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A combined Na and Cl treatment to promote grain growth in MOCVD grown CdTe thin films

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Abstract

The role of sodium (Na) in cadmium telluride (CdTe) thin film photovoltaic absorbers deposited on a metal-coated substrate is investigated. Introducing Na during the growth of the structure influences the morphological and crystallographic properties of the CdTe layer grown by metal-organic chemical vapour deposition (MOCVD). It is observed that the introduction of Na between the metal and CdTe layers induces a slight randomisation via promotion of (400) and (220) orientations. It is shown that the inclusion of Na between the substrate and the Mo back metal contact enlarges the CdTe grains following a $CdCl_2$ treatment by 50% but weakens the adhesion to the substrate. The introduction of Na between the Mo back contact and CdTe layer promotes the formation of large faceted grains for the as-grown films with an average grain size ten times larger than in the case of Na free deposition while maintaining good adhesion to the substrate. There is no further grain growth following $CdCl_2$ treatment however the CdTe grain size is still double that of the Na-free samples.

Keyword: Thin films; vapour deposition; MOCVD; CdTe; grain growth; sodium.

1 Introduction

Cadmium telluride (CdTe) based photovoltaics (PVs) is currently the leading thin-film material mainly due to its optimal direct energy band gap of 1.5 eV, high optical absorption coefficient and variety of scalable fabrication methods [1]. First Solar holds the record efficiencies for both small area and large module with 22.1 % [2] and 18.6 % [3], respectively, on-par with multi-crystalline silicon. These recorded efficiencies are for superstrate configuration where the incoming photons enter the structure through the transparent conductive oxide (TCO) via a transparent glass substrate. However the use of alternative lightweight, opaque and flexible substrates would provide an evident advantage in building integrated PV and for this the solar cell structure must be grown in the substrate configuration starting with the back contact. Additional advantages of the substrate configuration include further possible reduction in optical losses at the front surface and potential for better control of the junction formation following the absorber heat treatment. For CdTe in substrate configuration

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Amongst the variety of deposition techniques, metal-organic chemical vapour deposition (MOCVD) is capable of depositing high quality semiconductor and has been shown to be an effective technique for the deposition of polycrystalline CdTe PV cells [6]. The ability to fabricate the entire device structure using one method at atmospheric pressure and the potential to have an inline roll-to-roll process also provide further benefits of using this technique [7]. Impurities and dopants play a major role in PV devices and prime examples are chlorine (Cl) in CdTe and sodium (Na) in $CuInGaSe_2$ (CIGS) solar cells. Cl is fundamental to the "activation" of the CdTe film while Na affects grain size, crystal texture and conductivity in CIGS [8, 9]. The presence of Na in CdTe solar cells can result in increased grain size of the absorber layer, increased acceptor density and V_{oc} as it acts as a shallow acceptor in CdTe with low activation energy [10-13]. The increase in CdTe grain size is still paramount to reducing the volume of grain boundaries and defect concentration to increase device efficiency, and the role of Na merits further investigations. In this contribution, it is shown that it is challenging to control Na diffusion from the soda-lime glass (SLG) substrate through the molybdenum (Mo) back contact layer to create a high quality thin film. We subsequently investigate the morphological and structural properties of CdTe grown by MOCVD when Na is introduced via an evaporated sodium fluoride (NaF) thin layer and show that this results in relatively large grains suitable for PV applications.

2   Experimental procedures

Mo thin films (1.0 μm thick) were deposited on either SLG or quartz substrates (76 x 26 x 1 mm^3) using direct current (DC) magnetron sputtering with target currents of 1.5, 3 and 4.5 A, at room temperature and at argon (Ar) pressures of 3, 7 and 10 mTorr, from a rectangular target with dimensions 248 x 133 x 10 mm^3. A subset of Mo films was annealed in a tube furnace at temperature of 450 – 550 °C backfilled with 10 mbar of Ar after evacuating to 10^{-3} mbar in order to observe the effect of temperature on the back contact and Na content.

