

Electrochemical deposition of thin ZnTe films as a contact for CdTe solar cells

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ZnTe films doped with Cu were deposited by an electrochemical method for the first time directly onto CdTe/CdS/ITO/glass substrates to form a low resistance contact to CdTe. The depositions were carried out in an aqueous solution of ZnCl_2 , TeO_2 and CuCl_2 or CuSO_4 in which the substrate was externally short circuited to a Zn counter electrode to complete an electrochemical cell. Single phase films 50 nm to 300 nm thick were obtained for specific pH and TeO_2 concentrations and bath temperature. Complexing the Cu^{2+} with triethanolamine (TEA) allowed reproducible deposition of p-type ZnTe:Cu films. ZnTe:Cu/CdTe/CdS solar cells fabricated using this method have achieved AM1.5 efficiencies of 8.7%.

1. Introduction

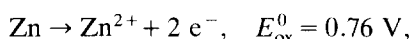
CdTe/CdS thin film solar cells have been made by a variety of techniques with efficiencies of about 10%, of which several methods are believed to be easily scaled for large area cell production [1,2]. One approach uses an n-i-p cell structure which takes advantage of the intrinsic nature of CdTe and solves the contact problem to the CdTe by using a p^+ ZnTe:Cu layer deposited by vacuum evaporation [1]. CdTe based cells are also candidate wide bandgap cells for tandem structures using CuInSe_2 based cells [3]. However, in the n-i-p CdTe cells, the optical absorption in the CdTe cell with the heavily doped ZnTe layer is about 60% from 400 nm to 1300 nm. This reduces the transmission through the device and limits the short circuit current of the narrow bandgap cell. To minimize the absorption, ZnTe films having the required electronic properties but which are continuous and thin (< 100 nm) are needed. It is not possible to deposit such continuous, thin ZnTe films by vacuum evaporation.

In this paper an electrochemical method to grow ZnTe having the required electronic properties and which are continuous and thin, is described. The approach is similar to that used by Bhattacharya et al. [4] and Murali et al. [5] for depositing CdTe and CdSe films respectively, where the substrate was short circuited to an easily oxidizable electrode (e.g. Al or Cd). This method has the advantage of simplicity in that it does not require instrumentation for potentiostatic or galvanostatic control. We also report results of CdTe/CdS devices using thin ZnTe:Cu as a primary contact. This approach has the additional advantage of

permitting alternative CdTe device designs which incorporate optical enhancing back-surface reflectors in cells with thin CdTe layers.

2. Electrodeposition of ZnTe films

ZnTe films were deposited electrochemically from an unstirred aqueous bath containing 0.1 M ZnCl_2 and about 10^{-4} M TeO_2 . The pH of the bath was adjusted between 3 and 4 using dilute HCl. The bath temperature was 50–60°C during the deposition. A conductive substrate, in most cases a 7059 glass/ITO/CdS/CdTe sample, and a zinc electrode were externally short circuited to form an electrochemical cell. The Zn electrode acts as both a source of electrons for the cathodic reaction and as a source of Zn^{2+} ions via the following reaction:



where E_{ox}^0 is the standard oxidation potential. The TeO_2 was brought into solution by dissolving it in a solution of NaOH, forming Na_2TeO_3 , with Te remaining in the +4 oxidation state. At the cathode, the dissolved zinc and tellurium are reduced simultaneously and instantly react to directly form ZnTe. Depositions were performed at pH from 2.0 to 5.0 and Te concentration from 10^{-3} M to 10^{-5} M to obtain the optimum condition for growth of ZnTe films. The deposition rate was monitored to determine when the Te was exhausted. Fig. 1a shows the time

