

Recrystallization in CdTe/CdS

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Abstract

Processing of CdTe/CdS solar cells requires annealing of CdS and CdTe/CdS in different ambients. It has been proven that the application of a CdCl₂ treatment (or its variant) is important for high efficiency solar cells. This treatment influences the structural and interface properties of the layers. We have grown CdS layers either by a chemical bath deposition (CBD) or a high vacuum evaporation (HVE) on different transparent conducting oxides (TCO): tin oxide doped with fluorine (FTO) and indium tin oxide (ITO) coated glass substrates. The CdTe layers have been grown by a HVE method. Effects of the CdCl₂ treatment on the recrystallization of CdTe and CdS have been studied with X-ray diffraction and scanning electron microscopy. An increase in the grain size of CdTe from about 0.5 to 3–7 μm, along with the loss of the preferred (111) growth orientation has been observed. The strain and recrystallization of CdTe, and intermixing of the CdTe and CdS layers strongly depend on the deposition and annealing temperatures. An optimum treatment and a minimum thickness of CBD–CdS is required for high efficiency solar cells. CdS layers and the method of their deposition also have a strong influence on the microstructure of CdTe and photovoltaic properties. Solar cells with efficiency of 11.2 and 2.5% are obtained with HVE and CBD grown CdS window layers. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: CdTe; CdS; Solar cells; Thin films; Recrystallization; Vacuum evaporation

Introduction

High efficiency CdTe/CdS photovoltaic devices have been obtained with different growth methods [1–3]. Recrystallization treatments are widely used for the CdS and CdTe layers grown by close space sublimation deposition (CSS) and high vacuum evaporation (HVE) techniques, they are essentially required for high efficiency. These recrystallization methods include a simple annealing in air (especially used for electrodeposited CdTe [4]), a CdCl₂ treatment either by vapour deposition of CdCl₂ on the CdTe or by dipping the layer in a CdCl₂–methanol solution and subsequent annealing in air or by annealing in a Cl₂ ambient. Several groups are involved to study the effect of the ‘CdCl₂ treatment’ on the properties of CdTe, CdS layers and junctions [5]. It is still not clear how the junction properties change in relation to recrystallization processes and to different deposition techniques of the window layer. Chemical bath deposition (CBD) grown CdS is preferred as window layer because of low optical absorption and good coverage properties on the TCO (ITO, FTO). However pinholes and incompatibility with PVD processes of CdTe deposition make them less attractive. Therefore PVD grown CdS layers are used for better reliability despite of the opti-

cal losses due to large thickness of 0.2–0.5 mm. The growth and properties of CdTe layers and solar cells may depend on the CdS/TCO substrate. As described in the followings we have investigated the structural properties of CdTe deposited on different type of CdS (CBD–CdS and HVE–CdS) grown on ITO and FTO substrates. Different kinds of post deposition treatments were applied to the layers, from an air-annealing to different CdCl₂ treatments at different temperatures.

Experimental details and results

Commercially available ITO and FTO coated soda lime glasses are used as front contact. CdS layers are grown either in a high vacuum evaporation chamber at a substrate temperature of 150°C (HVE–CdS) or by a chemical bath deposition (CBD–CdS) at 80°C with a solution of Cd salts, ammonia and thiourea. The thickness of the HVE–CdS is around 0.5 μm, whereas it is much lower, around 0.1 μm, for CBD–CdS. The CdS/TCO stacks are either annealed in vacuum at 450°C for recrystallization or left as-deposited, then CdTe is deposited in the same high vacuum chamber at a substrate temperature of 300°C. The CdTe layer is between three and four μm thick. The ‘CdCl₂ treatment’ includes vacuum evaporation of CdCl₂ layers of different thickness and annealing the stacks in air in the

