JOURNAL OF MATERIALS SCIENCE **39** (2004) 1515– 1518

Structural characterization of CdTe thin films developed on metallic substrates by close spaced sublimation

G. P. HERNÁNDEZ*, X. MATHEW‡, J. P. ENRÍQUEZ, B. E. MORALES
Centro de Investigación en Energía-UNAM, 62580, Temixco, Morelos, México
E-mail: xm@mazatl.cie.unam.mx

M. M. LIRA
Departamento de Fisica, CINVESTAV-IPN, D.F, Mexico

J. A. TOLEDO
Coordinación de Ingeniería Molecular, IMP, D.F, México

A. S. JUÁREZ, J. CAMPOS
Centro de Investigación en Energía-UNAM, 62580, Temixco, Morelos, México

Cadmium telluride (CdTe) is one of the most investigated semiconductors for photovoltaic applications in the last four decades and is one of the most promising photovoltaic materials due to low-cost, high-efficiency, nearly optimum band gap (1.5 eV) for efficient photo conversion, high optical absorption coefficient ($>10^4$ cm^{-1}) at band edge and the variety of deposition techniques available for its deposition as thin films. The close spaced sublimation (CSS) is one of the most promising methods to develop good quality CdTe films on large area substrates. There are various reports of the CdTe/CdS solar cells with efficiencies exceeding 16%, all prepared by CSS [1, 2].

In conventional solar cells, the CdTe is developed on the CdS window layer deposited on conducting glass substrates. But devices on glass substrates have the disadvantage of weight, inability to withstand high processing temperatures and are prone to damages. On the other hand devices on flexible metallic substrates can overcome all the above mentioned disadvantages of the glass based devices. Hence the development and characterization of CdTe on thin flexible metallic substrates are interesting. There are a number of reports regarding the characterization of CdTe thin films developed on CdS substrates by CSS, but practically no reports regarding the characterization of CdTe films developed on metallic substrates by CSS technique. We have deposited CdTe films on stainless steel by CSS at various source and substrate temperatures and the films were characterized using SEM and XRD. In this paper we are reporting the influence of the temperatures of substrate and source on the various structural parameters such as lattice parameter, grain size and stress. The investigations regarding the development of an interlayer between CdTe and the substrate are in progress and will be published in subsequent papers.

The CSS system consists of a graphite reactor enclosed in a quartz tube. The tube was evacuated and flushed with nitrogen gas and later pure nitrogen was admitted to a pressure of 10 mbar followed by 2 mbar oxygen and the final pressure of the CSS chamber was 12 mbar. The graphite plates were heated independently using two tungsten halogen lamps of 2 kW each and thermocouples were inserted into the graphite plates to monitor and control the temperature. The source of CdTe was a thick film of stoichiometric CdTe evaporated on a quartz glass. The metallic substrates were cleaned and loaded over the CdTe source. The

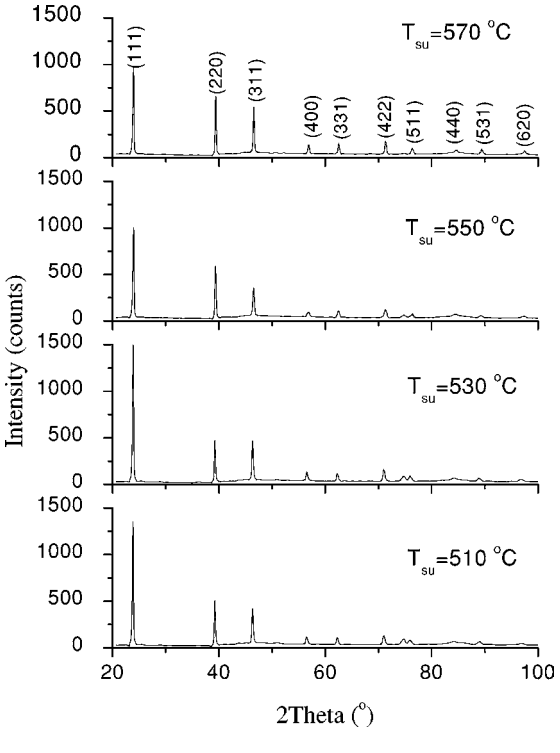

Figure 1 XRD patterns of the four films deposited at the same source temperature (T_{so}) of 630 °C, but with different substrate temperatures (T_{su}). The pressure and the environment in the CSS chamber were the same in all the cases.

