and after processing. It was demonstrated that while Na originates from the glass, it is also introduced by processing with impure CdCl<sub>2</sub>. Si has a profile that is substrate independent and cannot be attributed to glass. As expected, Br is introduced by bromine–methanol etching and was shown to be a potentially important contaminant. F is introduced by CHF<sub>3</sub> gas used during sputtering of ITO and CdS. Sn is not introduced from SnO<sub>2</sub> TCO, but SnO<sub>2</sub> is a barrier to In diffusion from ITO into CdTe. In does however come from both the TCO and from impurities in CdCl<sub>2</sub> used for processing.

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