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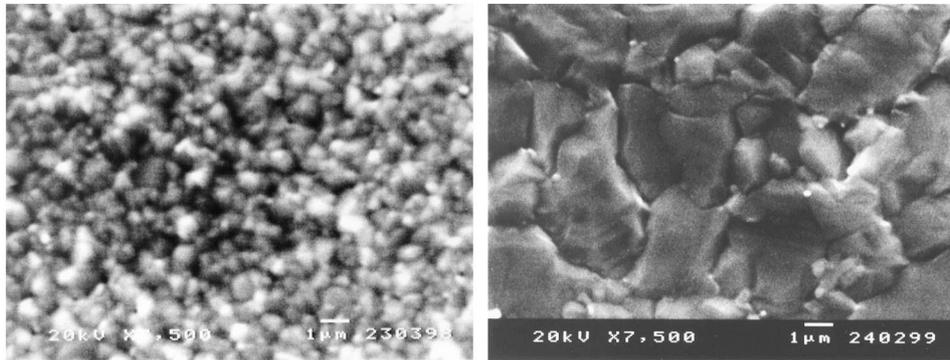


Fig. 1. Morphology of as-deposited CdTe on vacuum-annealed HVE-CdS (left) and vacuum-annealed CBD-CdS (right). The CdTe grains on CBD-CdS are 5–10 times larger than those on HVE-CdS.

temperature range of 350–450°C. For the air annealed samples no CdCl₂ is used. To finish the cells, the back contact is provided with a standard bromine-methanol etching followed by the deposition of a Cu/Au bi-layer and annealing in air at about 200°C.[5]

Morphology of CdTe

Scanning electron microscopy (SEM) was used to study the surface morphology of the CdTe layers. The morphology of as-deposited CdTe layers on CBD-CdS and HVE-CdS is quite different (see Fig. 1). The grain size of CdTe on HVE-CdS is in the range of 0.5–1 μm and the structure is very

compact. The CdTe on CBD-CdS consists of a few small grains of about 1 μm width and many large grains of about 5 μm width. The difference in the microstructure of CdTe is due to a different structure and morphology of the CdS layers. The CBD grown layers are cubic while HVE-CdS layers are predominantly hexagonal. As shown on Fig. 2, the grain size of CdTe on as-deposited CBD-CdS is very small, in the range of 0.5–1 μm. On the vacuum annealed CdS (recrystallized), large grains up to 5 μm and a few smaller CdTe grains are observed. The microstructure also depends on the TCO substrates, grains on FTO are almost two times larger than those on ITO. Similar results are observed for CdTe layers grown on HVE-CdS layers on different TCOs [4].

CdCl₂ treatments of the CdTe layers on vacuum annealed

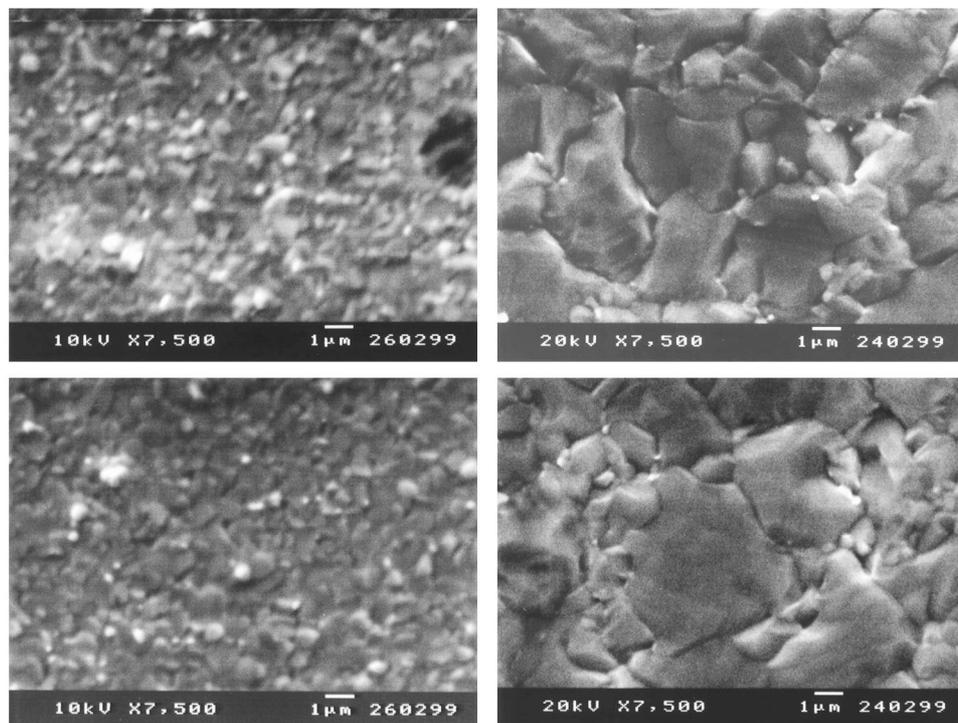


Fig. 2. Comparison of the as-deposited CdTe morphology on as-deposited (left) and vacuum-annealed (right) CBD-CdS layers on ITO (upper pictures) and FTO (lower pictures) substrates.

