



Influence of CdS growth process on structural and photovoltaic properties of CdTe/CdS solar cells

A. Romeo^a, D.L. Bätzner^a, H. Zogg^a, C. Vignali^b, A.N. Tiwari^{a,*}

^a*Thin Film Physics Group, Institute of Quantum Electronics, ETH Zürich, Technoparkstr. 1, 8005 Zürich, Switzerland*

^b*Centro Interfacolta' Misure, University of Parma, Viale delle Scienze 23/A, 43100 Parma, Italy*

Abstract

The morphology of CdS layers grown by chemical bath deposition (CBD) and high vacuum evaporation (HVE) have been investigated. The grains of CBD-CdS are more compact and smooth than those of HVE-CdS. The annealing and CdCl₂ treatment cause grain growth, which is stronger for the CdCl₂ treated samples. The grain-size of the as-deposited CdTe on CBD-CdS is about 5 times larger than of those grown on HVE-CdS. The structural and electrical properties of CdTe/CdS solar cells are strongly dependent on the CdS. The grain size of CdCl₂ treated CdTe layers are similar, irrespective of the transparent conducting oxide substrate and CdS deposition method. The efficiency of solar cells on thin CBD-CdS is low (about 5.6%) because of pin-holes and a large intermixing of CdTe-CdS. The cells on HVE-CdS yield a higher current density despite thicker HVE-CdS as compared to CBD-CdS. The efficiency of solar cells on HVE-CdS is 12.3%. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-efficiency CdTe/CdS photovoltaic devices have been obtained with different growth methods and recrystallization treatments [1–4]. It is known that the CdCl₂ treatment (deposition of CdCl₂ and annealing in air) on CdTe generally improves the

* Corresponding author. Tel.: + 41-1-4451474, Fax: + 41-1-4451499.

E-mail address: tiwari@iqe.phys.ethz.ch (A.N. Tiwari).

photovoltaic performance of solar cells. Also, a CdCl_2 treatment of the CdS window layers, applied in some laboratories, has yielded high-efficiency cells [3]. The growth and properties of CdTe layers and solar cells depend on CdS/transparent conducting oxides (TCO) substrates. Thin CdS layers grown by chemical bath deposition (CBD) are preferred as window layer because of low optical absorption losses and good covering properties on TCO. However pin-holes and irreproducibility is a concern for reliable industrial production. The CdS layers grown by physical vapor deposition (PVD) are more often used for better reliability and compatibility with PVD-CdTe processes, despite higher optical absorption losses in thicker (0.2–0.5 μm) CdS layers. We have investigated the properties of CdS, deposited by CBD or high vacuum evaporation (HVE) methods to find out which method is better suited and how the CdCl_2 treatment affects the properties of the CdS layers. The structural properties of the CdTe layers on different type of CdS layers have been investigated and correlated with the photovoltaic properties.

2. Experimental details and results

Commercially available ITO and fluorine doped SnO_x (FTO) coated soda lime glass substrates are used for the growth of solar cells. The sheet resistance of these transparent conducting oxide layers is above 10 ohm/square and the average optical transmittance is above 80%. CdS layers were 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) method at 80°C using a solution of Cd salt, ammonia and thiourea. The thickness of the HVE-CdS was varied in the range of 50–500 nm, however the optimum thickness is about 300 nm. Thinner (70–100 nm) CBD-CdS layers were used for high optical transmittance.

CdS layers were either annealed in vacuum at 450°C or treated with CdCl_2 before the growth of CdTe layers. For comparison, as-deposited CdS layers were also used. The CdTe layers were grown by evaporation of CdTe (6 nine pure) source material, at a substrate temperature of 300°C with a growth rate of 4 $\mu\text{m}/\text{h}$. The typical CdTe layer thickness is about 4 μm . An optimized CdCl_2 treatment [5,6] is applied on the CdTe/CdS stacks. The surface of the CdTe layer is etched in a bromine-methanol solution prior to the deposition of Cu/Au bilayers for back contacting on CdTe. It is known that Br-Methanol creates a Te-rich surface which yields an Ohmic contact on CdTe. After the metallization the cells were annealed at 200°C for 30 min.