*This work is part of the M.Sc. project of G. P. Hernández at CIE-UNAM.
‡Author to whom all correspondence should be addressed.

TABLE I Texture coefficient and preferred orientation grade of the CdTe films developed on stainless steel substrates by CSS

		Texture coefficient										
T_{S0}(°c)	T_{Su}(°c)	(111)	(220)	(311)	(400)	(331)	(422)	(511)	(440)	(531)	(620)	σ
610	510	0.54	0.47	0.82	1.09	0.68	0.74	1.09	2.50	1.07	0.99	0.54
	530	0.53	0.57	0.82	1.07	0.75	0.70	1.36	2.36	1.04	0.80	0.51
	550	0.41	0.39	0.77	1.48	0.57	0.70	1.40	2.36	0.96	0.98	0.57
	570	0.40	0.42	0.76	1.50	0.70	0.62	1.39	2.38	0.91	0.91	0.58
630	510	0.73	0.48	0.84	1.20	0.70	0.81	1.10	2.31	1.04	0.80	0.48
	530	0.78	0.43	0.85	1.28	0.67	0.94	1.17	2.07	0.98	0.83	0.42
	550	0.55	0.58	0.73	1.04	0.69	0.79	1.23	2.54	0.99	0.86	0.55
	570	0.42	0.53	0.90	1.17	0.77	0.98	1.34	2.16	1.22	0.93	0.55
650	510	0.86	0.34	0.68	1.27	0.71	0.86	1.33	2.17	0.95	0.84	0.47
	530	0.52	0.50	0.77	1.14	0.68	0.79	1.27	2.38	1.08	0.87	0.52
	550	0.58	0.51	0.71	0.88	0.81	0.85	1.24	2.56	1.22	0.63	0.57
	570	0.41	0.17	0.66	1.85	0.55	0.94	1.61	1.94	0.93	0.95	0.58
670	510	0.41	0.40	0.59	0.92	0.82	1.07	1.42	2.44	1.10	0.82	0.57
	530	0.46	0.38	0.70	1.13	0.71	0.88	1.29	2.43	1.16	0.86	0.55
	550	0.45	0.38	0.85	1.21	0.73	1.03	1.45	1.90	1.02	0.99	0.43
	570	0.56	0.31	0.80	1.58	0.63	0.97	1.65	1.64	0.96	0.90	0.45

The abbreviations T_{su} and T_{so} stand for temperature of substrate and source respectively. σ is the preferred orientation grade.

separation between the source and the substrate was 2 mm. The films were prepared with different source and substrate temperatures in the range 610–670 °C and 510–570 °C respectively. The XRD data were collected using a Rigaku X-ray diffractometer with CuK_α radiation at 1.54056 Å. The data were collected over a 2θ range of 20–100 degrees which facilitated an accurate study of all the peaks and a precise calculation of the lattice parameters.

We have analyzed sixteen films prepared under different conditions of source and substrate temperatures. Fig. 1 shows the X-ray diffraction patterns of four typical CdTe films deposited at substrate temperatures (T_{su}) of 510, 530, 550 and 570 °C, in each of these depositions the source temperature (T_{so}) was maintained constant at 630 °C. The XRD pattern shows the characteristic peaks of the cubic zincblende structure. It is clear from the figure that the substrate temperature influence the grain growth and the preferential orientation of the grains for the (111) plane decreases as the temperature increases. The preferred orientation of the crystallites along a crystal plane (hkl) in a thin film can be described by the term texture coefficient given in references [3, 4].

$$P_i = \frac{N(I_i/I_{i0})}{\sum_{i=1}^{N}(I_i/I_{i0})} \quad (1)$$

where P_i is the texture coefficient of the plane i, I_i is the measured integral intensity, I_{io} is the integral intensity of the JCPDS powder diffraction pattern intensity of the corresponding peak i and N is the number of reflections considered for the analysis. For the analysis we have considered the ten peaks of the cubic zincblende CdTe observed below $2\theta = 100°$. P_i is unity for each reflection in the case of a randomly oriented sample and values of P_i greater than unity indicate preferred orientation of the crystallites in that particular direction. The degree of preferred orientation of the sample as a whole can be assessed by the standard deviation σ of