Arsenic (As) doped CdTe thin films were grown by MOCVD on Mo coated substrates in a horizontal reactor, using purified H_2 as the carrier gas and with a growth temperature of 390 °C. The As doping of the CdTe absorber layer during the MOCVD growth is essential in order to achieve high p-type conductivity and high efficiency for superstrate configuration devices [14]. The organic precursors used were dimethylcadmium (DMCd), diisopropyltelluride (DiPTe) and trisdimethylaminoarsine (tDMAAs) for Cd, Te and As, respectively. An in-situ triple wavelength laser reflectometer was used to monitor the growing layer thickness of CdTe:As^+ (250 nm) and CdTe:As (2500 nm), where the As

10 min. In order to investigate the influence of Na on the properties of the CdTe films, three different sample layouts were prepared using quartz substrates: (i) CdTe/Mo/quartz, (ii) CdTe/Mo/NaF/quartz and (iii) CdTe/NaF/Mo/quartz where sodium fluoride (NaF, ~ 10 nm) was deposited by thermal evaporation at room temperature.

The thicknesses of the fabricated layers were examined at every stage using a Bruker Dektak XT stylus profilometer. Elemental depth profiling was performed using secondary ion mass spectroscopy (SIMS) using a Hiden Analytical gas ion gun and quadrupole detector. A primary Ar^+ beam with an impact energy of 4 keV and beam current of 600 nA was used to sputter over a 600×600 μm^2 rastered area. A 10% gating area was employed to remove any sidewall effects from the data. The depth profiles were then normalised and an average count was calculated for the measured sets. The film morphology of the CdTe thin films was investigated using a FEI Quanta 200 or Tescan Mira3 scanning electron microscope (SEM). The structure of the Mo and CdTe layers were examined using X-ray diffraction (XRD) carried out with a Siemens D-5000 diffractometer using a Cu K_α radiation source.

3   Results and discussion

3.1   Mo growth and Na diffusion

CdTe is normally deposited on SLG and generally includes barrier layer(s) such as Si_3N_4, Al_2O_3 or SiO_2 to prevent diffusion of impurities from the glass [10, 13, 15]. Na, a major constituent of SLG, is known to diffuse during thermal processes > 300 °C and has been shown to promote uncontrolled grain enlargement in CdTe deposited using vacuum evaporation [13, 16, 17]. For films grown by MOCVD this is also the case as is demonstrated next. Figure 1 shows the SEM surface micrographs of CdCl2-treated CdTe films deposited by MOCVD on Mo-coated quartz and SLG substrates. When deposited on quartz (figure 1 a) the CdTe grains are small (~ 0.5 μm) and compact whereas when deposited on SLG, grains grow larger (up to 5 μm) but the CdTe film is no longer continuous (figure 1 b), creating possible shunting paths in the solar cell structure, likely reducing its output power. It is therefore advantageous to adequately control grain growth while maintaining film continuity.
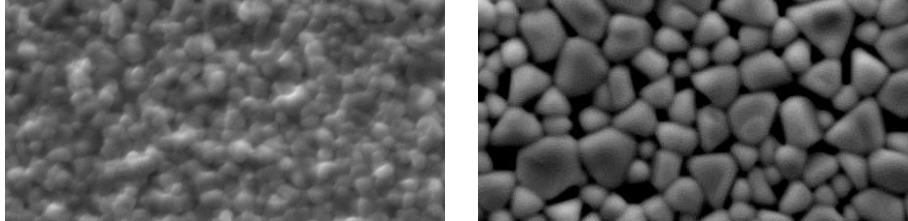
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Figure 1: SEM micrographs of CdCl$_2$-treated Mo/CdTe films deposited on (a) quartz and (b) SLG substrates.

In the case of CIGS, the rate of Na diffusion from the SLG substrate into the absorber is dependent on the Mo properties themselves [18] and it is expected that similar behaviour should occur in a CdTe thin film deposited on Mo/SLG. In order to optimise the Mo film layer, the influence of sputtering pressure and power (target current) on Na diffusion in Mo films were first explored. The Mo layer thickness was set at nominal value of 1.0 μm with sheet resistance $R_\square$ and resistivity ρ ranging from 0.16 – 0.59 Ω/□ and 16 – 66 μΩ·cm, respectively as shown in table 1. At deposition current of 3.0 and 4.5 A the resistivity increases with sputtering pressure as is usually observed in sputtered Mo where increased pressure yields less dense films and more intra grain voids, increasing resistivity [19]. It is noticed that at a lower deposition power of 1.5 A this trend is broken at the highest pressure, which results in the most conductive film. For a given deposition pressure the Mo film resistivity reduces as power increases in agreement with other reports [20-22].

Table 1: Electrical properties of as-grown Mo thin films deposited at room temperature. The thickness is 1.0 ± 0.1 μm for all films.