2.1. Morphology of CdS

Atomic force microscopy (AFM) was used to study the surface morphology of the CdS layers. The morphology of the as-deposited CBD-CdS and HVE-CdS layers are quite different (Fig. 1). The grain size of HVE-CdS is in the range of 0.1–0.3 μm and the layers are rough. The CBD-CdS consists of clusters of up to 0.5 μm but clearly these clusters are formed due to a coalescence of small grains of about 0.1 μm . The CBD-CdS layers are rather smooth. As shown on Fig. 2, the grain size of vacuum

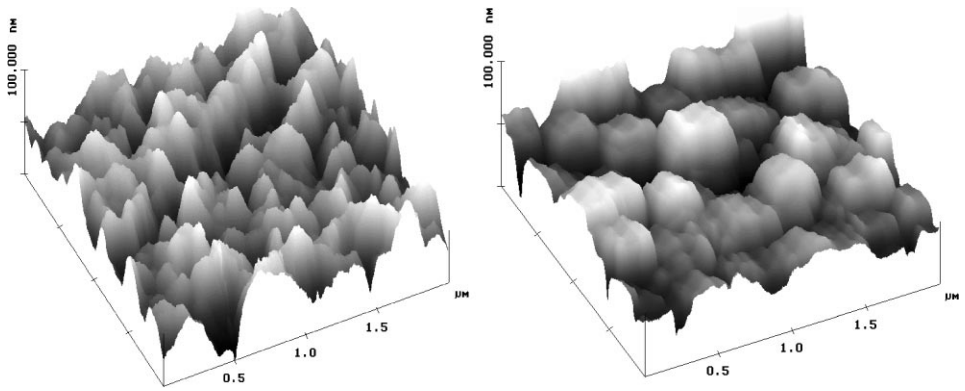


Fig. 1. Morphology of as-deposited HVE-CdS(left) and as-deposited CBD-CdS (right) layers on FTO substrate.

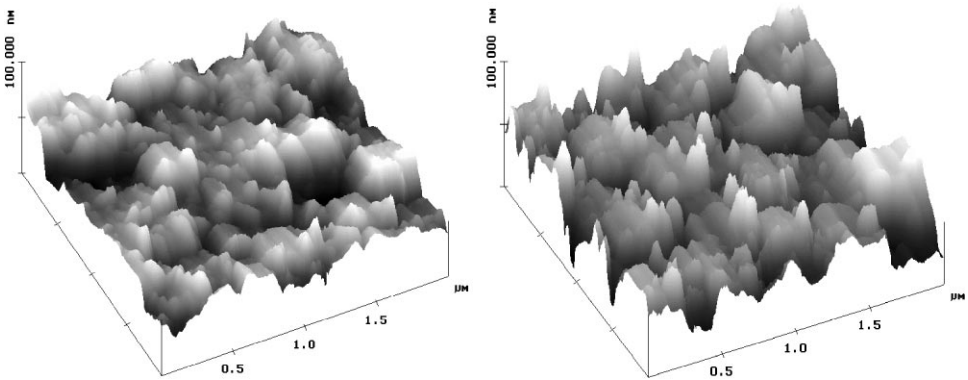


Fig. 2. Morphology of vac-annealed HVE-CdS (left) and vac-annealed CBD-CdS (right) layers on FTO substrate.

annealed HVE-CdS (recrystallized) is in the range of 0.3–0.5 μm and the layer is smooth. The effect of annealing in vacuum is different for the CBD-CdS. The grains, that on the as-deposited sample have a compact and smooth structure, are strongly recrystallized so that a flourished and rough structure is observed but its compactness is not lost (Figs. 1 and 2). The microstructure of the CdS also depends on TCO substrates. As shown in Fig. 3, the CdS grains on ITO are smaller and more homogenous than those on FTO. It should be mentioned that the morphology of CdS strongly depends on the morphology of the underlying TCO layer. The surface roughness of CdS may also depend on the thickness of the TCO layers.