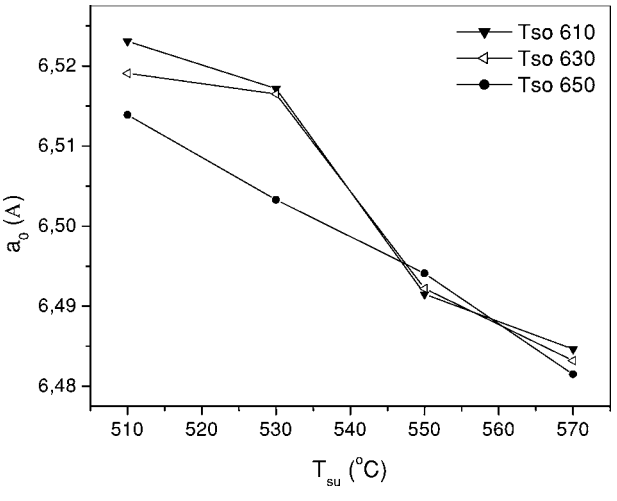

Figure 2 Dependence of the lattice parameter $\mathbf{a_o}$ on the substrate temperature (T_{su}) of the CdTe films prepared by CSS. The makers are experimental data and the line is a guide to the eye.

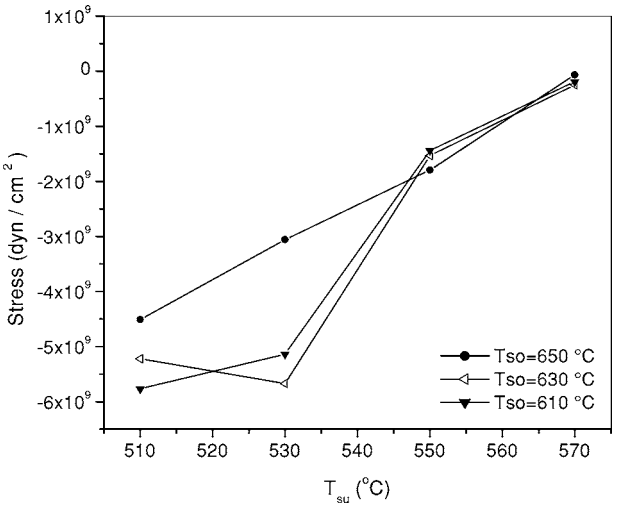

Figure 3 Variation in stress of the CdTe films when the substrate temperature (T_{su}) increases. The makers are experimental data and the line is a guide to the eye.

all the P_i values calculated for the sample [5].

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (P_i - P_{io})^2}{N}} \qquad (2)$$

where P_{io} is the texture coefficient of the powder sample which is always unity. The value of σ is an indicator of the degree of orientation of a sample and can be used to compare different samples. A value of zero for σ indicates that the sample is completely at random orientation. From Table I it can be seen that the value of σ is less than 0.6 for all samples which indicates that none of the samples possesses a significant orientation. Nevertheless, from the texture coefficient data we can see that in all samples (440) is the more preferred orientation.

