

ELECTRODEPOSITION OF (HgCd)Te FILMS

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Mercury cadmium telluride has been electrodeposited on metal substrates. The deposited films have been characterised by X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS). Cyclic voltammetry has been used as a probe to study the electrodeposition of the material. The deposition and stripping behaviour have been taken into account in discussing the mercury cadmium telluride formation.

Key words: Electrodeposition, mercury-cadmium telluride film, cyclic voltammetry

INTRODUCTION

Cadmium telluride (CdTe) has been identified as a potential material for low cost terrestrial photovoltaic (PV) applications. It is a direct bandgap semiconductor and its optical absorption matches the solar spectrum. Polycrystalline thin films of CdTe can be made by a variety of cost-effective deposition methods [1–4]. Heterojunction solar cells of the structure n-CdS/p-CdTe have been developed from electrodeposited CdS and CdTe films with an efficiency as high as 9.15% [4].

The major problem with thin film n-CdS/p-CdTe solar cells is the high resistivity of p-CdTe films (typical dark resistivity = 8×10^4 ohm.cm). Further, p-CdTe has a high work function ($\sim 5.6 - 5.7$ eV) and practically there is no suitable contact material to establish ohmic contact. To overcome these problems partially, CdTe is being gradually replaced by cadmium-rich mercury cadmium telluride (HgCd)Te in the fabrication of high efficiency-thin film electroplated heterojunction solar cells, since the resistivity of p-(HgCd)Te can be lower than that of p-CdTe. Further, forming ohmic contacts to p(HgCd)Te is found to be easier than with that of p-CdTe [5]. (HgCd)Te has all the desirable optical properties of CdTe like a large absorption and a more favourable and tunable bandgap.

$Hg_{1-x}Cd_xTe$ is a solid solution of CdTe and HgTe. The latter is a semimetallic compound. The two are completely miscible forming solid solutions of all compositions, with x values from 0 to 1. The bandgap in the alloys varies linearly with x values [6].

p-(HgCd)Te films with $0.05 < x < 0.15$ with a low resistivity and with an optical bandgap in the range 1.2 to 1.4 eV have been obtained by the electrodeposition technique [7]. Basol and Tseng report an efficiency of 10.6% for p(HgCd)Te/n-CdS solar cells fabricated by electroplating [8]. The physical properties of electrodeposited cadmium rich (HgCd)Te films have been reported by Neumann-Spallert et al [9]. Recently electrodeposition behaviour of (HgCd)Te system has been reported by Mori et al [10] using rotating ring disc electrode. They optimised the electrodeposition conditions for preparing homogeneous $Hg_{1-x}Cd_xTe$ layers with no contamination from Hg and Te as separate phases. The mechanism of electrodeposition of (HgCd)Te layers has been investigated [10–12].

This communication presents some of the investigations on the cyclic voltammetric behaviour of the deposition of (HgCd)Te system. XRD and AAS studies are also reported.

EXPERIMENTAL

(HgCd)Te layers were electrodeposited cathodically on conducting glass, titanium and molybdenum substrates at a potential range of -600 mV to -640 mV with respect to SCE. The procedure for (HgCd)Te electrodeposition is similar to that for CdTe [13]. The

aqueous bath was made up of 0.5 M CdSO₄ and 0.025 M TeO₂, heated to 353 K with the required quantity of HgCl₂ aq. (Hg²⁺ concentration of 0.025 M) added just before the deposition. The pH of the bath was 2.5. The duration of deposition was 1 h on substrates of Mo. The films were heat treated in air at 673K for 8 min., and characterised by XRD. The concentration of Cd in the layers was determined using a Perkin-Elmer Model 380 Atomic Absorption Spectrometer (AAS). Hg concentration was determined using Mercury Analyzer Model 5800 (ECIL), which could read concentrations down to 20 ng.

Cyclic voltammetric studies were carried out using platinum as the working electrode and a saturated calomel electrode (SCE) as reference and all the potential values are reported with respect to SCE. Na₂SO₄ (1N) was the supporting electrolyte throughout with CdSO₄, TeO₂ and HgCl₂ separately or together. Studies have been carried out at room temperature and at 353K.

RESULTS AND DISCUSSION

(HgCd)Te layers electrodeposited over Mo substrates are polycrystalline as shown by XRD (Fig.1). They exhibit a cubic structure with preferential orientation along the (220) and (311) directions. AAS studies indicate an approximate ratio of 0.9 : 0.1 for Cd : Hg electrodeposited (HgCd)Te layers. Cyclic voltammetry has been used to study the electrodeposition.