Pressure (mTorr)	Current (A)	$R_\square$ (Ω/□)	ρ (μΩ·cm)
3	1.5	0.59	53
7		0.59	66
10		0.16	16
3	3.0	0.40	40
7		0.41	51
10		0.47	54
3	4.5	0.27	22
7		0.33	34
10		0.39	39

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currents and the data is shown in figure 3. In the as-deposited state, the Na content does not vary significantly with changes in pressure but we note a small reduction in Na as the deposition pressure increases for higher deposition power. Figure 3 also displays the resistivity of the as-grown layer and although the parameters investigated here do not produce broad changes in resistivity (see for example [19]) there is a clear relationship between the Na SIMS count and film resistivity on all three series of samples: at a given deposition power, an increase in resistivity yields a lower Na diffusion in the Mo film (dashed and solid black lines, respectively in figure 3). In general, sputtering of Mo at lower Ar pressure yields denser films with less voids and porous grain [23] thus reducing the film resistivity as mentioned earlier. More interestingly is the fact that Na content in the as-deposited Mo film increases at lower pressure indicating that Na diffusion from the glass is greater for denser films.
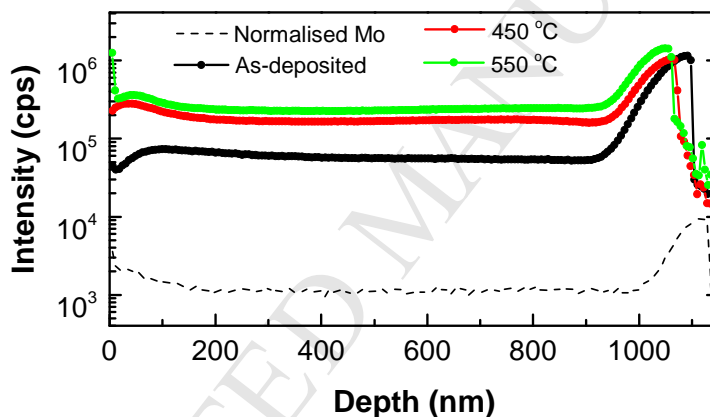

Figure 2: Na SIMS depth profiles in Mo films deposited at 10 mTorr and 4.5 A. The data has been normalised with respect to the Mo signal.

Figure 3 also includes the Na counts after heat treatment at 450 °C and 550 °C to mimic the range of CdTe post-deposition chloride treatment used to fabricate state-of-the-art solar cells. As expected it was observed that the Na content increases as the annealing temperature increases due to out-diffusion from the SLG substrate. At the lowest deposition current (figure 3 a), the Na content has a decreasing trend with sputtering pressure following annealing. At a deposition current of 3 A, saturation is observed as pressure increases.

Overall, these data indicate that it is difficult to predict the out-diffusion of Na from the glass especially when one considers the inhomogeneous concentration of constituents in SLG and a more robust approach is chosen, focusing on samples deposited on quartz substrate with an intentionally added NaF layer. For consistency and reproducibility purposes a Mo deposition current of 3 A was selected to carry out the next stage of this study on quartz substrates.
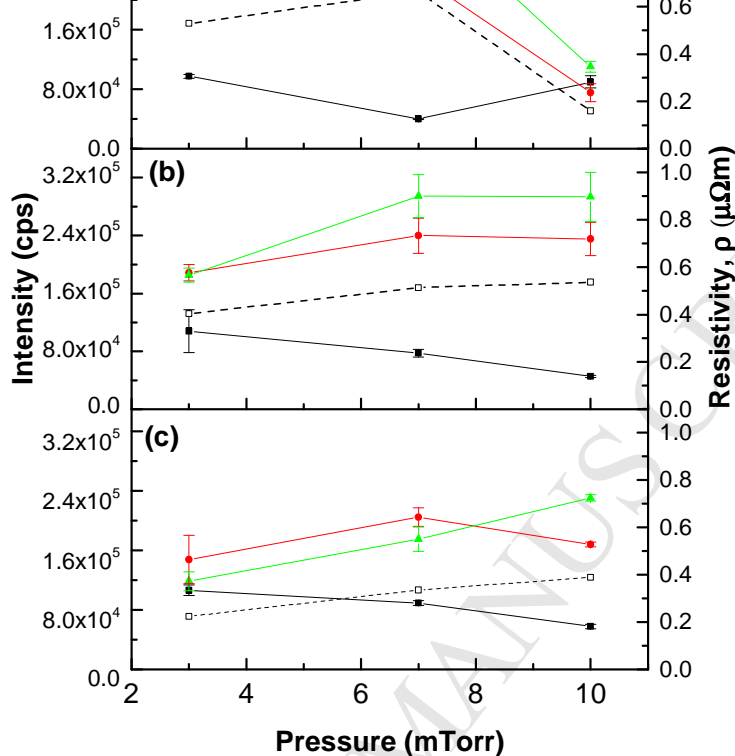
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Figure 3: SIMS analysis (filled symbols and solid lines) for sodium content in the Mo layer at different annealing temperatures at sputtering current of (a) 1.5 A (b) 3 A (c) 4.5 A. The resistivity plots of the as-grown layers are also shown (open symbols and dashed lines). The lines are a guide to the eye.

