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## Evidence for Amphoteric Behavior of Ru on CdTe Surfaces

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# Evidence for amphoteric behavior of Ru on CdTe surfaces

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Modification of large grain *p*-CdTe by Ru is shown to reduce the sub-band-gap response and increase minority-carrier diffusion length from 0.67 to 0.92  $\mu\text{m}$ . Contact potential difference (CPD) measurements on *n*- and *p*-CdTe show shifts in surface Fermi level in opposite directions corresponding to increase in barrier height in each case. The amphoteric nature of Ru on CdTe surfaces depending on conductivity type is thus inferred. The magnitudes of the changes in CPD are approximately equal to the increase of open circuit voltage  $V_{oc}$  observed in photoelectrochemical cells.

Surface modification of semiconductors has been shown to be a powerful technique for improving the properties of photoelectrochemical (PEC) solar cells.<sup>1</sup> While most of these investigations involved III-V compounds, Mandal *et al.*<sup>2</sup> have shown its application to PEC solar cells using large grain CdTe. In this case, along with increased open circuit voltage  $V_{oc}$  and fill factor, an improvement in short circuit current density  $J_{sc}$  was obtained.

In the present letter we report investigation of the surface properties of CdTe that are responsible for the observed behavior. Spectral response studies using a monochromator demonstrate a reduction of states within the band gap which is supported by broadband sub-band-gap measurements. Electron diffusion length in *p*-CdTe was also found to increase from 0.67 to 0.92  $\mu\text{m}$  due to reduction of surface recombination velocity. Finally contact potential difference (CPD) measurements using the Kelvin probe technique have demonstrated for the first time changes in surface Fermi level that were in good agreement with the changes in open circuit voltage for both *p*- and *n*-CdTe. Further, the changes due to Ru modification for each type were in opposite directions, as required for increased band bending, showing that Ru ions had opposite effective charge in the two cases, i.e., positively charged on *p*-CdTe and negatively charged on *n*-CdTe.

The experiments were conducted on Bridgman-grown large grain CdTe (grain size 2–3 mm) with resistivities of 28  $\Omega\text{ cm}$  for P-doped *p*-type and 8.7  $\Omega\text{ cm}$  In-doped *n*-type material. Hall effect measurements gave majority-carrier concentrations of  $1.25 \times 10^{16}$  and  $7.8 \times 10^{15}\text{ cm}^{-3}$  and mobilities of 18 and 428  $\text{cm}^2/\text{V s}$ , respectively. Photoelectrochemical experiments were conducted in  $\text{Sn}^{2+}/\text{Sn}^{4+}$  redox in 0.1 M HCl ( $\text{pH} = 1.2$ ) for *p*-CdTe and  $\text{Te}^{2-}/\text{Te}_2^{2-}$  redox in 5 M NaOH ( $\text{pH} = 12.0$ ) for *n*-CdTe in which stable operation has been reported.<sup>3</sup> Samples approximately  $0.3 \times 0.4\text{ cm}^2$  in area were first etched in conc.  $\text{H}_2\text{SO}_4\text{:K}_2\text{Cr}_2\text{O}_7$  (satd. soln.) in 3:7 ratio and washed in 0.1 M  $\text{Na}_2\text{S}_2\text{O}_8$  solution. Prior to modification samples were etched by 8 M conc. HCl to obtain a black matte surface and then immersed in 0.01 M  $\text{RuCl}_3$ , 3  $\text{H}_2\text{O}$  in 0.1 M  $\text{HNO}_3$  solution for 1–14 h. Samples were lightly washed in triple distilled water before use.

The spectral response of *p*-CdTe PEC cell determined before and after modification using a monochromator indicated a substantial reduction in photoresponse at energies

below the band gap of 1.48 eV as shown in Fig. 1. The response at shorter wavelengths is also considerably improved indicative of reduction of effective surface recombination velocity as discussed later. Evidence of removal of interface states in the band gap was also obtained using broadband tungsten-halogen illumination and single crystal GaAs and InP filters by a method described earlier.<sup>4</sup> The signal was detected using a PAR chopper and lock-in amplifier. Table I shows the response after different surface treatments.

