JOURNAL OF MATERIALS SCIENCE 31 (1996) 2047–2050

Influence of deposition potential and electrolyte composition on the structural and photoelectrochemical properties of electrodeposited mercury cadmium telluride

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Cadmium-rich $Cd_xHg_{1-x}Te$ (CMT) thin films were grown by cathodic electrodeposition. Two main fabrication parameters were taken into account: deposition potential and mercury content in solution. Different layers of CMT deposited by varying these two parameters were studied by X-ray diffraction, energy dispersive X-ray spectrometry and photoelectrochemical measurements. It was shown that surface structure, composition and quantum efficiency of CMT can be controlled with these two variables. Multigap structures were also been considered.

1. Introduction

Nowadays $Cd_xHg_{1-x}Te$ (CMT) has very interesting applications as a semiconductor, owing to the fact that the amount, x, of mercury in it varies between 1.45 and 0 eV [1]. This characteristic is very useful because it allows $Cd_xHg_{1-x}Te$ to be used as an infrared detector or as a p-layer in the construction of high-efficiency solar cells. This work focused on the latter use.

Recent advances [2–4] have shown that the main advantage of using $Cd_xHg_{1-x}Te$ in solar cells lies in the construction of multilayers/multigaps in order to obtain optimum benefit from the solar spectrum. Electrodeposition is of special interest because of its low cost, ease and use in the industry [2, 5, 6]. Nevertheless, many problems remain in the electrodeposition techniques in growing thin films of $Cd_xHg_{1-x}Te$ [7].

In this work, two different ways of producing changes in the CMT composition were studied. The photoelectrochemical study provided amazing details about the quantum efficiency of these films.

2. Experimental procedure

For the preparation of $Cd_xHg_{1-x}Te$ films, the well-known system consisting of a standard three-electrode electrochemical cell was used. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a large (3×3 cm^2) platinum sheet. Two different types of working electrode (substrate) were used: titanium plate and SnO_2 glass to allow optical properties and the growth process on the different substrates to be studied. These studies are still in progress.

The titanium plate (3×1 cm^2) was cleaned as follows: cleaning in distilled water; degreasing by boiling in trichlorethylene, acetone and methanol, for about 5 min in each; etching for 2 min in nitric acid 60%; etching for 45 s in HF 7%; boiling in 10% oxalic acid solution. The plate was left in this solution for about 3 days, the time necessary to change the colour of the solution (transparent–Brown–transparent). The substrates were kept in this solution until they were required for use.

The SnO_2 glass substrates (3×1 cm^2) were degreased as the titanium plates. Before use they were etched about 10 s to clean their surface. It was observed that during the deposition, the films deposited on the etched substrates were much more resistant and the layer was more firmly adhered than those grown on the unetched substrates.

The films were grown by electrodeposition at a constant potential in an aqueous solution containing 0.5 M $CdSO_4$; 10^{-3} M TeO_2 and concentrations of $HgCl_2$ which varied from 5×10^{-5}–2×10^{-4} M. The pH was adjusted to 1.6 with H_2SO_4. Nitrogen was bubbled before the deposition and passed over the electrolyte during the electrodeposition to avoid different kinds of oxidation and undesirable "acidifying effects" near the electrodes. The temperature of the solution was maintained at 90 °C when the titanium substrate was used, and lowed to 70 °C with SnO_2 substrates because of sticking effects. Films adhere better to titanium substrates than to the glass substrates. This is basically due to the differences in roughness and conductivity of the surfaces. Current densities registered during growth were between 2 and 4 mA cm^{-2} (depending on the deposition potential) for the titanium substrate, and between 0.2 and 0.4 mA cm^{-2} when SnO_2 was used. The electrodeposition was favoured by stirring the solution.

Certain experimental variables in this technique can modify the stoichiometry of the grown film: for example, $[Hg^{2+}]$, V_d, T, pH, and stirring. We are interested in the two most important: $[Hg^{2+}]$ in the solution and the deposition potential, V_d. By controlling these two variables monolayer films and films made of different layers have been grown.