A CdCl_2 treatment was applied to the HVE-CdS layers. After this recrystallization treatment a big change in the shape and size of the CdS grains is observed (Fig. 4). It appears that the CdCl_2 treatment recrystallizes the CdS layers in such a way that

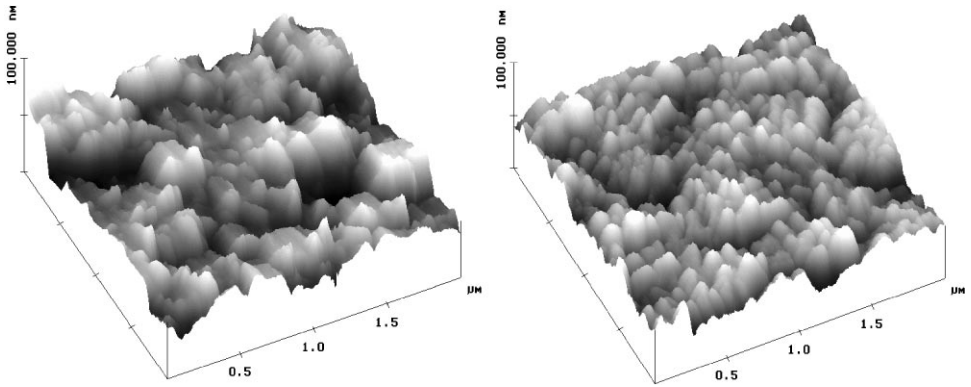


Fig. 3. Morphology of vac-annealed HVE-CdS layers on FTO (left) and ITO (right).

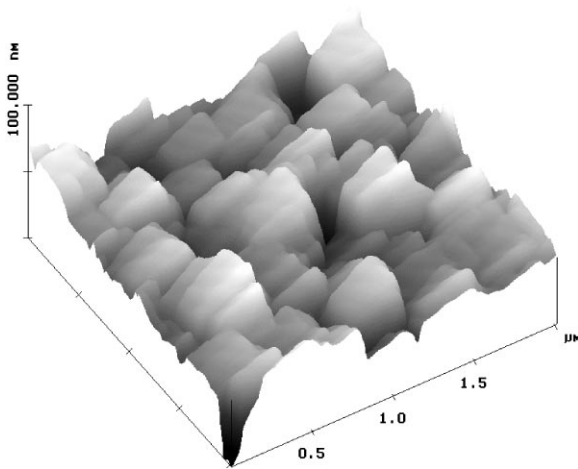


Fig. 4. Morphology of CdCl_2 treated HVE-CdS on FTO substrate.

some of the small grains coalesce together and form bigger grains of $0.5 \mu\text{m}$ width. Also, the shape of the grains is completely different, after the treatment the surface is smoother and the grains are predominantly rectangular in shape.

2.2. Morphology of CdTe

Scanning electron microscopy (SEM) was used to study the surface morphology of the CdTe layers grown on different CdS layers. Due to the different structures of CBD-CdS and HVE-CdS layers the as-deposited CdTe layers grow with different morphologies (Fig. 5). The grains of CdTe on HVE-CdS are in the range of $0.5\text{--}1 \mu\text{m}$. The CdTe on CBD-CdS appears to consist of some small grains of about $1 \mu\text{m}$ and

