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BRIEF COMMUNICATIONS

Correlation of Fermi Level Shift with Photovoltages at Ruthenium-Modified CdTe Surfaces

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The effect of ruthenium surface modification is shown to considerably improve the properties of CdTe-based photoelectrochemical (PEC) solar cells. Contact potential difference (CPD) measurements on *n*- and *p*-CdTe show shifts in surface Fermi level in opposite directions corresponding to an increase in barrier height in each case. The magnitudes of the changes in CPD are approximately equal to the increase of open-circuit voltage, V_{oc}, observed in photoelectrochemical cells.

Chemical modification of semiconductor surfaces by metal ions such as ruthenium is known to enhance open-circuit voltages at electrolyte interfaces and also to stabilize the surface against dissolution. It had been suggested that the ions interact with surface states in the bandgap to remove Fermi level pinning. An alternative explanation is provided here through measurement of contact potential difference (CPD) which shows that the effect of Ru ions is to alter the surface Fermi level. The shift is in opposite directions for *n*- and *p*-CdTe but increases the barrier height in the dark for both cases. The magnitude of the shift is in fairly good agreement with the measured increase in open-circuit voltage at CdTe–electrolyte interfaces.

Since the pioneering experiments of Parkinson *et al.* (*1*), who first demonstrated the beneficial effects of modification of *n*-GaAs surfaces by ruthenium treatment, similar behavior has been demonstrated on several other semiconductors including InP (2), CdSe (*3*), and CdTe (*4*). The observed increase in open-circuit voltage in solar cells has been attributed to removal of pinning by surface states due to strong interaction with electropositive Ru ions. The exact mechanism of surface modification, however, remains intriguing in view of the suggestion of Aspnes (*5*) that an alternative explanation may lie in the shift of the surface Fermi level. The present experiments using

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the Kelvin CPD measurement technique are, to the authors' knowledge, the first to demonstrate directly that (i) shift of the surface Fermi level does indeed occur, (ii) it is in opposite directions for *n*- and *p*-CdTe but such as to cause an increase in barrier height in both cases, and (iii) the magnitude of the shift is in fairly good agreement with the increase in barrier height observable at electrolyte interfaces.

The experiments were conducted on Bridgman-grown large-grain CdTe (grain size 2–3 mm) with resistivities of 28 ohm-cm for *P*-doped *p*-type and 8.7 ohm-cm In-doped *n*-type material prepared in our laboratory. Hall effect measurements gave majority-carrier concentrations of 1.25×10^{16} and 7.8×10^{15} cm^{-3} and mobilities of 18 and 428 cm^2/V-sec, respectively. CPD measurements used the classical Kelvin technique (*6*) and were conducted in a nitrogen ambient using a gold reference electrode vibrated at 100 Hz. A PAR 5101 lock-in amplifier was used for signal detection while the voltage null was measured using a Keithley 510 B DMM. The measurements on several specimens 0.6×0.4 cm^2 in area were reproducible to within ±5 mV. Samples were first etched in concentrated $H_2SO_4 : K_2Cr_2O_7$ (saturated solution) in a 3 : 7 ratio and washed in 0.1 *M* $Na_2S_2O_4$ solution. Prior to modification samples were etched in 8 *M* concentrated HCl to obtain a black matte surface and then immersed in 0.01 *M* $RuCl_3 \cdot 3H_2O$ in 0.1 *M* HNO_3 solution for 30 sec to 1 min. The CPD values before modification, after matte etching, and after modification are given in Table I for *p*- and *n*-CdTe.

It is observed that on both *n*- and *p*-CdTe the effect of matte etching is to make the CPD more positive; i.e., the energy bands bend upward at the surface. However, the effect of Ru modification thereafter causes the band to bend downward in *p*-type but upward in *n*-CdTe. Thus depletion layer conditions are enhanced in both cases, resulting in an increase in barrier height. The effect of 0.1 *M* HNO_3 without $RuCl_3$ was negligible, as was confirmed by control experiments.

