Mercury cadmium telluride solar cell with 10.6% efficiency

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Cd-rich mercury cadmium telluride (MCT) is a promising material for thin-film solar cell applications. In this letter we present data on the deposition of MCT films by a simple electroplating technique and report on the highest efficiency polycrystalline MCT thin-film solar cell to date, which has an efficiency of 10.6% under AM1.5 illumination.

There is considerable interest in electroplated semiconductors for photovoltaic applications because of the well-known attractive features of the electrodeposition technique, i.e., its simplicity, low cost, and scalability. Although various elemental and compound semiconductors have been successfully electrodeposited in thin-film form, only a few of these materials were developed to a point where photovoltaic cells with appreciable efficiencies could be demonstrated. To date, the most successful devices made on electrodeposited semiconductors have been those which utilized electroplated II-VI compounds such as CdS, CdTe, and $Hg_{1-x}Cd_xTe$ (MCT).

The cathodic electrodeposition of CdTe from aqueous electrolytes was first carried out by Panicker *et al.* who demonstrated that uniform films with controlled stoichiometry could be obtained using this simple technique.[1] High efficiency heterojunction solar cells of the structure CdS/p-CdTe were later developed[2,3] and an efficiency of 9.15% was reported.[4] These cells utilized electroplated CdS window layers and type converted p-type CdTe material.[5,6] Although reasonable short circuit currents and open circuit voltages were routinely observed in the all-electroplated CdS/p-CdTe devices, good fill factors were difficult to obtain especially in any sizable device. The fill factor value for the 9.15% efficient cell of Ref. 4, for example, was only 0.595. The main reason for this is the high series resistance introduced by the bulk of the high resistivity p-CdTe film as well as by the ohmic contact made to it. The dark resistivity of a typical electroplated and type converted p-CdTe layer is in the order of 8×10^4 Ω cm. The resistance of an ohmic contact made to such a film is expected to be very high.[7]

To partially overcome the difficulty associated with contacting high resistivity p-CdTe, we have proposed and demonstrated the use of Cd-rich MCT in place of p-CdTe in electroplated heterojunction solar cells.[8,9] The resistivity of electrodeposited and type converted p-MCT can typically be around 8×10^3–8×10^4 Ω cm depending upon its stoichiometry. Because of the lower resistivities attainable in p-MCT films, good ohmic contacts to this material are easier to obtain. An all-electroplated CdS/p-MCT thin-film cell with 1.38 cm^2 area and 9.4% efficiency has already been reported.[10] Here we present data on a device which achieved over 10% efficiency.

The plating solution used in this work was prepared in a manner[8] similar to those previously described for CdTe deposition.[5] First a 0.5-M solution was obtained dissolving CdSO$_4$ in DI water. This solution was then purified for about 2 h using an inert graphite anode and a platinum cathode.

The cathode potential was kept at -620 mV with respect to a Ag-AgCl reference electrode and the solution temperature was around 90 °C during this electrolysis period. Following the purification step 0.015 M Cl$^-$ was added into the electrolyte using HCl. Although the reasons are not fully understood, addition of a small amount of Cl$^-$ into the plating bath was found to be beneficial especially in terms of improving the short circuit currents of the devices.[8] After adjusting the pH to around 1.6, 38 ppm of HTeO$_2^+$ was introduced into the electrolyte by applying a potential of 500 mV to a pure Te anode. The resulting plating solution could be used to deposit CdTe films. To obtain MCT layers of different stoichiometry, various concentrations of Hg^{+2} ions were introduced into the electrolyte using HgCl$_2$. MCT deposition was carried out on glass/indium tin oxide (ITO)/CdS substrates at 90 °C using two anodes, one carbon and one tellurium. The QRP (quasi rest potential) was kept around -650 mV during the deposition. The sheet resistance of the ITO was 10 $\Omega/\square$. The CdS layer was electroplated on the ITO[5] and its thickness was around 800 Å. The as-deposited MCT films were 1.2–1.3 μm thick and they were n type. Scanning electron microscope (SEM) pictures revealed some loose particles on their surfaces. Energy dispersive analysis of x rays (EDAX) indicated that these particles were more Hg rich in their composition compared to the bulk of the underlying film. Also, the number of particles per unit area was an increasing function of $(1 - x)$.[10] The CdS/p-MCT junction was formed by heat treating the CdS/MCT structure in air for 8 min at 400 °C. This treatment converts the n-type MCT film into p type and forms an active junction between the p-MCT film and the CdS layer. The device was completed by first etching the p-MCT surface and then vacuum depositing the gold or nickel ohmic contact over it. The etching procedure consisted of a 1–2 s dip into an acidic solution (one part by volume H$_2$SO$_4$ and one part by volume of saturated K$_2$Cr$_2$O$_7$ solution) followed by a 15-min soak in hydrazine at room temperature.[11] The acidic etch leaves behind a surface layer which is rich in tellurium and oxides. The treatment in hydrazine removes a highly resistive thin film of oxide from the top of this surface layer.