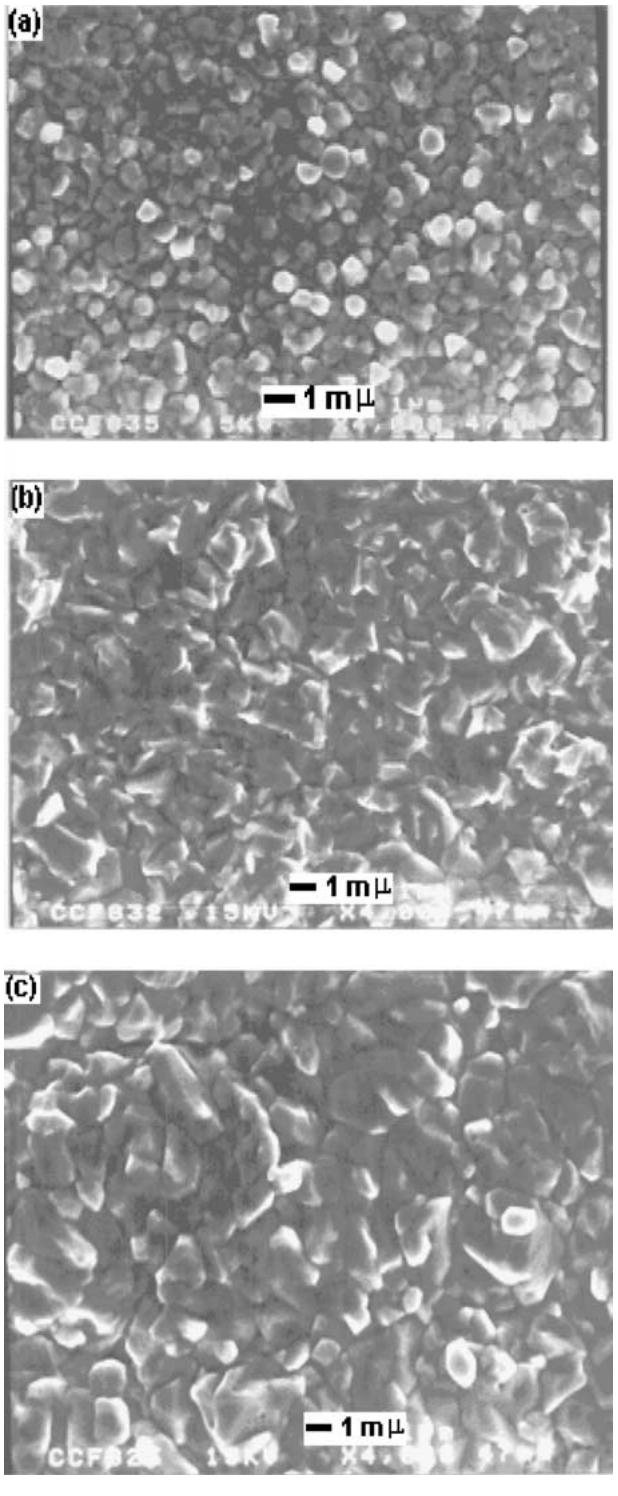

Figure 4 SEM micrographs of the three CdTe films prepared by CSS at different substrate temperatures of (a) 530 °C, (b) 550 °C and (c) 570 °C. Source temperature remained constant at 630 °C.

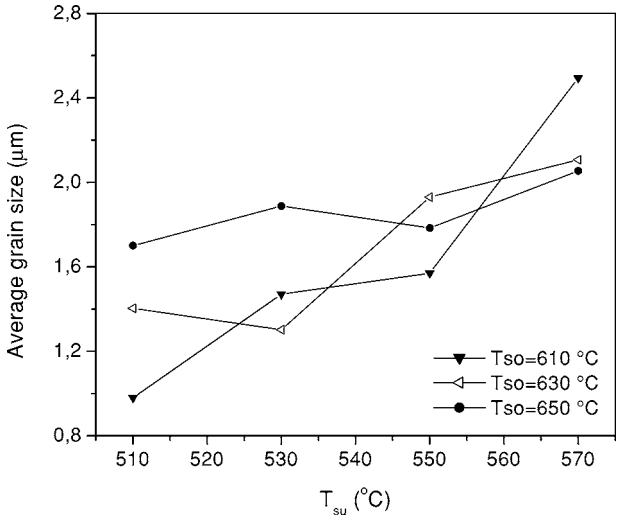

Figure 5 Dependence of the average grain size of the films on the substrate temperature (T_{su}). The makers are experimental data and the line is a guide to the eye.