TABLE I

CHANGES IN CPD ON RU MODIFICATION

	V_{CPD}	
Surface condition	*p*-CdTe	*n*-CdTe
Before modification	−0.50	−0.20
After matte etching	−0.35	+0.20
After Ru modification	−0.70	+0.28

Although these experiments were carried out in a nitrogen ambient, the results may be compared with studies in photoelectrochemical systems in which the original experiments of Parkinson *et al.* (*1*) had been conducted. The redox systems used were $Sn^{4+/2+}$ in 0.1 *M* HCl at pH = 1.2 for *p*-CdTe and 0.025 *M* Te^{2-}/Te_2^{2-} in 5 *M* NaOH for *n*-CdTe in which stable operation has been reported (*7*). High-purity argon was bubbled through the redox solutions initially and during the experiments. Study of the dark I–V characteristics revealed a significant decrease in reverse saturation current density J_0 and in ideality factor *n* due to Ru modification; e.g., for *p*-CdTe J_0 decreased from 2.5×10^{-7} to 3.78×10^{-8} A/cm^2 and *n* from 2.21 to 1.52, and for J_0 of *n*-CdTe decreased from 8.6×10^{-8} to 4.2×10^{-9} A/cm^2 and *n* from 2.12 to 1.16. When illuminated with an AM1 intensity tungsten–halogen lamp, short-circuit current density J_{sc} for *p*-CdTe increased from 3.24 to 4.1 mA/cm^2 and the fill factor from 0.40 to 0.49 and for *n*-CdTe, J_{sc} increased from 3.4 to 5.2 mA/cm^2 and the fill factor from 0.42 to 0.51. An increase in V_{oc} also occurred, which is indicative of increased band bending and change in surface potential, and values are given in Table II.

The changes in CPD given in Table I can obviously be used to derive the corresponding changes in barrier height V_{bi} due to Ru

TABLE II

CHANGE IN V_{oc} ON Ru MODIFICATION

Material	V_{oc} Unmodified	V_{oc} Modified
p-CdTe	0.65	0.86
n-CdTe	0.36	0.76

modification. Assuming the work function of the gold reference electrode to be 5.10 eV and the electron affinity and bandgap of CdTe to be 4.28 and 1.50 eV, respectively, the barrier height of *p*-CdTe is found to change from 1.02 to 1.22 eV, while that for *n*-CdTe changes from 0.52 to 1.00 eV on modification. While the absolute values of barrier height are expected to be influenced by the presence of ions in the electrolyte, the observed changes in V_{oc} on modification (Table II) are in remarkably good agreement with the measured changes in CPD, viz., 0.21 eV vs 0.20 for *p*-CdTe and 0.40 eV vs 0.48 eV for *n*-CdTe. This supports an earlier inference from Schottky barrier studies on *n*-InP (*8*) that Ru ions interact strongly with the underlying semiconductor controlling the band bending.

The shift in surface Fermi level and an increase in V_{oc} on modification can only be attributed to additional surface charge provided by the Ru ions. From the observed changes in V_{oc}, using the theory of Kingston and Neustadtar (*9*), the density of surface charge was computed to be $+3.4 \times 10^{15}/\text{cm}^2$ for *p*-CdTe and $-1.26 \times 10^{15}/\text{cm}^2$ for *n*-CdTe. Our calculated values are supported by recent XPS measurements (*10*) 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 were also observed, the latter being expected to contain the additional surface charge. The presence of the thin oxide layer may account for the much-improved stability, the decrease in photocurrent density for *p*-CdTe after modification being found to be only 4.7% in 130 hr compared with 89% over the same period prior to modification. In conclusion it is shown that the effect of Ru-surface modification of CdTe induces excess surface charge and thus a change in the surface Fermi level as verified by CPD measurements. The excess surface charge caused an increase in band bending, thereby increasing the V_{oc} in PEC solar cells.

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