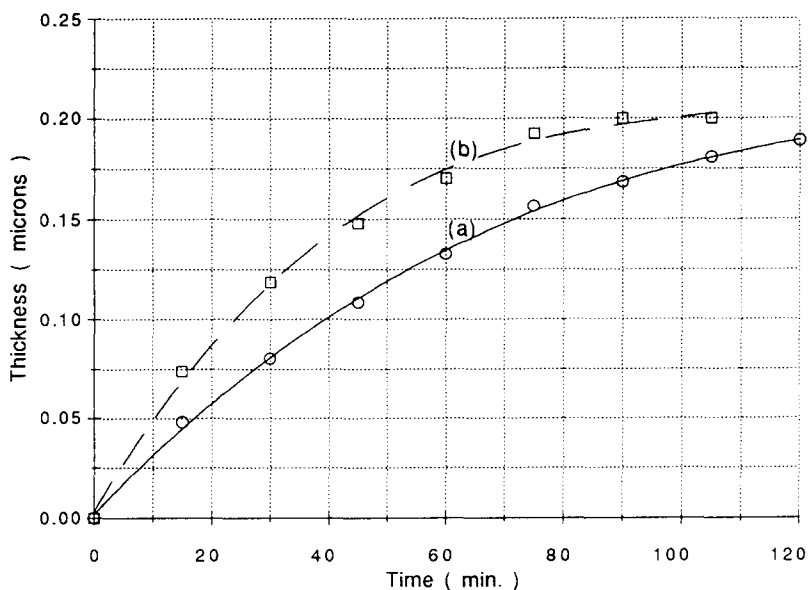


Fig. 1. ZnTe film deposited as a function of deposition time: (a) no Cu in bath and (b) 10^{-4} M/l Cu in bath.

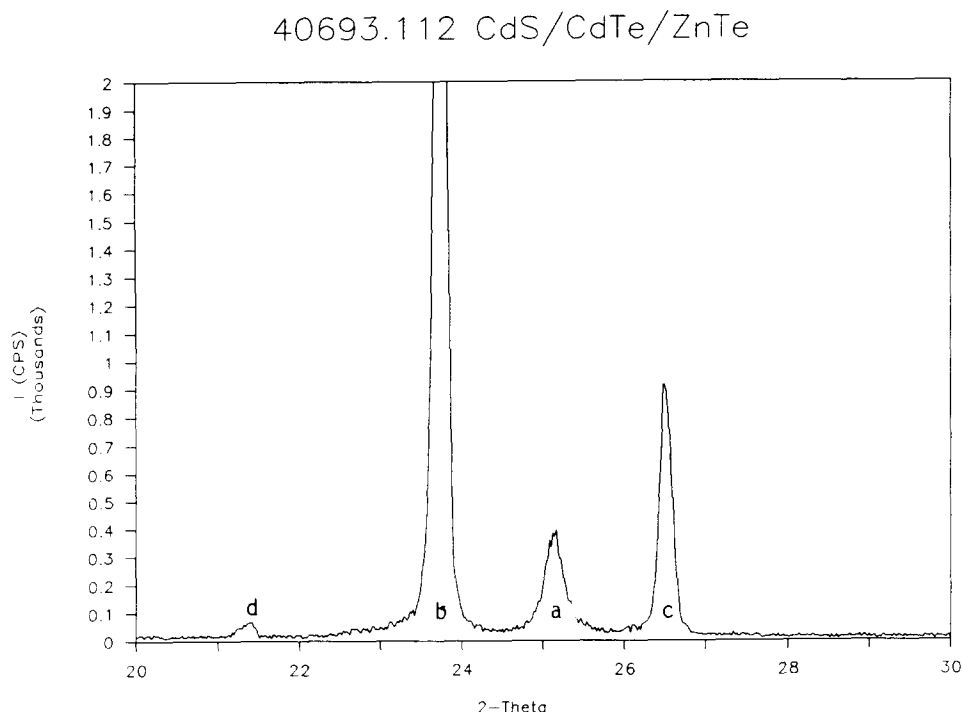


Fig. 2. X-ray diffraction spectrum of ZnTe film on 7059/ITO/CdS/CdTe showing (a) the ZnTe (111) peak, (b) the CdTe (111), (c) the CdS (002), and (d) the In₂O₃ (012) peak from the ITO substrate.

dependence of the ZnTe film deposition onto a 7059/ITO/CdS/CdTe substrate. In this case, the pH was 3.1–3.3, the volume was 50 ml, the area of the substrate was $\sim 1.9 \text{ cm}^2$, and the Zn electrode area was 1.6 cm^2 . A nearly linear growth rate was observed over about 1 h of deposition after which it tended to saturate, suggesting exhaustion of the Te in the solution. On further addition of TeO₂ to the solution and adjusting the pH, growth of ZnTe proceeded in a similar fashion confirming that the growth was limited by the availability of tellurium. It can be observed from fig. 1a that a $0.2 \mu\text{m}$ thick ZnTe film could be grown from a single deposition within about 120 minutes using a solution volume of 50 ml.

