CdTe photoelectrochemical solar cells—Chemical modification of surfaces

K C MANDAL, S BASU and D N BOSE

Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

Abstract. Chemical modification of both n and p type CdTe has been found to improve the performance and stability of PEC solar cells. The surfaces, modified by Ru^{3+}, have been examined by a variety of techniques. Modification results in enhanced barrier height at the surface due to the formation of a passivating oxide layer.

Keywords. Solar cells; cadmium telluride; surface modification.

1. Introduction

High efficiency PEC solar cells with GaAs and InP as photoelectrodes have been developed using the technique of chemical modification of surfaces, originating from the work of Parkinson *et al* (1978) and Heller *et al* (1980). Tufts *et al* (1987) recently reported a 15% efficiency n-GaAs PEC cell with Os^{3+} surface modification which is suitable for a charge transfer $> 30,000$ C/cm^2.

While most of these experiments have been successful on III-V semiconductors, Bose *et al* (1986) were the first to demonstrate that such surface modification was equally effective on both n and p type CdTe. This paper attempts to summarize the experiments conducted on CdTe surfaces as well as the performance of PEC solar cells. It may be recalled that two alternative mechanisms of chemical modification have been proposed: (i) removal of surface state pinning by Heller (1981) and (ii) electrocatalytic effect by Borbavello *et al* (1982). While the former results in a decrease of hole recombination at the surface the latter gives rise to increased hole transfer into the electrolyte. The present results show unambiguous evidence of decrease of surface recombination velocity and removal of surface state pinning which is also evident at the CdTe/air interface. Similar result was earlier reported on n-InP electrolyte interfaces (Bose *et al* 1984a) as well as Schottky barriers (Bose *et al* 1984b).

2. Experimental

The investigations were conducted on Bridgman-grown CdTe which was doped with In (donor) or P (acceptor) to provide large grain polycrystalline material with the properties as given in table 1.

Table 1. Properties of Bridgman-grown bulk CdTe.

Type	Resistivity (ohm-cm)	Carrier conc. (cm^{-3})	Mobility (cm^{2}V^{-1}s^{-1})
p	28	1.25×10^{16}	16
n	8.7	1.7×10^{15}	428

Surface modification was carried out as described earlier by etching for 30 s to 1 min in 8 M HCl to obtain a black matte surface and then immersing in 0·01 M $RuCl_3$ $3H_2O$ in 0·1 M HNO_3 for 15 min which was the optimum period. Comparison was also made with effects of Pt^{4+} and Pd^{2+} by immersing in respective chlorides. Unmodified surfaces were prepared by etching in $H_2SO_4:K_2Cr_2O_7$ and finally washed in 2% bromine-methanol.

## 2.1	Results

n and p-CdTe were used as photoelectrodes in Te^{2-}/Te_2^{2-} and Sn^{2+}/Sn^{4+} redox electrolytes respectively in which stable performance has been reported. Details of the experiments have been described elsewhere (Mandal *et al* 1986, 1987). Apart from dark I-V, C-V and solar cell characteristics, spectral response and $\ln(1-\eta)$ vs $V_b^{1/2}$ plots were also determined. From the intercepts, the values of diffusion lengths before and after modification were found. The results are summarized in table 2.

Similar experiments were conducted using Pt^{4+} and Pd^{2+} which showed that while the former had some beneficial effect, the latter degraded the cell properties.

## 2.2	Surface characterization

To examine the reasons for surface modification, corroborative studies were conducted on measurement of contact potential difference (CPD) (Bose *et al* 1986), sub-band gap spectroscopy and electrochemical photocapacitance spectroscopy (EPS) (Bose *et al* 1988). These experiments proved that (i) negative surface charge developed on n-CdTe and positive on p-CdTe increasing the barrier height in each case such that $\Delta V_{CPD} \simeq \Delta V_{oc}$. (ii) The order of magnitude in sub-band response reduced on modification in both cases. (iii) Discrete levels (surface and bulk) present in CdTe were altered on matte etching and further changed on surface modification. Mid-gap recombination centres disappeared while states which were suitable for minority carrier transport appeared near the band-edges.