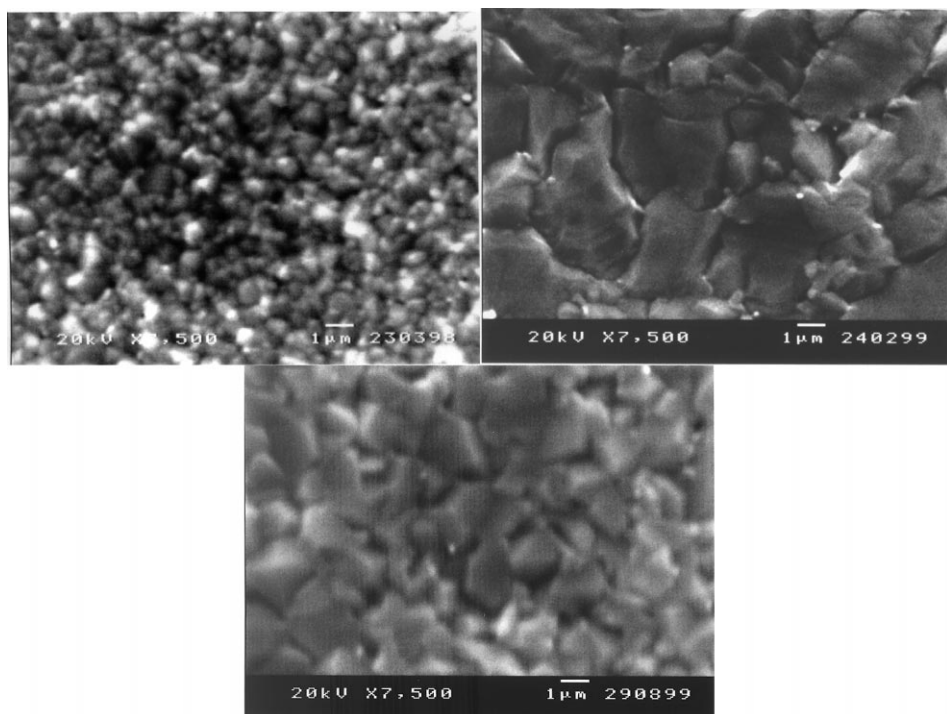


Fig. 5. Morphology of as-deposited CdTe on vac-annealed HVE-CdS (left), vac-annealed CBD-CdS (right) and on HVE-CdS treated with CdCl_2 (bottom). The CdTe grains on CBD-CdS are 5 to 10 times larger than those on HVE-CdS, and on the treated CdS the grains are of intermediate size.

many large grains of about $5\ \mu\text{m}$ width. The grains of the CdTe on CdCl_2 -treated HVE-CdS are larger compared to those on vacuum-annealed HVE-CdS but smaller than those of CdTe on vacuum-annealed CBD-CdS.

Post deposition treatments with CdCl_2 were performed on the CdTe layers grown on vacuum annealed CBD-CdS, HVE-CdS and CdCl_2 treated HVE-CdS. After this recrystallization treatment, a big change in the shape and size of the CdTe grains is observed (Fig. 6). For the CdTe on vacuum annealed HVE-CdS, a many-fold increase in the grain size and formation of wide grain boundaries are observed. The CdTe on CBD-CdS also is recrystallized in such a way that an entirely different microstructure and morphology of CdTe is created. There is insignificant change in the grain size of CdTe grown on the CdCl_2 treated HVE-CdS but the morphology is changed: the layer is more compact and the grain boundaries are reduced.

2.3. Recrystallization and intermixing in 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 $\text{Cu-K}\alpha$ source. Fig. 7 shows the XRD patterns of CdTe