3.2 Using NaF to control CdTe grain growth

Both Na and F have previously been investigated in CdTe superstrate devices with some success. Na is a shallow acceptor (Na_{Cd}) in CdTe [24], while F, like Cl, is a donor (F_{Te}). In the case of F, the literature reports investigations where F is used in conjunction with Cl as a replacement to $CdCl_2$ using CdF_2 [25] or HCF_2Cl [26]. The combined used of CHF_3 treated CdS and HCF_2Cl treated CdTe leads to efficiency as high as 15.8% [27]. It is likely that both Cl and F are incorporated in the CdTe and demonstrates that F (along with Cl) can contribute to effective p-doping of CdTe via the formation of complexes [28]. Extrinsic doping of CdTe using NaF [10] and NaCl [10, 29] leads to degraded device performances due to excessive CdS-CdTe intermixing irrespectively of the halogen (Cl, F) species. The performance of the superstrate device can be maintained if the NaF layer is deposited at the back of the structure, *i.e.* after the CdTe deposition [13], likely protecting the pn junction from degradation. On the other hand, when the presence of Na in the structure is carefully controlled the open circuit voltage, a key limitation for CdTe technology, of the device can be improved owing to an increase in acceptor concentration while a small drop in short circuit current

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plasma used in the sputtering of the CdS layer ($[F]=10^{17}$ at/cm³ for the as-deposited CdS), F segregates at the surface of the CdTe following CdCl₂ treatment with a SIMS signal in the absorber itself equal to the background detection limit. Secondly, Emziane found a significant amount of Na to be present in CdTe devices (up to 10^{18} at/cm³) even when using Na-free substrate and this is due to the large concentration of impurities in the raw CdCl₂ powder material. The use of Na, or NaF, is yet to be explored in substrate configuration and the following section provides new insights on the effect of NaF on MOCVD-grown CdTe.
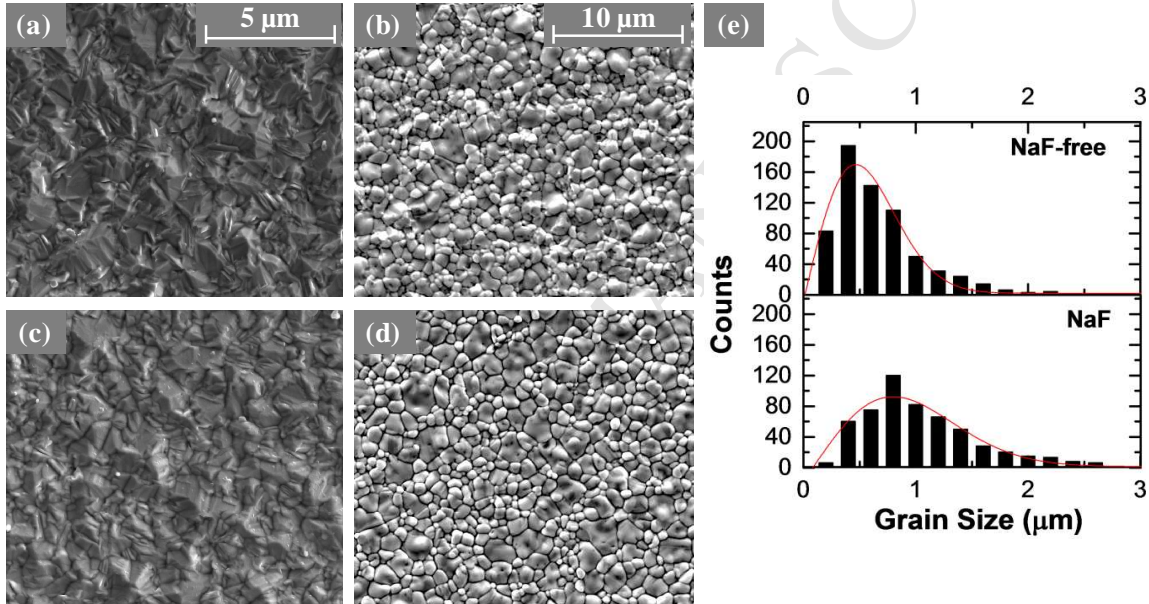