The values used in our experiments for these variables were: $[Hg^{2+}] = 10^{-4}$, 2×10^{-4}, 5×10^{-5} M, $V_d = -550$, -600, -650 mV.

Two methods were used to obtain films of $Cd_xHg_{1-x}Te$ with different mercury contents: (a) deposition at a fixed potential but using electrolitic baths with different values of $[Hg^{2+}]$; (b) deposition using one electrolyte with a fixed value of $[Hg^{2+}]$ but with changing deposition potential.

Multilayer films with different compositions of mercury in each layer were also prepared, by applying consecutively to the substrate two of the potentials mentioned above, in a solution with a fixed value of $[Hg^{2+}]$.

The thickness of all the samples was controlled during the deposition using the relation between charge transfer and deposited mass with the well-known Faraday's law, and after deposition it was verified with a Talystep. Each deposited layer was 1 μm thick.

The samples were analysed by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDAX) techniques in order to determine their structure and composition. Photoelectrochemical characterization to study quantum efficiency was also performed.

The XRD equipment was a Siemens Diffraktometer D5000, using CuK_α radiation. The EDAX equipment was a Philips electronic microscope XL30 and a Philips EDX analyser PV 9900. This equipment is able to obtain qualitative and quantitative analysis of the films, detecting concentrations less than 0.1%. The variation of the Hg/Te ratio with depth in the multilayers was studied by irradiating their edges with a fixed 20 kV electron beam.

Photoelectrochemical measurements were carried out using a solution 0.1 M Na_2S and 0.1 M S in a conventional single-compartment cell, with a flat quartz window for illumination of the semiconductor electrode, coupled to a potentiostat whose output was fed into a Lock-in amplifier. Monochromatic illumination experiments were performed with a stabilized 150 W xenon lamp coupled to a high-intensity monochromator and using chopped light (27 Hz). These measurements show that all the samples exhibit n-type conduction.

3. Results and discussion

The study of the structure of $Cd_xHg_{1-x}Te$ is not easy because of the small difference in the "lattice constants" of CdTe and HgTe (6.482 and 6.460 Å respectively). However the intensities, position and width of the peaks, allow us to confirm the existence of the ternary semiconductor in our films.

The effect of varying $[Hg^{2+}]$ in the solution when a constant potential of -650 mV was applied was studied first. Metallic cadmium appears in all the films, but with the amounts becoming increasingly smaller when mercury in solution was increased. Mercury was not observed to be isolated. peaks of $Cd_xHg_{1-x}Te$ (CMT) were the highest and narrowest when the film was deposited in $[Hg^{2+}] = 2 \times 10^{-4}$ M ($x = 0.85$) .

The effect of varying V_d while the mercury content in solution was fixed, was also studied. Cadmium was observed to be in the single phase except for voltages less or equal to -600 mV (Fig. 1) which is in