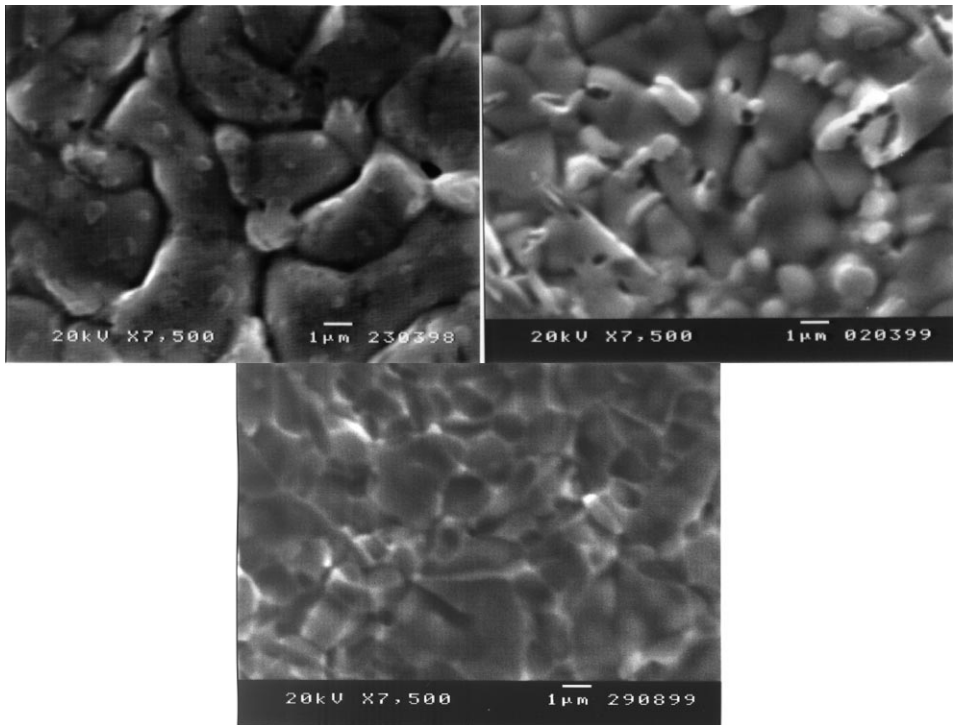


Fig. 6. Morphology of CdCl₂-treated CdTe on vac-annealed HVE-CdS (left), on vacuum annealed CBD-CdS (right), and on CdCl₂ treated HVE-CdS (bottom).

layers grown at a substrate temperature of 150°C on vacuum annealed CdS layers grown by CBD and HVE. The as-deposited CdTe layers exhibit a strong (111) preferred orientation in both the cases. With the increase in the substrate temperature the preference for the (111) orientation is decreased. Fig. 8 shows the XRD of as-deposited CdTe layers grown at 300°C on different CdS/FTO/glass samples (vacuum annealed HVE- and CBD-CdS and CdCl₂ treated HVE-CdS). CdTe layers on vacuum annealed and CdCl₂-treated HVE-CdS are (111) oriented. In contrast, the XRD pattern of CdTe on vacuum annealed CBD-CdS exhibit (111), (311) and (422) peaks of similar intensities, indicating that the layer is not (111) oriented.

Therefore, the crystallographic orientation of the CdTe layers on CBD-CdS is always influenced by the deposition temperature of CdTe layers, which is not the case for CdTe on HVE-CdS.

It seems that there is a correlation between the size of the CdS grains and the orientation of the CdTe that grows on it. The CdTe layers are more (111) oriented on highly recrystallized CdS layers of larger grain size, like the CdCl₂ treated CdS.

The loss in the texture of CdTe is further enhanced by annealing in air and also with the application of the CdCl₂ treatment. XRD patterns of the CdCl₂ treated (annealed at 430°C) CdTe deposited on different CdS layers were also measured (Fig. 9).

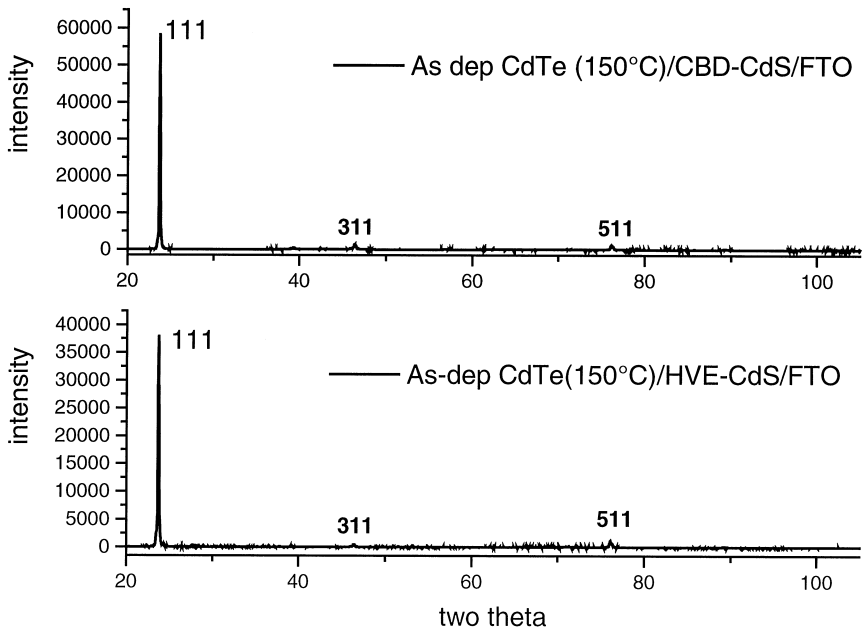


Fig. 7. XRD patterns of CdTe deposited at 150°C on vac-annealed CBD-CdS (top), and on vac-annealed HVE-CdS (bottom).