Room temperature deposition

Voltammetric behaviour of Cd²⁺ in Na₂SO₄ shows that Cd²⁺ to Cd⁰ conversion takes place at -820 mV (Fig.2). The stripping peak is observed at -690 mV. For Te⁴⁺ ions in Na₂SO₄, the deposition peak is not clearly observed whereas the stripping peaks are observed at $+430$ mV and $+480$ mV. Hg²⁺ ions in Na₂SO₄ show that Hg²⁺ to Hg⁰ conversion and vice versa take place at $+60$ mV and $+210$ mV respectively (fig. not given).

Cd²⁺ and Te⁴⁺ system

The voltammogram in Fig.3 shows the behaviour of Cd²⁺ and Te⁴⁺ ions when both are present in Na₂SO₄. Prior to bulk deposition some reaction is taking place between -300 and -750 mV as seen from Fig.3. This behaviour is expected for the deposition of cadmium telluride. The stripping of cadmium is observed at -690 mV. There is no shift in cadmium stripping whereas a shift towards more positive potentials is observed for the tellurium stripping (viz. at $+520$ mV). This stripping behaviour suggests tellurium is not present as Te⁰, when cadmium deposition occurs around -780 mV. Since the codeposition of Cd and Te to form CdTe is not indicated as evidenced by the stripping behaviour, it is likely that the Te formed during the cathodic cycle might have undergone further reduction [14]. It is presumed that even in the presence of excess cadmium ions, the reduced tellurium does not combine with cadmium ions to form cadmium

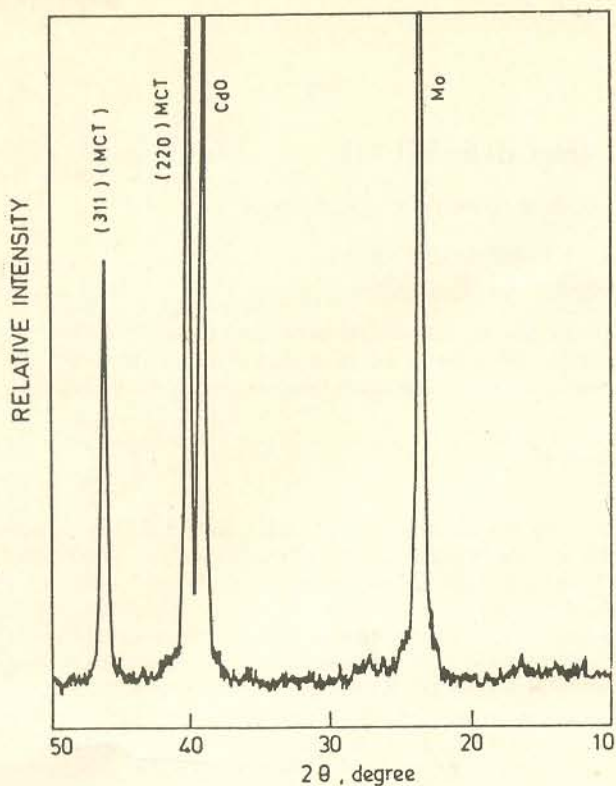


Fig. 1: XRD of the electrodeposited (HgCd)Te films heat treated at 673K for 8 min.

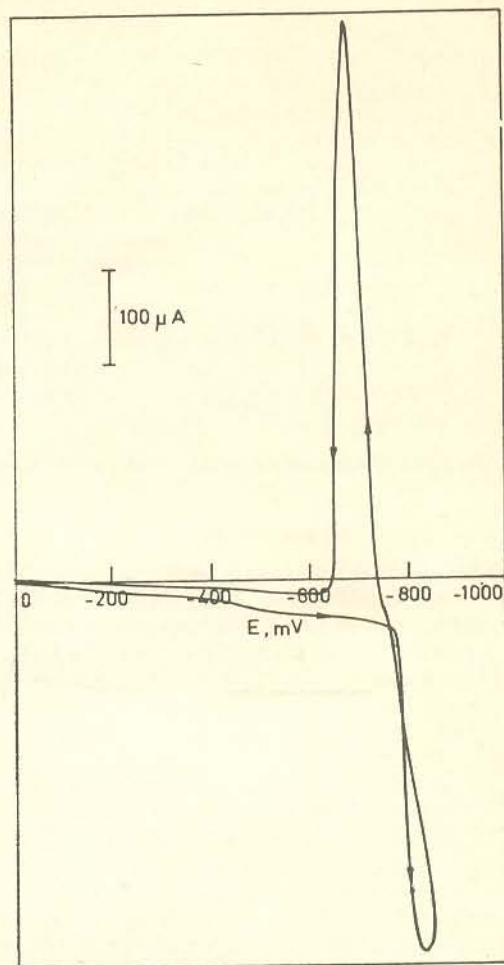


Fig. 2: Cyclic voltammogram of a solution containing 0.05M CdSO₄ in 0.5M Na₂SO₄ at 303K