Figure 1 shows the Hg to Te atomic ratios in the electrodeposited MCT layers as a function of the electrolyte composition. These data were taken from 16 films, plated from three different baths. The films were first freed of the Hg-rich loose particles on their surfaces and then they were dissolved into nitric acid for atomic absorption spectroscopy measurements to determine their stoichiometry. The points in Fig. 1 reflect the initially measured values of the Hg^{2+}/
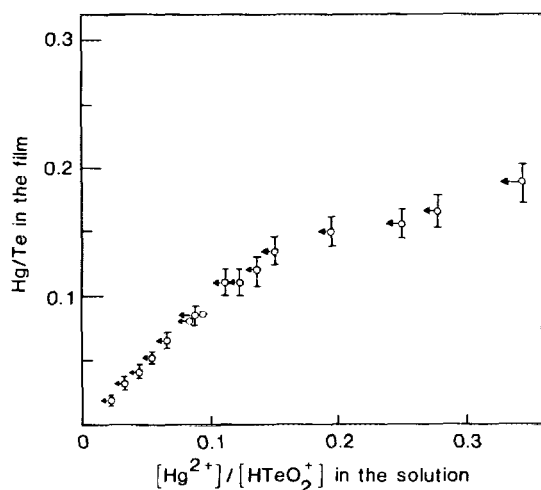
FIG. 1. Stoichiometry of the electroplated MCT films as a function of the electrolyte composition.

$HTeO_2^+$ ratios in the electrolytes. The arrows indicate the variation of the mercury concentration in the solution during plating. The vertical bars, on the other hand, show the variation of the Hg/Te ratio in different parts of the films and the error involved in the measurements. It should be noted that at high mercury concentrations Hg^{2+} exchanges with the Te anode in the solution. As a result, some of the mercury in the electrolyte is lost to this reaction.

Figure 2 shows the illuminated current-voltage characteristics of a CdS/p-MCT heterojunction. The J_{sc}, V_{oc}, and fill factor (FF) values for this 1.48 cm^2 area device are 27.03 mA/cm^2, 0.62 V, and 0.633, respectively, yielding an efficiency value of 10.6%. The measurement was made under an AM1.5 illumination intensity of 100 mW/cm^2 and there was no A/R coating on the glass substrate through which the light entered the device. The MCT film of this cell was deposited from an electrolyte which had a composition of $Hg^{2+}/HTeO_2^+ \cong 0.1$. From Fig. 1 the expected mercury to

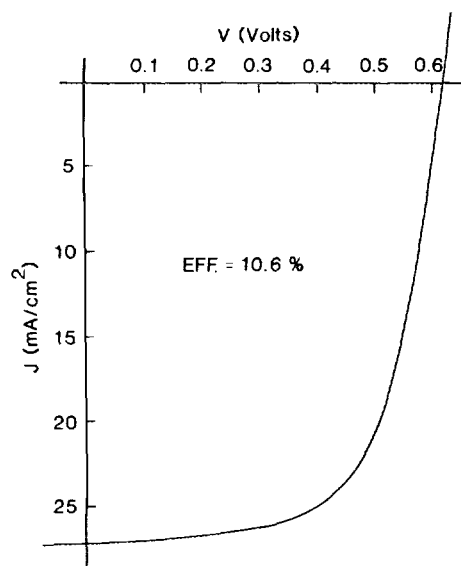FIG. 2. Illuminated I-V characteristics of an electroplated CdS/p-MCT solar cell. 100 mW/cm^2, AM1.5 illumination. Area = 1.48 cm^2, V_{oc} = 0.62 V, J_{sc} = 27.03 mA/cm^2, FF = 0.633.