The loss of the (1 1 1) preferred orientation is common to all the layers, but it is more evident for the CdTe deposited on the vacuum annealed CBD-CdS where the (3 1 1) peak is predominant. In the case of CdTe on vacuum annealed HVE-CdS the (1 1 1) orientation is still stronger, but the (3 1 1) and (4 2 2) peaks have now a strong intensity so that the (1 1 1) preferred orientation is lost, and there is a more random orientation. The CdTe layers on CdCl₂ treated CdS is also randomly oriented, many of the XRD peaks have almost similar intensities (between 800 and 1300 counts).

The crystallographic rearrangements in CdTe are related to the stress in the layer and to the application of the CdCl₂ sintering flux and high temperature annealing. The creation of new grains as a result of the 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 annealing at 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. Pin holes in CdTe/CdS and almost total intermixing of CdS-CdTe also deteriorate the performance of solar cells on HVE-CdS window layers with thickness < 100 nm.

To study the intermixing and stress in the CdTe layers, the in-plane lattice parameters were accurately determined from the Nelson–Taylor plot [7,8]. As given in Table 1, the as-deposited CdTe layers have a high in-plane lattice constant compared to the recrystallized layers. As an example, the lattice parameter of the as-deposited CdTe on HVE-CdS decreases from 6.499 to 6.446 Å after the CdCl₂

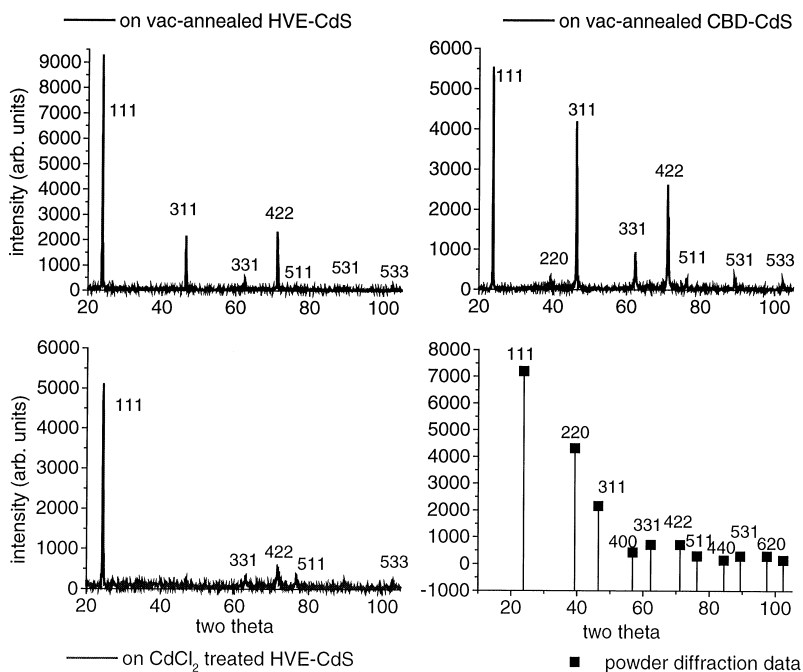


Fig. 8. XRD patterns of the as-deposited CdTe grown at 300°C on different CdS layers on FTO.

treatment. This is because of the relaxation of the compressive stress which is generated due to the lattice and thermal mismatch between the CdTe and the underlying substrate. The lattice parameter of the CdTe layer deposited at 150°C is 6.484 Å which is very near to the value obtained from the powder diffraction data (6.481 Å). This indicates that the stress in the low-temperature grown layer is insignificant. The lattice parameter may also decrease because of the intermixing of CdS into the CdTe layer. These effects are also evident for CdTe on CBD-CdS. In the case of CdTe on the CdCl₂ treated CdS, the lattice parameter of the as-deposited CdTe is not as high as for the one deposited on the vacuum annealed CdS, and after the CdCl₂ treatment the lattice parameter does not decrease so much. This is due to a change in the structure of the CdS, probably the lattice constants of vacuum annealed and CdCl₂ treated CdS are different, because of crystallographic structural transformation of phases. It appears that the influence of the CdCl₂ treatment on the recrystallization of CdTe and CdS-CdTe intermixing is less pronounced for CdCl₂ treated CdS window layers. This could be a reason for the slightly lower efficiency of the devices made with a treated CdS, it probably needs a different optimization.