Figure 4: SEM micrographs of CdTe thin films with the following configurations: (a-b) Na-free (CdTe/Mo/Quartz), (c-d) CdTe/Mo/NaF/quartz with (a-c) as-grown and (b-d) CdCl₂-treated. The Mo was deposited at a DC current of 3 A and Ar pressure of 10 mTorr. Grain size (diameter) distribution histograms are shown in (e) for CdCl₂-treated films. Top: CdTe/Mo/quartz and bottom: CdTe/Mo/NaF/quartz.

Figure 4 shows the impact of NaF (10 nm) on the surface morphology of MOCVD-grown CdTe films with and without CdCl₂ treatment for the layout CdTe/Mo/(NaF/)quartz. The micrographs were analysed using the Gwyddion software package to determine the grain size (grain pixel area modelled to a circular shape) distribution and were fitted to a Rayleigh function to obtain average values. Throughout the text "grain size" refers to the diameter of the modelled grain. In the as-grown state the grains show very small < 0.2 μm pyramid shaped structures (figure 4 a and c), with a marginal increase for the Na containing film (figure 4 c). Following CdCl₂ treatment, the grains become more rounded with less sharp faceted edges and a grain growth is observed as expected for MOCVD-grown CdTe thin films [32] (figure 4 b and d). The histograms in figure 4 e show the grain size distributions

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Films prepared with the layout CdTe/Mo/NaF/quartz were not suitable for further possible processing due to delamination of the CdTe/Mo film during the pn junction formation trials. This is due to the weak adhesion between Mo and NaF, where NaF dissolves in the aqueous solution. A more robust approach is to deposit the NaF after the Mo back contact deposition. Figure 5 shows the effect of Na on CdTe/NaF/Mo/quartz layout with varying Mo sputtering pressure. Compared to layout CdTe/Mo/NaF/quartz (figure 4 c), there is a clear morphological change: large faceted CdTe grains are formed in the presence of Na even in the as-deposited state. Pre-CdCl$_2$ treatment (figure 6 a) the CdTe grain size average is 1.9 μm at pressure of 3 mTorr and 1.6 μm for films deposited at higher pressure of 7 and 10 mTorr. The three sets of data showed broad distributions with grain sizes ranging between 0.5 – 4 μm. As with the previous example the CdCl$_2$ annealing step yields more rounded grains and smoother films: the root mean square roughness values of samples shown in figure 5 were 225 nm and 195 nm before and after CdCl$_2$ treatment, respectively. On the other hand, the histograms in figure 6 b show a reduced average grain size of ~ 1 μm following CdCl$_2$ with a narrower distribution regardless of the back contact sputtering pressure. The cross section images, also shown in figure 4, do not reveal measurable differences between the two sets of samples.
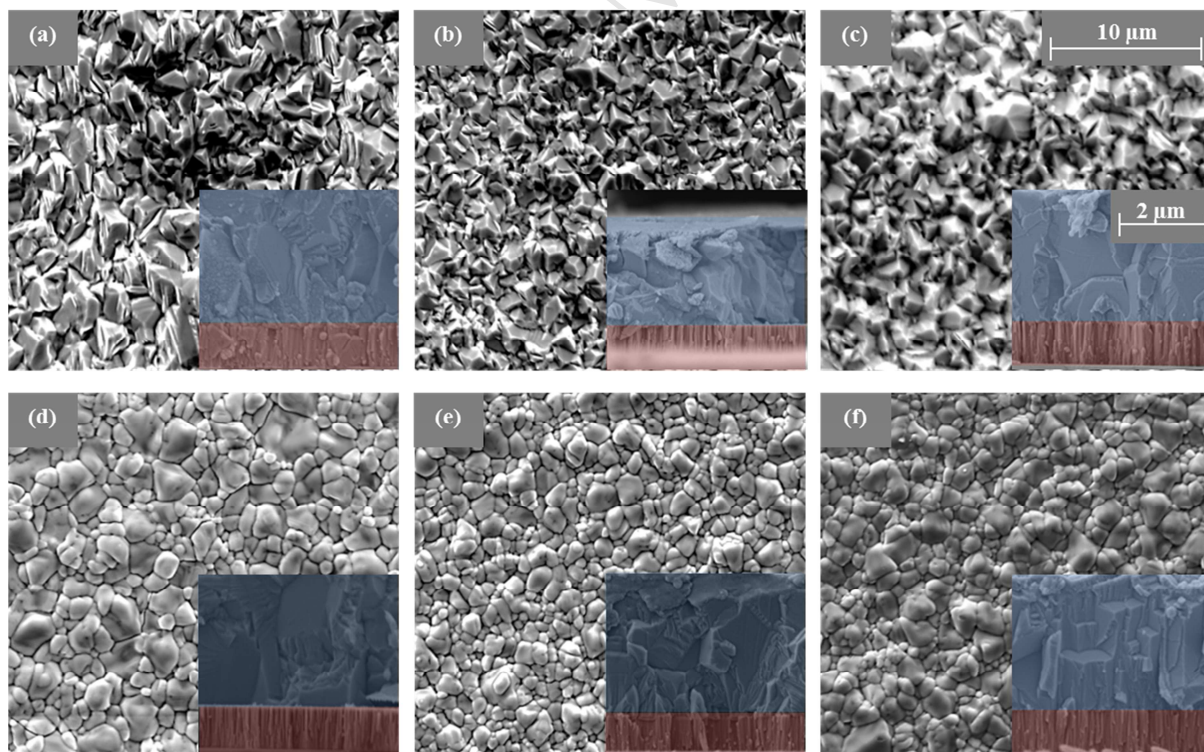