tellurium ratio in this film is around 0.1. Although one loses a small amount of mercury during the annealing process, this does not affect this ratio appreciably especially at the low Hg levels. In a measurement made on a similar film we found that the original mercury content decreased by about 1% as a result of the heat treatment. This is within the experimental error involved in determining the film compositions reported in this paper. The optical bandgap of an electroplated MCT film with $(1 - x) = 0.09$–0.1 is around 1.27–1.31 eV.[9] Consequently, the short circuit current value of the device in Fig. 2 is much better than that of an electroplated CdS/p-CdTe cell. The V_{oc} value, on the other hand, is smaller as expected. The fill factor is also better than that of a typical electroplated CdS/p-CdTe device, More importantly, fill factor values of better than 0.6 are quite reproducible in CdS/p-MCT cells. This point is demonstrated by Table I which gives the measured FF values for 22 electroplated CdS/p-CdTe and CdS/p-MCT solar cells. These devices were fabricated on 22 different films which were sequentially deposited. The areas of the devices were 1.5–1.7 cm^2. It can be seen from Table I that the FF values of the CdS/p-CdTe devices are more scattered than that of the CdS/p-MCT cells.

Relatively low resistivity of the p-MCT suggests that this material may be beneficially utilized as a "buffer" layer between the p-CdTe film and the contact metal in a CdS/p-CdTe device. An experiment was carried out to test this idea. Figure 3 shows the results of a heat treatment made on two completed devices to compare the thermal stability of their ohmic contacts. Device D was a regular CdS/p-CdTe cell. Device E had a 0.3-μm-thick MCT layer ($1 - x = 0.16$) deposited on the CdTe film before the sample was subjected to the type conversion annealing at 400 °C. Since some interdiffusion between the CdTe and MCT will take place at this temperature,[12] the resulting mercury concentration profile near the surface is expected to be graded after the anneal. It is observed from Fig. 3 that after 55 h of heat treatment in air at 150 °C the fill factor of device E is much more stable than that of device D. It is known that the resistance of an ohmic contact to p-CdTe increases when it is subjected to heat treatment.[7] The reason for this is the fact that ohmic contacts to p-CdTe can only be made as tunneling junctions and therefore their quality is very sensitive to the barrier thickness at the metal/CdTe interface which may change as a result of any thermal processing. Presence of a low resistivity region at the contact/film interface naturally improves the tunneling properties of this contact and thus improves its temperature stability.

In conclusion, we have demonstrated that Cd-rich mercury cadmium telluride thin films with controlled stoichiometry can be obtained by a simple electrodeposition tech-

TABLE I. Comparison of the FF values obtained for 22 electroplated CdS/p-CdTe and CdS/p-MCT devices.

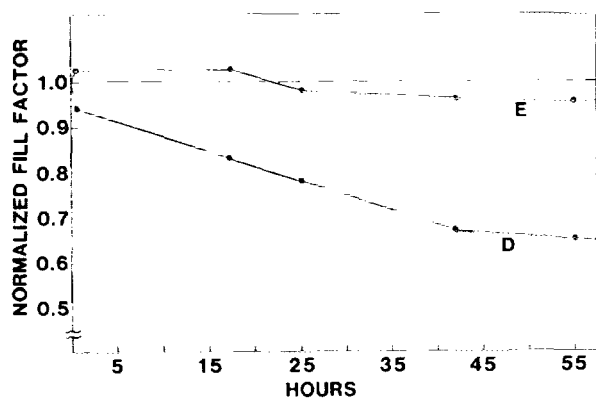| Cell type	Fill factor value (%)										
CdS/p-CdTe	59	59	61	58	52	56	57	55	58	56	54
CdS/p-MCT	60	62	63	64	61	60	60	64	64	64	63

FIG. 3. Temperature stability of ohmic contacts made to a CdS/p-CdTe device (device D) and to a CdS/p-CdTe/p-Hg$_{0.16}$Cd$_{0.84}$Te device (device E). Test temperature: 150 °C.

nique and that this material can be utilized to fabricate thin-film solar cells with over 10% efficiency. The reported efficiency of 10.6% is the highest to date for any electroplated cell.

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