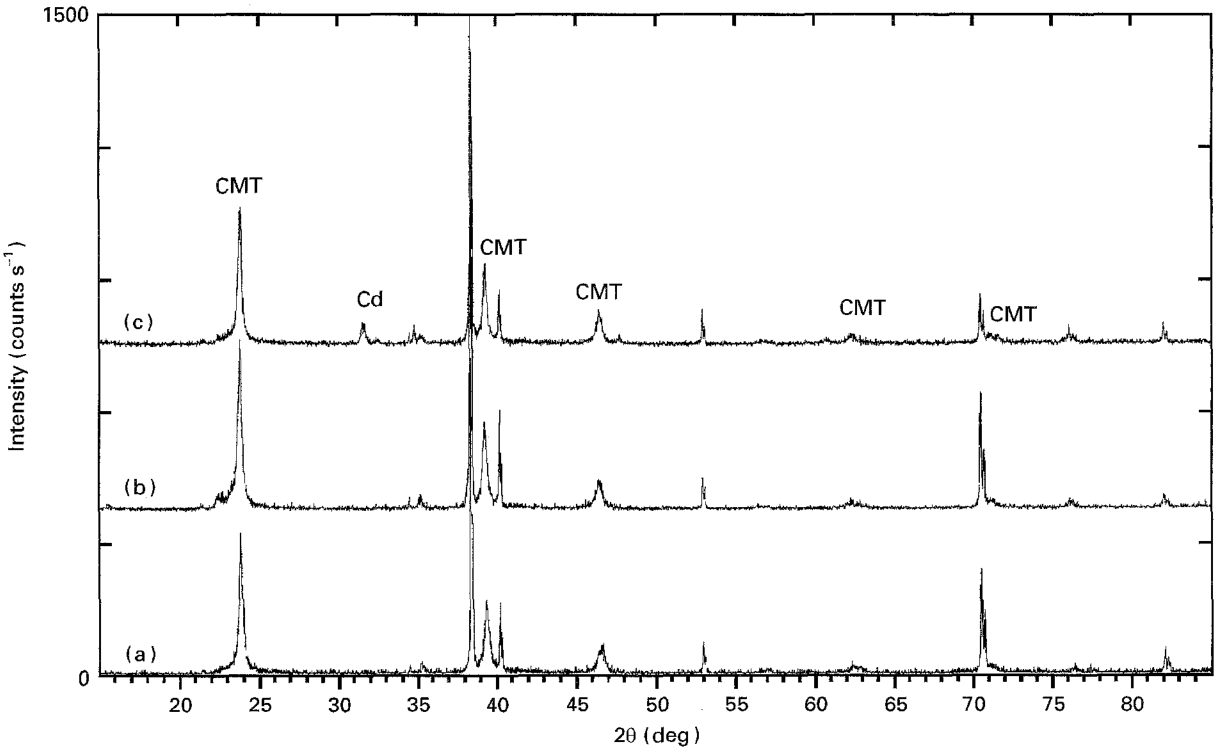

Figure 1 XRD patterns of $Cd_{0.85}Hg_{0.15}Te$ samples deposited at (a) -550 mV, (b) -600 mV and (c) -650 mV.

TABLE I Relative intensities for $Cd_xHg_{1-x}Te$ samples with different values of x, grown at different deposition potentials

d(Å)	I_r(%)					
	− 550 mV		− 600 mV		− 650 mV	
	$x = 0.85$	$x = 0.9$	$x = 0.85$	$x = 0.9$	$x = 0.85$	$x = 0.9$
3.74	44.89	30.25	33.68	33.52	38.06	16.82
2.29	23.62	15.23	17.58	15.17	22.69	9.65
1.95	9.53	8.23	6.23	5.35	10.08	3.91
2.81 (Cd)	–	–	–	–	6.24	17

TABLE II Hg/Te ratio in films deposited in different electrolytic baths at − 600 and − 550 mV

$[Hg^{2+}]$	Hg/Te ratio	
	− 600 mV	−550 mV
5×10^{-5}	0.12	0.08
10^{-4}	0.13	0.12
2×10^{-4}	0.27	0.29

TABLE III Hg/Te and Cd/Te ratios of CMT samples deposited in a bath of 10^{-4} M Cl_2Hg applying different potentials

V_{dep} (mV)	Hg/Te rate	Cd/Te rate
− 550	0.12	0.55
− 600	0.13	0.56
− 650	0.18	1.90