2.4. Photovoltaic properties

The efficiency of solar cells does not depend on the grain size of the CdTe only but that is also influenced by the CdTe-CdS intermixing and pinholes/weak spots which

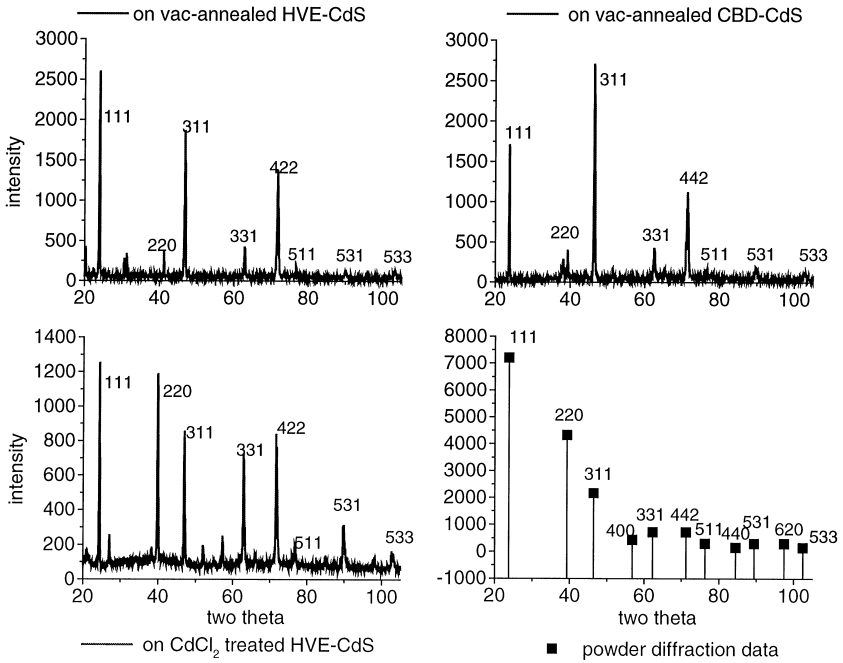


Fig. 9. XRD patterns of CdTe on different CdS layers.

Table 1
Table of 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
HVE-CdS (vac-annealed)	As-deposited at 150°C	6.484
HVE-CdS (CdCl ₂ -annealed)	As-deposited at 300°C	6.482
HVE-CdS (CdCl ₂ -annealed)	Treated with 600 nm CdCl ₂	6.477
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 (vac-annealed)	As-deposited at 150°C	6.487

are mainly generated in CBD-CdS/TCO substrates. Solar cells on thin (about 70 nm) CBD-CdS exhibit poor and irreproducible performance: pinholes are clearly visible after the CdCl₂ treatment of CdTe/CdS stacks. The annealing treatment causes strain relaxation and creation of pinholes, it is also possible that almost all of the CdS layer is consumed (intermixed) in the CdTe during the annealing treatment. Therefore the cells have low efficiency on shorts. The annealing treatment is essential for the conductivity-type conversion and junction activation.

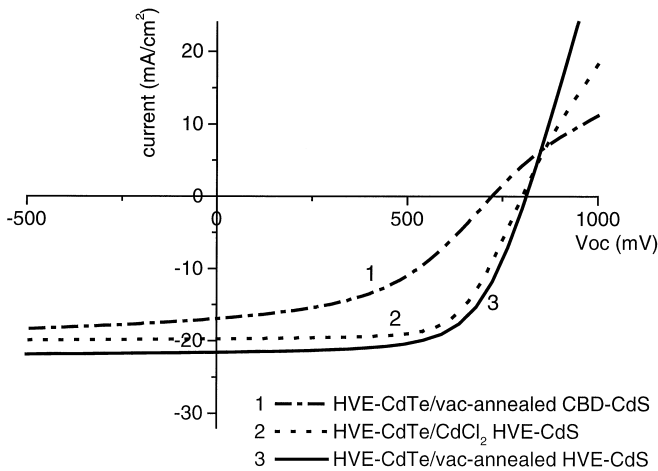


Fig. 10. I - V graphs of the solar cells made with three different CdS layers.