Figure 5: SEM micrographs of CdTe thin films as-deposited (top row) or following CdCl$_2$ heat treatment (bottom row) deposited on NaF/Mo/quartz at varying Mo pressures: (a, d) 3 mTorr, (b, e) 7 mTorr and (c, f) 10 mTorr.
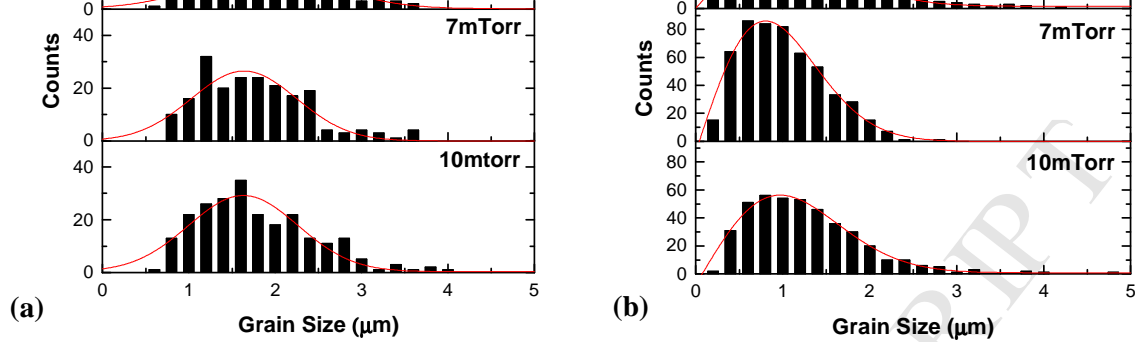
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Figure 6: Grain size distribution of CdTe films as a function of Mo sputtering pressure for the layout CdTe/NaF/Mo/quartz. (a) Pre-CdCl₂ treatment and (b) post-CdCl₂ treatment. Note the change of scale between (a) and (b).
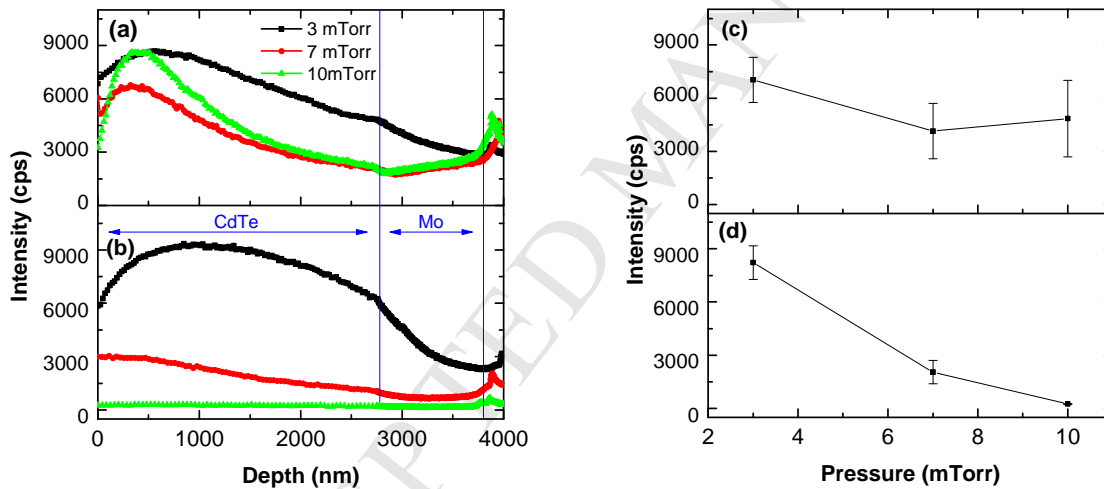