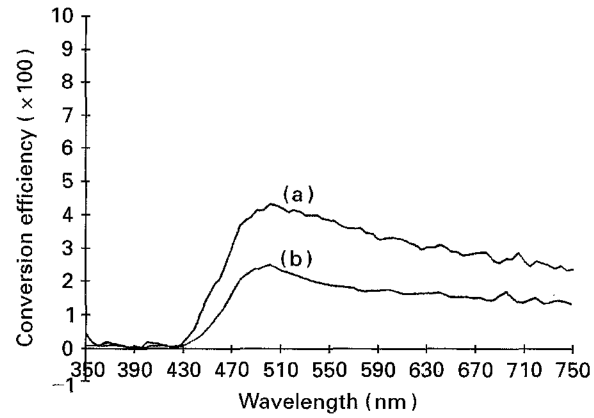

Figure 2 Quantum efficiency of both sides of a $Cd_{0.85}Hg_{0.15}Te$ sample: (a) face not in contact with the platinum electrode; (b) face adjacent to the platinum electrode.

agreement with the results of Cd–Hg–Te voltamographs [7, 8]. It was observed that changes in intensities when applying $V_d = -600$ mV were less abrupt than when using − 650 or − 550 mV, which can indicate a predominant deposition of CMT instead of CdTe and HgTe, see Table I. It was also observed that the higher the temperature of the electrolyte during deposition, the more crystalline were the films.

The Hg/Te and Cd/Te ratios in the film were studied by EDAX. CdTe films grown at different potentials were initially analysed. Samples deposited at − 550 mV showed a lack of cadmium in its composition structure. At − 650 mV the effect was the contrary. On the face adjacent to the platinum sheet during electrodeposition, and only at − 650 mV, small balls of cadmium (about 10 μm diameter) could be seen and the Cd/Te ratio increased sharply. This was probably due to the high deposition rate (the intensity registered was double) when the negative potential increasingly approaches the cadmium deposition potential [7].

On the opposite face (not adjacent to the platinum electrode) we found a Cd/Te value of 0.7, the face was more homogeneous and there was a total absence of cadmium grains. Posterior photoelectrochemical study of both sides of it was very revealing. A potential of − 600 mV gives to the sample a good surface structure and homogeneity with a Cd/Te value of 0.7.

Thus, it was observed in this first EDAX study that deposition potentials of − 650 mV or more negative, are not good for the obtention of these films owing to problems of high deposition rate, hydrogen evolution in the solution, and excess cadmium as a single phase.

An increase in the mercury deposited on the film with increasing $[Hg^{2+}]$ in the electrolitic bath was observed, see Table II. This dependence is almost linear, but only when $[Hg^{2+}]/[HTeO_2^+]$ goes from 0 to 0.2 [9].

Using a solution with $[Hg^{2+}] = 10^{-4}$ M, the dependence of Hg/Te, Cd/Te in the films with the deposition potential used during the deposition was studied an increase in the amount of mercury deposited as the potential became more and more negative was observed, see Table III; this is of interest because in this way V_d can control mercury deposition and thus the energy band gap of the material. The behaviour of cadmium and tellurium was studied previously CdTe.

Some multilayer samples were analysed by EDAX by irradiating their edges with a fixed 20 kV electron beam (depth profile). It was observed that the same dependence existed between V_d and mercury deposited in the film in the different layers of the sample. This kind of "multigap structure" is especially interesting for photoelectrochemical studies [4].

The EDAX study revealed significant differences on the surface and in the composition of both sides of the same sample. Photoelectrochemical measurements on these faces showed important differences in the quantum efficiency, as can be seen in Fig. 2. Those differences are even bigger in multilayer samples (Fig. 3). The face not in contact with the platinum electrode presents a higher quantum efficiency (even double) than the other face. This difference is maximum at 510 nm where the peak of the curve is situated. Defects, grains of cadmium and less homogeneity are clearly negative in order to obtain optimum profit from the solar energy.