The physical properties of the surfaces were examined using XPS, SIMS and Raman spectroscopy (Bose *et al* 1985; Bose and Holz 1987). These results can be summarized as follows: (i) the unmodified surfaces (n and p) had a thin surface layer of Te on stoichiometric CdTe; (ii) the modified surfaces were covered by a layer of $TeO_{2\pm x}$ with depletion of Cd towards the outer surface; (iii) Ru was detected on the modified surface but its charge state could not be determined.

Table 2. Comparison of properties of n and p-CdTe before and after Ru surface modification.

Type	Surface	L_p (μm)	s (cm/s)	J_0 (A/cm²)	n	V_{fb} (V)	J_{sc} (mA/cm²)	V_{oc} (V)	F.F	Stability
n	Unmod.	0·12	4×10^4	$8·6\times10^{-8}$	2·12	−0·97	3·4	0·52	0·42	
	Mod.	0·17	$8·6\times10^3$	$4·2\times10^{-9}$	1·16	−1·20	5·2	0·78	0·51	
p	Unmod.	0·72	$1·8\times10^5$	$2·8\times10^{-7}$	2·72	+1·02	2·17	0·63	0·38	18 h
	Mod.	0·99	$3·5\times10^4$	$5·1\times10^{-8}$	1·54	+1·20	3·23	0·92	0·48	336 h

3. Discussion

The above results can be explained on the basis of Heller's (1981) theory of removal of surface state pinning due to strong chemisorption of Ru^{3+}, since reduction of active surface state density within the band-gap has been directly demonstrated. Further, the grain boundary passivation leading to increase in J_{sc} also occurs. The interaction of Ru with CdTe surface has also been shown in the solid-state Schottky barrier in which increase in ϕ_b and decrease in ideality factor n has been found (Mandal *et al* 1988). This is in contrast with the observation of Tufts *et al* (1987). However improved minority carrier transport to redox electrolyte may also be occurring due to creation of favourable energy states.

The efficacy of Ru treatment in the present case is considered to be due to the following factors: (a) variable valency of Ru which allows amphoteric behaviour, (b) smallest atomic radius in its family permitting strong surface interaction and (c) strongly oxidizing nature vis-a-vis Pt and Pd, the latter being known to be a hydrogenation catalyst. Surface modification by appropriate ions is thus a powerful tool for improving the properties of semiconductor surfaces and interfaces and may find application in diverse fields.

References

Borbavello E, Kalyansundaran K, Graetzel M and Pelezetti E 1982 *Helv. Chim. Acta* **65** 243

Bose D N, Ramprakash Y and Basu S 1984a *J. Electrochem. Soc.* **131** 850

Bose D N, Roy J N and Basu S 1984b *Mat. Lett.* **2** 455

Bose D N, Hegde M S, Basu S and Mandal K C 1985 *Proc. 18th IEEE Photovoltaic Specialists Conf.* (New York: IEEE Press)

Bose D N, Basu S, Mandal K C and Mazumdar D 1986 *Appl. Phys. Lett.* **46** 472

Bose D N and Holz M 1987 *Mat. Lett.* **5** 291

Bose D N, Basu S and Mandal K C 1988 *Proc. 7th Int. Conf. on Thin Films, New Delhi*

Heller A 1981 *Am. Chem. Soc. Symp. Ser.* **146** 57

Heller A, Miller B, Lewerenz H J and Bachmann K J 1980 *J. Am. Chem. Soc.* **102** 6555

Mandal K C, Basu S and Bose D N 1986 *Solar Cells* **18** 25

Mandal K C, Basu S and Bose D N 1987 *J. Phys. Chem.* **91** 4011

Mandal K C, Basu S and Bose D N 1988 (to be published)

Parkinson B A, Heller A and Miller B 1978 *Appl. Phys. Lett.* **33** 521

Tufts B J, Abrahams I L, Santangelo P S, Ryba G N, Casagrande L G and Lewis N S 1987 *Nature (London)* **326** 861