Figure 7: SIMS depth profiles showing the Na content in the as-grown CdTe thin films (a) CdTe/NaF/Mo/quartz and (b) CdTe/Mo/NaF/quartz. The Mo was sputtered at pressures of 3, 7 and 10 mTorr and target current of 3 A. The data was normalised against the Mo signal intensity. Note the linear scale on the intensity axis. The average counts in the CdTe layer are shown in (c) and (d), respectively.

Sodium SIMS depth profiles are displayed in figure 7 a and b for the as-grown CdTe films deposited using the following configurations: CdTe/Mo/NaF/quartz and CdTe/Mo/NaF/quartz. An average count was calculated at the three different Ar pressures for each of the configurations and is shown in figure 7 c and d. The greatest sodium content is seen at the lowest sputtering pressure (3 mTorr) in both cases while for higher Mo deposition pressures the Na profiles are of similar shape and intensity. The layout CdTe/Mo/NaF/quartz yields the greatest variations in Na as a function of sputtering pressure (figure 7 d) and this reemphasises the fact that the Mo layer controls the rate of diffusion. Comparing the Na content for the films with the configuration of CdTe/NaF/Mo/quartz (figure 7 a and c) and their

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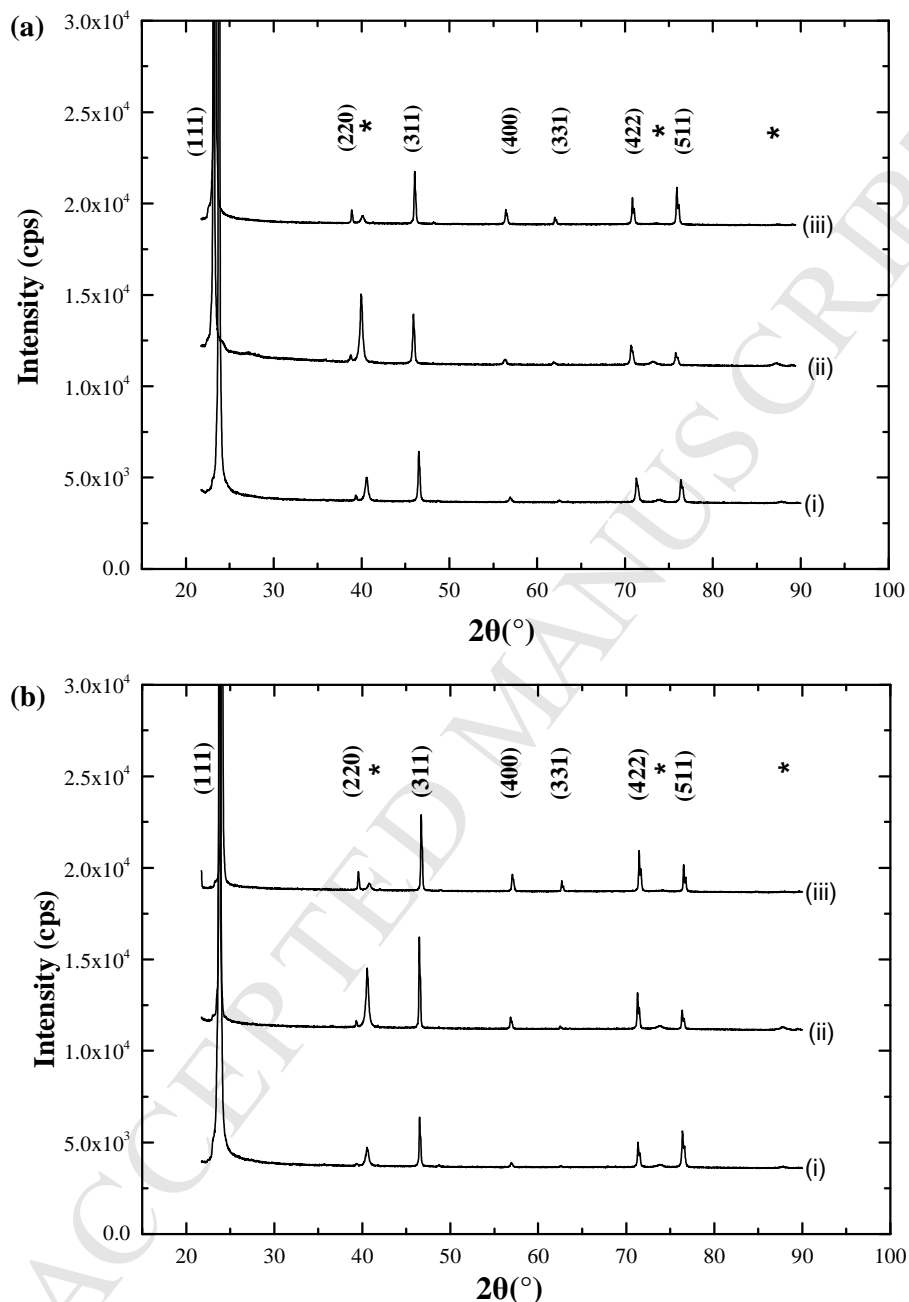
Figure 8: XRD patterns for as-grown (a) and CdCl$_2$-treated (b) samples deposited at constant current of 3 A with the following configurations: (i) NaF-Free, (ii) CdTe/Mo/NaF/quartz, (iii) CdTe/NaF/Mo/quartz. The Mo was deposited at Ar pressure of 10 mTorr. The peaks corresponding to the Mo layer are marked by the asterisks.