The lattice parameter, $\mathbf{a_o}$, of the samples were calculated from the peak positions in XRD patterns and using the method developed by Nelson and Taylor [6, 7]. The lattice parameter calculated from different peaks were plotted against $\cos^2\theta(\sin^{-1}\theta + \theta^{-1})$. The relationship between these two parameters is linear and the intercept at $\cos^2\theta(\sin^{-1}\theta + \theta^{-1}) = 0$, gives the lattice constant of the sample. The lattice parameter $\mathbf{a_o}$ of different samples prepared at different source and substrate temperatures is shown in Fig. 2. It is clear from Fig. 2 that the films deposited at lower substrate temperatures shows larger values for the lattice parameter than the powder sample $\mathbf{a}_{\text{powder}} = 6.481$ Å, which suggests that the film is submitted to compressive stress in the plane parallel to the substrate surface and for higher substrate temperatures the lattice parameter approaches the value of bulk CdTe. In electro deposited CdTe films it has been reported that the lattice parameter of the as deposited film is larger than that of the powder sample and upon annealing the lattice parameter decreases and for longer annealing durations the value becomes less than that of the powder sample [8]. In this case the stress changes from compressive to tensile due to the annealing; there are good number reports in the literature regarding the influence of post deposition heat treatments on the lattice parameter [8–12].

Fig. 3 shows the variation in stress of the CdTe thin films deposited with different source and substrate temperatures. As we can see the substrate temperature has a noticeable influence on the stress of the film. It can be seen that the stress decreases as the substrate temperature increases and approaches zero when the T_{su} is more than 570 °C.

Fig. 4 shows the SEM micrograph of CdTe films deposited at a source temperature of 630 °C and with substrate temperatures 530, 550 and 570 °C respectively. It can be seen that the films prepared at higher substrate temperatures have better morphological parameters such as grain size, free of voids, and close packed

structure. The grain sizes were measured by line-intercept method. Fig. 5 shows the dependence of average grain size on the substrate temperatures. As we can see from the figure, the average grain size increases with substrate temperature.

Acknowledgments

This work was partially supported by CONACYT and PAPIIT-UNAM through the projects 38542-U and IN115102 respectively.

References

1. J. BRITT and C. FEREKIDES, *Appl. Phys. Lett.* **62** (1993) 2851.
2. T. ARAMOTO, S. KMAZAWA, H. HIGUCHI, T. ARITA, S. SHIBUTANI, T. NISHIO, J. NAKAJIMA, T. TSUJI, A. HANAFUSA, T. HIBINO, K. OMURA and M. MUROZONO, *Jpn. J. Appl. Phys.* **36** (1997) 6304.
3. K. H. KIM and J. S.CHUN, *Thin Solid Films* **141** (1986) 287.
4. CHARLES S. BARRETT and T. B. MASSALSKI, in "Structure of Metals: Crystallographic Methods, Principles and Data", 3rd ed. (McGraw Hill, NY, 1966) p. 205.
5. H. R. MOUTINHO, M. M. AL-JASSIM, D. H. LEVI, P. C. DIPPO and L. L. KAZMERSKI, *J. Vac. Sci. Technol.* A **16** (1998) 1251.
6. A. TAYLOR and H. SINCLAIR, in Proceedings of the Physical Society, Vol. 57 (The Physical Society, London, 1945) p. 126.
7. J. B. NELSON and D. P. RILEY, *Proc. Phys. Soc.* **57**, (1945) 160.
8. B. QI, D. KIM, D. L. WILLIAMSON and J. U. TREFNY, *Electrochem. Soc.* **143** (1996) 517.
9. A. ROMEO, D. L. BATZNER, H. ZOGG and A. N. TIWARI, *Thin Solid Films* **361** (2000) 420.
10. K. D. ROGERS, J. D. PAINTER, D. W. LANE and M. HEALY, *J. Electronic Mater.* **28** (1999) 112.
11. L. R. CRUZ, L. L. KAZMERSKI, H. R. MOUTINHO, F. HASOON, R. G. DHERE and R. DE AVILLEZ, *Thin Solid Films* **350** (1999) 44.
12. H. R. MOUTINHO, M. M. AL-JASSIM, F. A. ABUFOLTUH, D. H. LEVI, P. C. DIPPO, R. G. DHERE and L. L. KAZMERSKI, "26th IEEE Photovoltaic Specialists Conference" (Anaheim, California, 1997).

Received 1 July
and accepted 12 August 2003