and as-deposited CBD–CdS were performed. After this recrystallization treatment a big change in the shape and size of the CdTe grains is observed (see Fig. 3). It appears that the CdCl₂ treatment recrystallizes the CdTe layers in such a way that some of the small grains coalesce together while some of the bigger grains divide into small grains and reorient themselves. As result an entirely different microstructure and morphology of CdTe is created. As shown in Fig. 3 the size and shape of recrystallized CdTe on as-deposited and annealed CdS are almost similar for FTO but quite different in case of ITO substrates.

X-ray diffraction of CdTe

The crystallographic orientation of different types of CdTe/CdS stacks were investigated with X-ray diffraction. The measurements were performed with a Siemens D-500 diffractometer and Cu K α source. Fig. 4 shows the XRD pattern of CdTe/CBD–CdS(vacuum-annealed)/FTO/glass samples. The as-deposited CdTe at a substrate temperature of 150°C exhibits a strong (111) preferred orientation. With increase in the substrate temperature the preference for the (111) orientation is decreased, as is shown for a layer grown at 300°C. The loss in the texture of CdTe is further enhanced by annealing in air and also with the application of the CdCl₂ treatment. The intensities of the (311) and (422) peaks are slightly lower than the intensity of the (111)

peak of the 300°C deposited or air annealed layers. However the intensity of the (111) peak is lower than that of the (311) peak of the CdCl₂ treated layers, implying that the layers are not (111) textured. The air annealed and CdCl₂ treated samples show an additional peak at 39 degrees, which we believe may be due to the intermixing of CdTe with CdS, the intensity of this peak is high for CdCl₂ treated samples suggesting an enhanced intermixing.

The CdTe layers on HVE-grown CdS also exhibit qualitatively a similar behaviour (see Fig. 5) [5]. The air annealing and CdCl₂ treatment reduce the (111) preferred orientation which depends on the annealing temperature and the amount of CdCl₂. The as-deposited layers at a substrate temperature of 300°C have a very intense (111) peak but the intensities of the (311) and (422) peaks are up to 40% of the (111) intensity (higher as compared to the powder data). For the CdCl₂ treated layers at 390°C the intensity of the (111) peak is lower than that of the (422) peak. Therefore, the (111) preferred orientation is completely lost and the layer has a predominance of the (422) orientation. For the layers annealed at higher temperatures of 430°C, the intensity of the (111) peak is again higher than the other peaks. This suggests that at high temperatures the grains rearrange towards the as-deposited structure, nevertheless the (111) orientation is still not as predominant as it was for the as-deposited CdTe layers. The crystallographic rearrangements are related to the stress in the layer and to the application of annealing at