It is seen that there is an increase in response on matte etching followed by a substantial decrease on Ru modification. While the polished surface appears to have large response for photon energies near the band edge, the matte surface is characterized by large photoresponse below the absorption edge of both filters. This is discussed later in connection with the CPD measurements.

The minority-carrier diffusion length  $L_n$  in *p*-CdTe was measured in the electrolyte using the equation  $1/\eta = 1/$

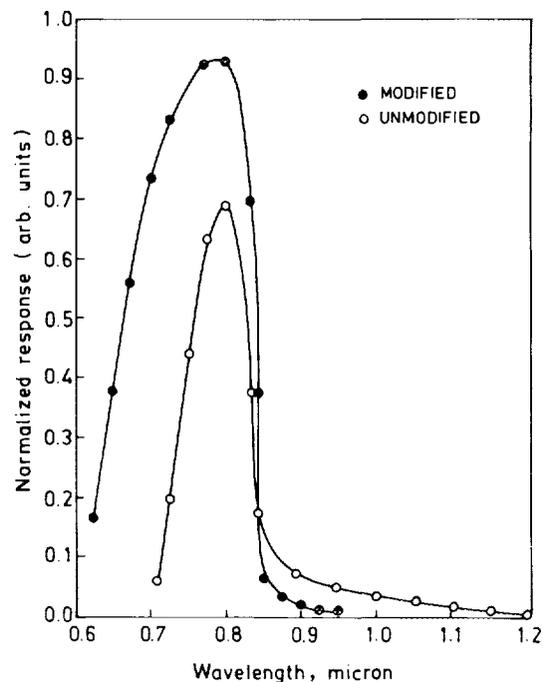


FIG. 1. Normalized spectral response in the current mode of *p*-CdTe photoelectrode in  $\text{Sn}^{2+}/\text{Sn}^{4+}$  redox in 0.1 M HCl ( $\text{pH} = 1.2$ ) before and after Ru modification.

TABLE I. Sub-band-gap response on *p*-CdTe.

Surface treatment	Sub-band response	( $\times 10^{-6}$ V)
	GaAs filter ( $E_g = 1.43$ eV)	InP filter ( $E_g = 1.34$ eV)
Polished and etched	45	15
Matte etched	61	42
Ru modified	12	3
6 h AM1 illumination	11	2

( $\alpha L_n + 1$ ). Monochromatic radiation was incident on the sample, the source intensity being calibrated using a Si *p-i-n* diode. The optical absorption coefficient of the specimen, determined using a Beckman spectrophotometer, was in good agreement with the literature in the range 0.50–0.83  $\mu\text{m}^{-1}$ .<sup>5</sup> Plotting the quantum efficiency  $1/\eta$  vs  $1/\alpha$  (Fig. 2), the diffusion length could be determined from the slope of the curve.  $L_n$  was thus found to increase from 0.67 to 0.92  $\mu\text{m}$  on modification. It can be shown that the change in depletion layer width  $W_d$  on modification is small, from 0.29 to 0.31  $\mu\text{m}$  and hence the change in  $L_n$  is not merely due to increased band bending.

Jastrzebski *et al.*<sup>6</sup> have shown that in the presence of surface recombination the effective diffusion length is reduced from the bulk value  $L_0$  to  $L_{\text{eff}}$ , where

$$L_{\text{eff}}^2 = L_0^2 \left( 1 - \frac{s}{s+1} \right) \exp\left( -\frac{Z}{L_0} \right)$$

and  $s$  = reduced surface recombination velocity  $SL_0/D$ , with  $D$  the diffusion coefficient. Considering excitation at the surface, i.e.,  $Z = 0$ , it is found that for  $L_0 = 1 \mu\text{m}$  the observed increase in  $L_{\text{eff}}$  corresponds to a decrease in  $S$  from  $1.8 \times 10^5$  to  $0.35 \times 10^5$  cm/s.