X-ray diffraction was used to analyse the crystallographic properties of the deposited layers. For CdTe, the following peaks for the (111), (220), (311), (400), (331), (422) and (511) planes, which correspond to the diffraction angles of 23.76°, 39.32°, 46.43°, 56.82°, 62.35°, 71.22° and 76.3° were

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In both the as-grown and CdCl$_2$-treated state, the samples without NaF and with layout CdTe/Mo/NaF/quartz display a very low intensity for (220), (400) and (331) peaks (i and ii in figure 8) in comparison with the sample CdTe/NaF/Mo/quartz (iii in figure 8). [111] is the dominant direction for all films.

The effects of growth conditions on texture and preferred orientation of the samples were investigated by calculating texture coefficient C_{hkl} and preferred orientation σ as explained in [32]. The σ values are used to compare the degree of orientation between different samples, so that lower σ values indicate more randomly oriented samples. The reference sample (*i.e.* random sample) would have texture coefficients of 1 and preferred orientation of 0 while for a fully aligned sample the C_{hkl} would be 7 (as 7 peaks were used in the calculation) for that particular direction and 0 for the others. The calculated σ values for the Na-free samples ranged between 1.5 to 1.7 indicating less randomly oriented samples compared to the samples with Na that had a σ value ranging between 0.7 – 0.9. The texture coefficient C_{111} increases post-CdCl$_2$ treatment for samples prepared without NaF; however the opposite was observed when Na is present. Moreover, the decrease in C_{111} correlates with an increase in C_{400} and C_{220}. This shows an increase in crystallite orientation in the (400) and (220) directions for samples that have both NaF and CdCl$_2$ deposited even though the favoured preferred orientation of the films is still long the (111) plane.

4   Conclusion

The effect of sodium and sodium fluoride on the morphological and structural properties of CdTe thin films has been investigated. The microstructural investigation shows that the presence of NaF between the back-contact layer and CdTe film was found to lead to a marked increase in grain size of the as-deposited CdTe absorber, with average grain sizes up to 1.9 µm compared with < 0.2 µm for Na-free CdTe. Post-CdCl$_2$ treatment the grains transformed from faceted to round shape with a reduction in grain size (1.0 µm) but still significantly larger than sample processed without Na (0.5 µm). Na doping is only viable when induced after the Mo back deposition due to poor adhesion between the glass, NaF and Mo layers. NaF does not induce large crystallographic changes and the films remains (111) orientated with a small promotion of (400) and (220) crystallites. This combined NaF and Cl treatment provides a new avenue for the development of MOCVD CdTe thin films which should be further exploited at device level in substrate configuration.

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- Introducing Na after Mo back-contact causes a ten-fold increase in CdTe grain size.
- Introducing Na prior the back-contact causes delamination during further processing.
- CdCl$_2$ treatment softens the surface with an apparent reduction in grain size.