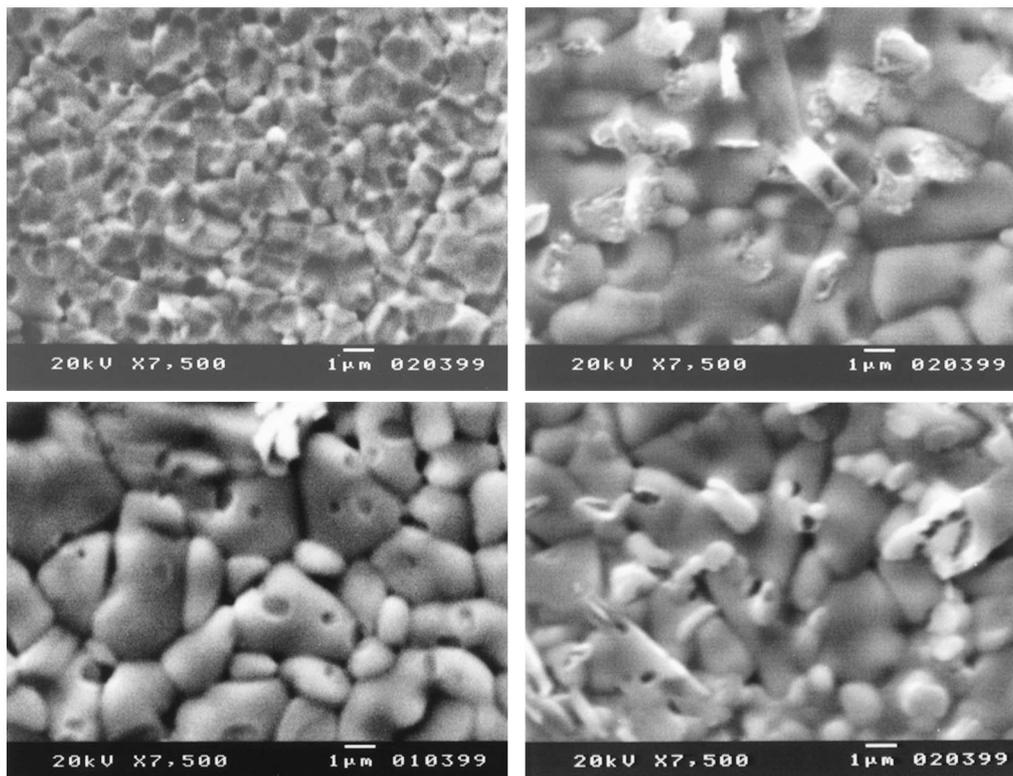


Fig. 3. Morphology of CdCl₂ treated CdTe on as-deposited CBD–CdS (left) and on vacuum annealed CBD–CdS (right); upper row is for ITO substrates, lower row is for FTO substrates.

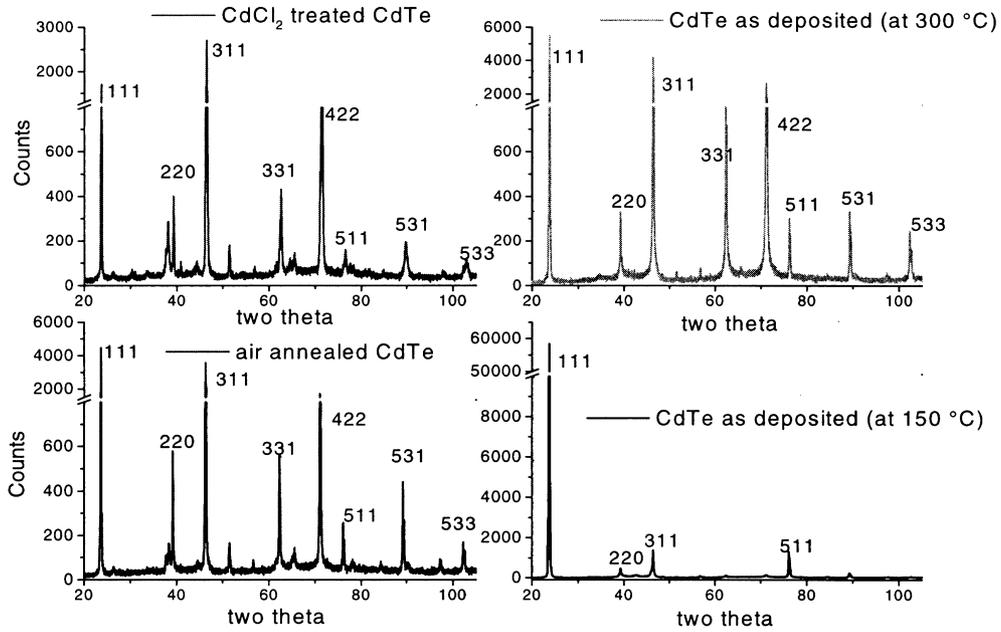


Fig. 4. XRD patterns of CdTe/CBD-CdS (annealed in vacuum)/FTO/Glass.