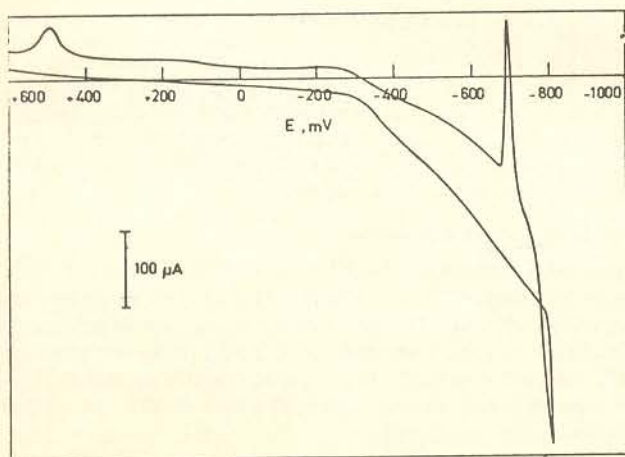


Fig. 3: Cyclic voltammogram of a solution containing 0.05M CdSO₄ and 0.001M TeO₂ in 0.5M Na₂SO₄ at 303K

telluride on the electrode surface. So there is no possibility for the cadmium telluride formation under this condition.

Hg²⁺ and Te⁴⁺ system

When Te⁴⁺ is added to Hg²⁺ ion, reduction of Hg²⁺ to Hg⁰ is not clearly observed and Te⁴⁺ to Te⁰ reduction is expected to take place after the reduction of Hg²⁺ occurs (Fig. 4). The stripping peak for mercury is shifted to +260 mV and no stripping for tellurium is observed. It may be inferred from these observations that HgTe is formed. At room temperature, formation of mercury telluride appears to be more probable.

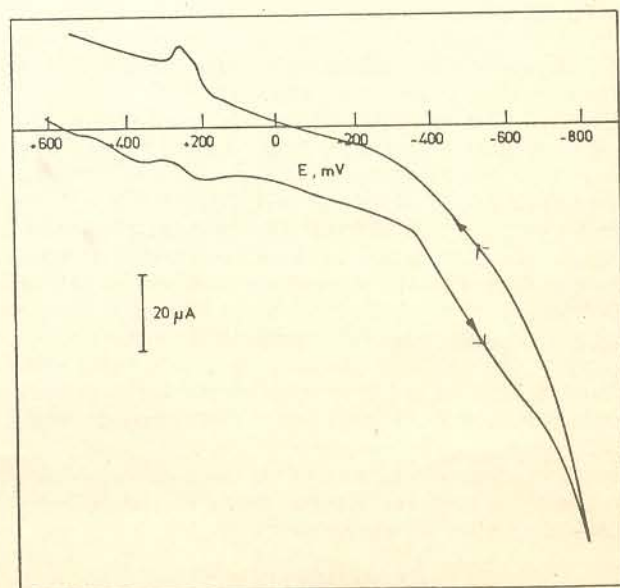


Fig. 4: Cyclic voltammogram of a solution containing 0.001M HgCl₂ and 0.001M TeO₂ in 0.5M Na₂SO₄ at 303K

Hg²⁺ and Cd²⁺ system

When Hg²⁺ and Cd²⁺ ions are both taken, the voltammogram shows that there is no codeposition. Deposition and stripping of Hg are observed at +60 mV and +210 mV respectively, while for cadmium these occur at -800 mV and -690 mV respectively. As observed from the stripping peak, the conversion of Cd²⁺ to Cd⁰ is higher on Hg surface than on Pt. This shows that mercury gets deposited on the electrode surface first. Cadmium deposition and stripping take place over the deposited Hg surface.

Hg²⁺, Cd²⁺ and Te⁴⁺ system

Figure 5 shows the voltammogram when Hg²⁺, Cd²⁺ and Te⁴⁺ are present in Na₂SO₄. Deposition of HgTe is seen to take place prior to Cd and Cd is expected to deposit over these layers. The deposition and stripping behaviour of Cd are unaltered. Stripping of mercury is observed only at +280 mV and in addition no Te stripping is observed as seen for the HgTe system. These observations indicate that the deposition of Cd²⁺ over HgTe is more probable than its deposition over Hg⁰. In this ternary system Hg-Cd-Te, when Cd²⁺ to Cd⁰ conversion takes place, and occurs on HgTe surface and not on Hg⁰ as is observed in the binary Hg²⁺ and Cd²⁺ system. It leads one to conclude that at room temperature, the codeposition of the ternary (HgCd)Te may not be possible.