The relations between quantum efficiency and different stoichiometries of $Cd_xHg_{1-x}Te$ (different values of mercury deposited on the film) were also studied. As can be seen in Fig. 4, films with $x = 0.9$ are the most efficient in light conversion, much higher than $x = 0.85$ or 0.7 films, and this must be taken into account in order to grow multilayer films. This effect can be explained with the help of the solar spectrum

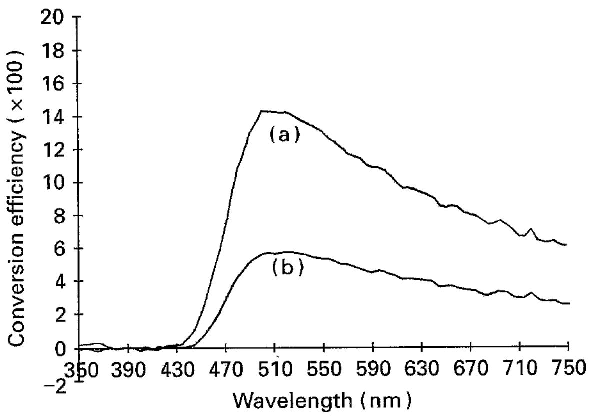

Figure 3 Quantum efficiency of both sides of a multilayer $Cd_{0.85}Hg_{0.15}Te/Cd_{0.95}Hg_{0.05}Te$ sample: (a) face not in contact with the platinum electrode; (b) face adjacent to the platinum.

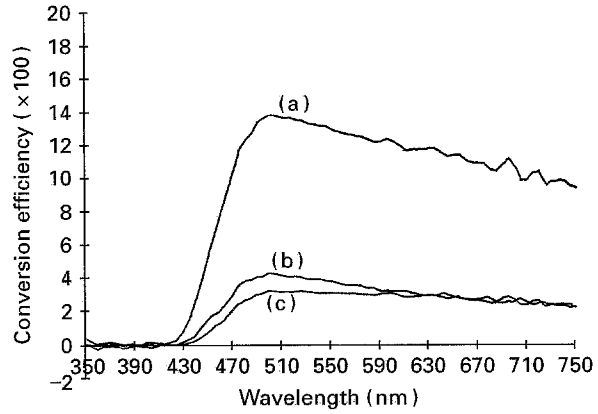

Figure 4 Spectral response of the quantum efficiency in CMT films: (a) $Cd_{0.9}Hg_{0.1}Te$; (b) $Cd_{0.85}Hg_{0.15}Te$; (c) $Cd_{0.7}Hg_{0.3}Te$.

curve shape and with information about defects and film growth obtained from X-ray diffraction and EDAX.

4. Conclusions

Two different methods of obtaining electrodeposited $Cd_xHg_{1-x}Te$ films with different values of $1 - x$ (mercury deposited) have been studied, which imply different values of the energy band gap. (a) changing the deposition potential during electrodeposition (-550, -600, -650 mV). More negative potentials gave more mercury deposited in the film; (b) using solutions with different $[Hg^{2+}](5 \times 10^{-5}, 1 \times 10^{-4}, 2 \times 10^{-4}$ M). High $[Hg^{2+}]$ in solution gave more mercury deposited in the film. Structural and photoelectrochemical studies on these films showed:

1. CMT thin films can be obtained by cathodic electrodeposition;
2. the higher the solution temperature during deposition, the higher was the crystallinity of the samples;
3. the best potentials for the electrodeposition of cadmium-rich CMT are less negative than -650 mV in order to obtain homogeneity, an absence of singles phases and good Hg/Te ratios;
4. differences exist between films deposited on opposite sides of the substrate. These differences are in composition, surface structure and most importantly in quantum efficiency;
5. the best profit of the solar spectrum takes place with films $x = 0.9$ then $x = 0.85$ and finally $x = 0.7$;
6. multilayer films (multigap structures) are more efficient in light conversion than the single films (monogap).

Acknowledgements

We thank Dr L.M. Peter and the Electrochemistry Group, University of Southampton, where the photoelectrochemical measurements were carried out, for their assistance, and the Servicio Interdepartamental de Investigación (SIDI) for the XRD and EDAX measurements.

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Received 25 April
and accepted 23 November 1995