high temperature and on the CdCl₂ sintering flux. The creation of new grains as a result of a disintegration of some large grains is due to the relaxation of the excessive strains in the lattice. The coalescence of small grains into bigger ones is caused by the CdCl₂ sintering flux and by the high temperature. Because of this composite nature of the CdTe layers, XRD peaks corresponding to the crystallographic

planes of the as-deposited CdTe grains and ‘regenerated grains’ are observed. Glancing angle XRD patterns with varying angle of incidence revealed a difference in the crystalline state of bulk and surface of the CdTe layers in relation to the post-deposition treatment. The intensity of the (220) peak of the CdTe surface is very high compared to the bulk of the layers. For example in the as-deposited

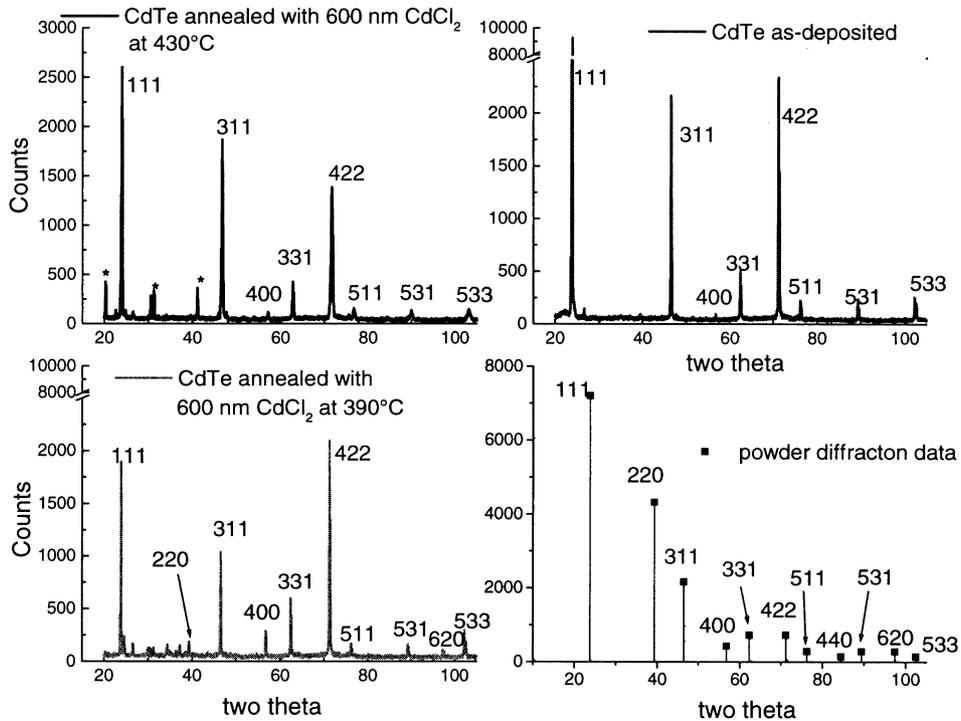


Fig. 5. X-ray diffraction patterns of CdTe/HVE-CdS (annealed in vacuum)/FTO/glass.

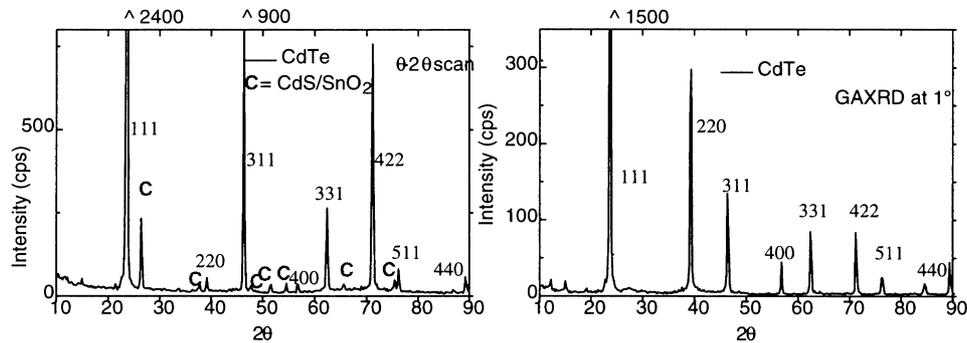


Fig. 6. XRD glancing angle pattern (right) and XRD bulk pattern (left) of HVE-CdTe as-deposited.

case the ratio of (111)/(220) is 5 for the surface and 24 for the bulk (see Fig. 6). This is indicative of a different microstructure compared to the bulk of the CdTe.