Since Aspnes<sup>7</sup> had suggested that surface modification may also cause a shift in surface Fermi level, CPD measurements were carried out using the Kelvin vibrating probe

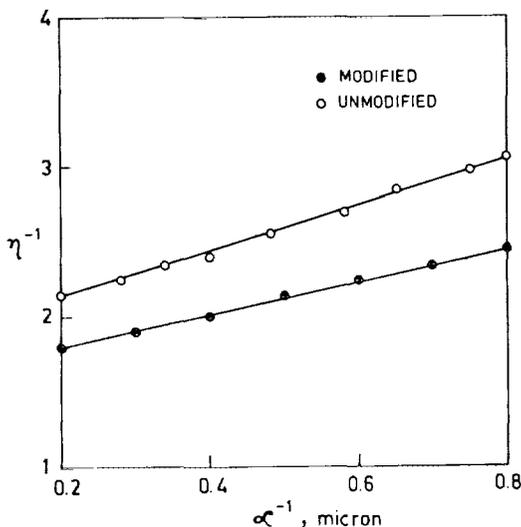


FIG. 2. Plot of inverse quantum efficiency ( $\eta^{-1}$ ) vs inverse absorption coefficient ( $\alpha^{-1}$ ). The  $L_n$  values are calculated from the slope of the plots. (O) 0.67  $\mu\text{m}$ ; (●) 0.92  $\mu\text{m}$ .

TABLE II. CPD measurements on *n*- and *p*-CdTe.

Surface condition	<i>p</i> -CdTe		<i>n</i> -CdTe	
	$V_{\text{CPD}}$	$V_{\text{oc}}$	$V_{\text{CPD}}$	$V_{\text{oc}}$
Polished and etched	-0.50 V	0.65 V	-0.20 V	0.36 V
Matte etched	-0.35 V	...	+0.20 V	...
Ru modified	-0.70 V	0.86 V	+0.28 V	0.76 V

technique. Experiments were conducted in a nitrogen ambient using a gold reference electrode vibrated at 100 Hz. A lock-in amplifier was used for signal detection while the voltage null was measured using a Keithley 510B DMM. Measurements on several specimens were reproducible to within  $\pm 15$  mV. Table II gives the changes in CPD after different surface treatments.

It is observed that on matte etching the CPD becomes more positive for both *n*- and *p*-CdTe indicating that the bands bend up due to creation of acceptorlike states at the surface. This is similar to usual observations on ground or damaged surfaces of elemental semiconductors. Thereafter the effect of Ru modification causes the CPD to change in opposite direction for the two cases, i.e., bands bend down at the surface for *p* type and bend up for *n*-CdTe. Thus the barrier heights are increased in both cases, the changes being -0.20 V for *p*-CdTe and +0.48 eV for *n*-CdTe. Also shown in Table II are the values of open circuit voltages  $V_{\text{oc}}$  under AM1 illumination when these electrodes are used in PEC solar cells. It is seen that the increases in  $V_{\text{oc}}$  in the two cases are 0.21 V and 0.40 eV, in fairly good agreement with the changes in  $V_{\text{CPD}}$ .

The shift in surface Fermi level and increase in  $V_{\text{oc}}$  on modification can be attributed to additional surface charge which is positive for *p*-CdTe and negative for *n*-CdTe. From the observed changes in  $V_{\text{oc}}$ , using the theory of Kingston and Neustadter,<sup>8</sup> the density of surface charge can be calculated to be  $+3.4 \times 10^{15}/\text{cm}^2$  for *p*-CdTe and  $-1.6 \times 10^{15}/\text{cm}^2$  for *n*-CdTe. Our calculated value is supported by recent XPS measurements<sup>9</sup> which demonstrate a fairly high concentration of Ru atoms. A change in the surface stoichiometry (Cd:Te) ratio on modification and formation of a stable Te-rich oxide layer was also observed, the latter being expected to contain the additional surface charge. The presence of the oxide layer may account for the much improved stability, the decrease in photocurrent density after modification being found to be only 4.7% in 130 h compared with 89% over the same period prior to modification. In conclusion, it is shown that the effect of Ru surface modification of CdTe is a change in the surface Fermi level as determined from CPD measurements which is opposite in direction for *n*- and *p*-CdTe. The excess surface charge causes an increase in band bending increasing the  $V_{\text{oc}}$  in PEC solar cells. The growth of a passivating oxide layer helps to reduce the interface state density and the surface recombination velocity leading to an increase in effective diffusion length.

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