Solar cells were also prepared on thicker (~ 150 nm) CBD-CdS layers. Fewer pinholes were observed after the CdCl₂ treatment but the cells exhibit low efficiency in the range of 5–6% (typical values are $V_{oc} = 720$ mV, $I_{sc} = 17$ mA/cm², f.f. = 0.45). Cells with thin (< 100 nm) HVE-CdS also yield low efficiency with V_{oc} in the range of 500–650 mV and f.f. of 0.4. The measurement suggest that cells with CBD-CdS should be treated with a very small amount of CdCl₂. High-efficiency cells are obtained when the HVE-CdS layers thickness is about 300 nm. As shown in Fig. 10, the highest efficiency obtained for a solar cell on HVE-CdS is 12.3% ($V_{oc} = 800$ mV, $I_{sc} = 23$ mA/cm², f.f. = 0.67). The solar cell with CdCl₂ treated CdS exhibits an efficiency of 11.2% ($V_{oc} = 780$ mV, $I_{sc} = 22$ mA/cm², f.f. = 0.65).

The poor performance of the cells with 5.6% efficiency is attributed to the presence of pinholes and excessive intermixing.

3. Conclusions

The microstructure of CdS layers on TCOs depends on the method of deposition and post-deposition treatment. The crystallization and morphology of the CdTe are strongly affected not only by the CdCl₂ treatment alone but also by the CdS deposition method and the structure of the CdS window layers on the TCO substrates. 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 CdCl₂ treatment cause growth or even disintegration of grains in the CdTe layers. The as-deposited CdTe layers on HVE-CdS grow with (111) preferred orientation in the substrate temperature range of 150–300°C: CdTe layers grown at low temperature (150°C) are highly (111) oriented but layers grown at 300°C are comparatively less (111)

oriented. The CdCl_2 treatment reduces the texture. The post-deposition annealing treatments release the mismatch-induced stress in CdTe and also influence the intermixing of CdS-CdTe which is very much dependent on the properties of the CdS layers. The performance of solar cells on thin CBD-CdS and HVE-CdS is poor because of pinholes or excessive intermixing of CdS into the CdTe layers. Highest efficiency of 12.3% was obtained on about 300 nm thick vacuum annealed HVE-CdS layers. Solar cells on CdCl_2 treated CdS have slightly lower (11.2%) efficiencies, probably due to a weaker intermixing of the layers.

References

- [1] R.W. Birkmire, E. Eser, *Ann. Rev. Mater. Sci* 27 (1997) 625.
- [2] D. Bonnet, Proceedings of the 14th European Photovoltaic Solar Energy Conference, 30 June–4 July 1997, Barcelona, Spain.
- [3] N. Romeo, A. Bosio, R. Tedeschi, V. Canevari, Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, 6–10 July 1997, Vienna, Austria.
- [4] M.E. Ozsan, D.R. Johnson, S. Oktik, M.H. Patterson, D. Sivapathasundaram, J.M. Woodcock, Proceedings of the 12th European PVSC, 11–15 April, Amsterdam, The Netherlands.
- [5] A.Romeo, H. Zogg, A.N. Tiwari, Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, 6–10 July 1997, Vienna, Austria.
- [6] A. Romeo, D.L. Bätzner, H. Zogg, A.N. Tiwari, E-MRS 1999 Spring Meeting, June 1–4 1999, Strasbourg, France.
- [7] H.R. Moutinho, M.M. Al-Jassim, F.A. Abulfotuh, D.H. Levi, P.C. Pippo, R.G. Dhere, L.L. Kazmerski, Proceedings of the 26th PVSC, September 30–October 3 1997, Anaheim, CA, USA.
- [8] A. Taylor, H. Sinclair, Proceedings of the Physical Society, Vol. 57, The Physical Society, London, 1945, p.126.