Stress, intermixing and photovoltaic performance

XRD measurements were analysed to study the intermixing and stress in the CdTe layers. The in-plane lattice parameters were accurately determined from the Nelson–Taylor plot [6,7]. As given in Table 1, the as-deposited layers have a high in-plane lattice constant compared to the recrystallized layers. As an example the lattice parameter of as-deposited CdTe on HVE–CdS decreases from 6.499 to 6.446 Å for the CdCl₂ treated layers. This is because of the relaxation of the compressive stress which is generated by the lattice and thermal mismatch between the CdTe and the underlying substrate. The lattice parameter may also decrease because of the intermixing of CdS in to the CdTe layer. These effects are more pronounced for CdTe layers grown on CBD–CdS. For example the lattice parameter decreases from 6.487 to 6.449 Å because of the intermixing of CdS/CdTe. A careful analysis of the data presented in Fig. 4 proved that the position of the (333)/(511) peak of CdTe shifts from 76.2 to 75.6° after the CdCl₂ treatment and

Table 1
Lattice parameter of CdTe on different window layers

Window layers	Condition of CdTe/CdS stacks	CdTe lattice parameter (Å)
HVE–CdS (vac-annealed)	As-deposited at 300°C	6.499
HVE–CdS (vac-annealed)	Treated with 600 nm CdCl ₂	6.446
CBD–CdS (vac-annealed)	As-deposited at 150°C	6.487
CBD–CdS (vac-annealed)	As-deposited at 300°C	6.481
CBD–CdS (vac-annealed)	Treated with 50 nm CdCl ₂	6.480
CBD–CdS (as-deposited)	Treated with 50 nm CdCl ₂	6.449

an additional peak at 77.6° is measured which is assigned to the intermixed CdTe–S compound [8].

The photovoltaic properties of the solar cells do not depend on the grain size only but also on the intermixing and pinholes which are mainly generated on CBD–CdS/TCO substrates. The CBD–CdS layers are thin (about 70 nm) and the annealing treatments cause strain relaxation and creation of pinholes. It is possible that almost all of the CdS layer is consumed into the CdTe. Therefore despite of large grained CdTe layers the solar cells exhibit poor performance: either shorts (in case of CdCl₂ treated) or low efficiencies are measured.

The highest efficiency of a solar cell on CBD–CdS is 2.5% ($V_{oc} = 500$ mV, $I_{sc} = 14.6$ mA/cm², f.f. = 0.35), while for the layers on HVE–CdS the efficiency is 11% ($V_{oc} = 811$ mV, $I_{sc} = 21.4$ mA/cm², f.f. = 0.64). The cells with 2.5% efficiency were made without a CdCl₂ treatment (only air annealing), and the poor performance is attributed to the presence of pinholes and excessive intermixing which is increased in the CdCl₂ treated case.

Conclusions

The crystallization and morphology of the CdTe is strongly affected not only by the CdCl₂ treatment but also by the deposition method and the structure of the CdS windows on the TCO substrates, they also affect the influence of the post-deposition treatment on CdTe. On CBD-grown CdS window layers, large grain CdTe is obtained even in the as-deposited condition. In contrast the CdTe grain size on HVE–CdS is small and post-deposition treatment is required to increase the grain size. The air annealing or CdCl₂ treatment cause growth or even disintegration of grains in the CdTe layers. The CdCl₂ treatment reduces the texture. At a low annealing temperature (around 390°C) the (111) preferred orientation is completely lost, however it is partly regained by increasing the annealing temperature. The post deposition treatments release the mismatch induced stress in CdTe and also influence the intermixing of CdS–CdTe. Despite of the large grain size of CdTe on CBD–CdS, low efficiency cells are obtained because of a

pronounced intermixing. In fact, because of pinholes or the almost total consumption of the thin CdS into the CdTe layers the CdCl₂ treated cells show electrical shorts.

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