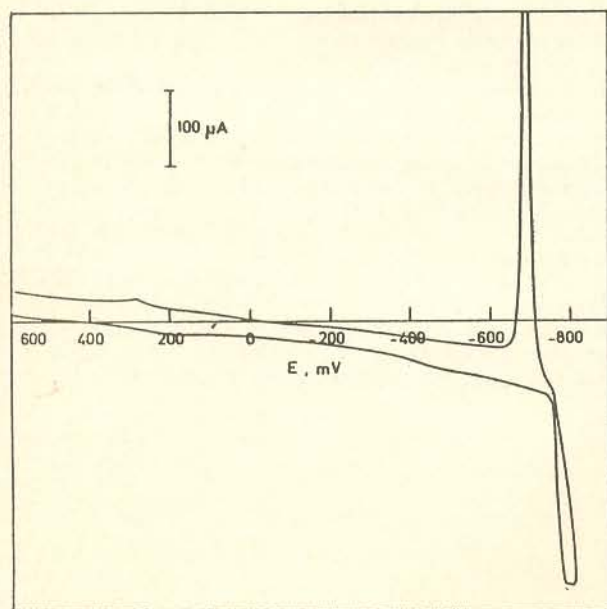


Fig. 5: Cyclic voltammogram of a solution containing 0.001M HgCl₂, 0.001M TeO₂ and 0.05M CdSO₄ in 0.5M Na₂SO₄ at 303K

Deposition at 353 K

Cyclic voltammogram of Cd²⁺ at the elevated temperature of 353 K (Fig. 6 curve a) shows deposition at -700 mV and stripping at -650 mV. The voltammogram for Te⁴⁺ system shows the Te stripping peak at +420 mV. For the Hg²⁺ system, the voltammogram shows deposition at +180 mV and stripping at +310 mV.

Cd²⁺ and Te⁴⁺ system

Figure 6 (curve b) shows the voltammogram for the system Cd²⁺ and Te⁴⁺ ions. On polarisation, Cd²⁺ to Cd⁰ conversion takes place at -670 mV, stripping occurring at -600 mV. There is not much change observed for the tellurium deposition while the stripping peak is

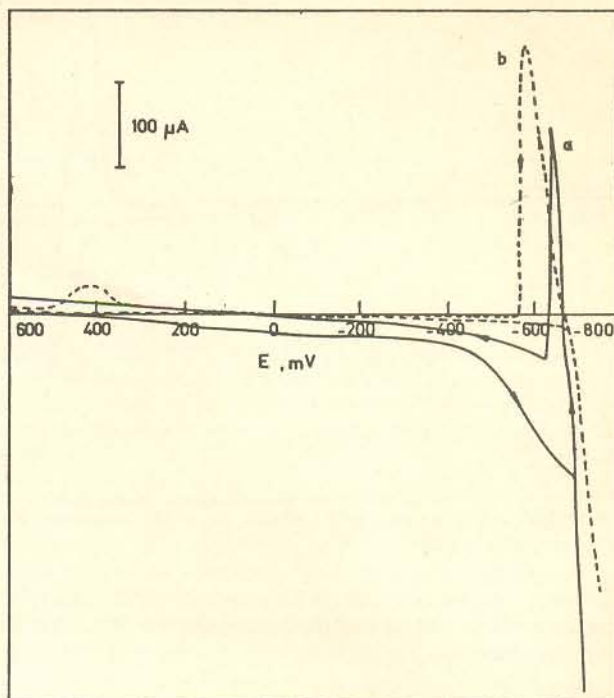


Fig. 6: Cyclic voltammogram of a solution (at 353K) containing (a) 0.05M CdSO₄ (b) 0.05M CdSO₄ and 0.001M TeO₂

shifted by +30 mV anodically to +450 mV. This shows that both Cd and Te are not present as Cd⁰ and Te⁰ pointing to the probability of formation of CdTe species. It may be noted from the voltammogram that cadmium is not deposited in the elemental form.

Hg²⁺ and Te⁴⁺ system

The voltammogram obtained from a solution containing Te⁴⁺ and Hg²⁺ (figure not given) shows the deposition potential for Hg is not much shifted. A new transition is observed at -200 mV. The reduction of tellurium may take place at this potential region and Te may deposit along with mercury, forming HgTe layers. Stripping peaks for both mercury and tellurium get shifted to +400 mV and +480 mV respectively. This shows that HgTe formation takes place in this region.

Hg²⁺ and Cd²⁺ system

Figure 7 shows the behaviour of Cd⁰, Hg⁰ deposition. The deposition of mercury takes place at +180 mV and stripping at +340 mV. The stripping of cadmium is observed at two potentials viz. -610 mV and -580 mV. The reduction of Cd²⁺ to Cd⁰ in presence of Hg²⁺ ions takes place in two steps as observed from the shoulder at -650 mV and at -700 mV. During Cd deposition, Cd amalgam may form in addition to cadmium. Cd seems to be deposited as Cd amalgam initially and further nucleation takes place on this. So stripping is observed at more positive values of -580 mV and -610 mV.

Hg²⁺, Cd²⁺ and Te⁴⁺ system

When Hg²⁺, Cd²⁺ and Te⁴⁺ ions are present in the solution the deposition of Te and Hg are not clearly observed (Fig.8). The nucleation loop [12] for Cd²⁺ to Cd⁰ is not observed. The cadmium stripping peak in the present system is observed at +550 mV, which is more positive to that of pure Cd⁰ stripping at +650 mV. Mercury stripping and tellurium stripping are observed at +350 mV and +450 mV respectively. Mercury stripping behaviour is similar to that of CdHg stripping and tellurium stripping to that of CdTe. It is seen from these studies that at 353K (HgCd)Te deposition takes place between -600 mV and -750 mV and the deposition may occur through the

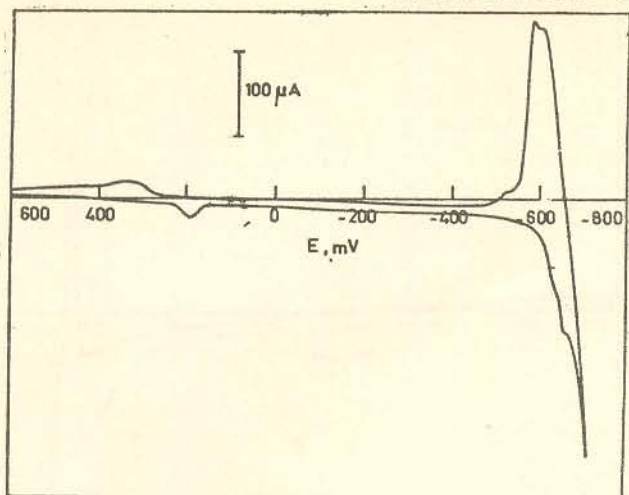


Fig. 7: Cyclic voltammogram of a solution (at 353K) containing 0.05M CdSO_4 and 0.001M HgCl_2

formation of CdTe and CdHg . During the deposition of Cd° , codeposition of Hg° and Te° leads to the formation of $(\text{HgCd})\text{Te}$ films. At room temperature $(\text{HgCd})\text{Te}$ formation is not favoured.

CONCLUSION

The cyclic voltammetry studies reported herein show that the electrochemical formation of $(\text{HgCd})\text{Te}$ is not favoured at room temperature while at the elevated temperature of 353K, its formation occurs. A comparison of XRD data of the films with the product obtained by other methods confirms the formation of the compound at 353K $(\text{HgCd})\text{Te}$ formation seems to occur through the deposition of CdTe and CdHg .

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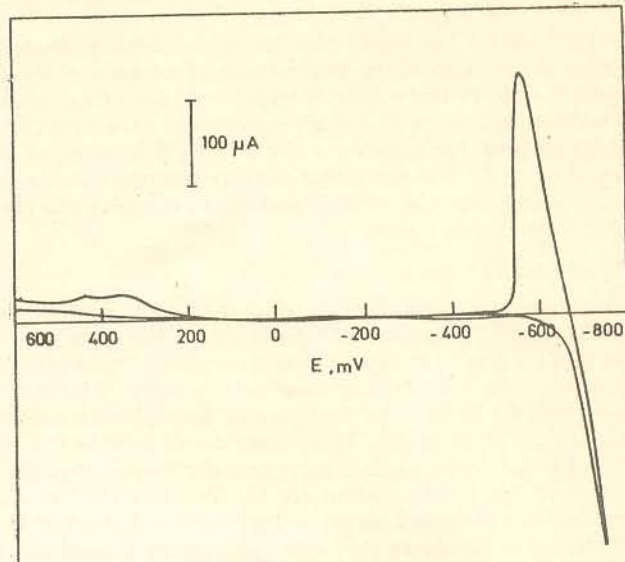


Fig. 8 Cyclic voltammogram of a solution (at 353K) containing 0.05M CdSO_4 , 0.001M HgCl_2 and 0.001M TeO_2

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