Single phase ZnTe films were deposited when the pH was 3–4 and the Te concentration was 10^{-4} M or less. To confirm this, the films were analyzed by X-ray diffraction. The X-ray diffraction pattern of a typical ZnTe film deposited on 7059/ITO/CdS/CdTe is shown in fig. 2. The sharp (111) peak at $2\theta = 25.20^\circ$ establishes the formation of a highly oriented cubic phase ZnTe film. The other peaks are due to CdTe, CdS, and ITO. At lower pH, free Te was deposited and above pH = 5, the solution became cloudy, due to precipitation of TeO₂. Increasing the Te ion concentration in solution by adding TeO₂ is limited by the solubility of TeO₂ at a given pH and temperature [6]. Since Te is less electropositive than Zn, the Te would be more likely to deposit as the element from its ions in an

electrochemical bath than Zn from its ions. Hence, very low concentration of Te in the solution must be maintained compared to the Zn^{2+} ions. Similar considerations apply to electrodeposition of other II–VI compounds such as CdTe [7].

To dope the ZnTe films p-type, Cu was incorporated during growth by reduction of a Cu complex added to the bath. Use of a Cu *complex* was necessary to reduce the formation rate of free Cu compared to ZnTe. The Cu complex was prepared by adding triethanolamine (TEA) to an aqueous solution of CuSO_4 . This was added to the ZnTe bath to give a Cu concentration from 10^{-5} to 10^{-3} M. Outside this range either insufficient Cu was incorporated into the film or other compounds of Cu and Te were formed. Fig. 1b shows the time dependence of Cu-doped ZnTe growth on a 7059/ITO/CdS/CdTe substrate for a bath of 0.1 M ZnCl_2 , about 10^{-4} M TeO_2 , and 10^{-4} M CuSO_4 in TEA, with a total volume of 50 ml, a pH of 3.1–3.3, a substrate area of $\approx 2.3 \text{ cm}^2$ and a 1.3 cm^2 Zn electrode. The ZnTe:Cu deposition rate is higher than for the undoped films, and the deposition saturates earlier than in the 50 ml volume used.

3. CdTe devices with a ZnTe contact

For solar cell fabrication, ITO/CdS/CdTe substrates were coated with a solution of methanol containing 1% by weight of CdCl_2 and then heat treated in dry air for 30 minutes at 400°C , as described elsewhere [8]. A mild, 0.01%, Br_2 -methanol etch for 5 s was then used to remove any surface residue resulting from the heat treatment since it was found that ZnTe did not grow uniformly on unetched surfaces. A ZnTe film, 50–100 nm thick, doped with Cu was then electrochemically deposited as described above. A robust contact, either Cu/Au, Ni or ITO, was deposited onto the ZnTe:Cu to complete the solar cells. The device area was scribed to nominally 0.08 cm^2 . The performance of the cells was optimized in a 150°C air heat treatment [8]. I – V characteristics were measured at 32°C under 87.5 mW/cm^2 ELH illumination and the current was normalized to

Table 1

Device parameters for CdS/CdTe/ZnTe:Cu cells using ITO/Ni, Cu/Au, and Ni robust contacts measured under ELH simulation, normalized to 100 mW/cm^2 at 32°C

Contact	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)
ITO/Ni	0.766	17.9	54.6
	0.679	19.0	54.2
	0.709	16.3	68.3
Cu/Au	0.754	17.4	60.5
	0.616	20.1	55.1
	0.703	16.8	69.0
Ni	0.676	20.1	51.7
	0.628	18.2	54.9
	0.616	15.2	74.8

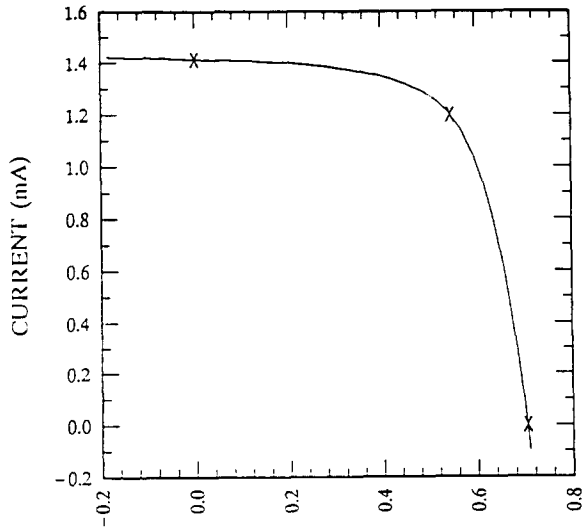


Fig. 3. Current-voltage measurement of ITO/CdS/CdTe/ZnTe:Cu/Cu/Au Cell #40691.231-1 at SERI under SERI AM1.5 global illumination at 25°C.

100 mW/cm². A summary of the device results for cells with the best I - V parameters having different contacts to the ZnTe:Cu is presented in table 1.

The device results are independent of the contact to the ZnTe:Cu indicating

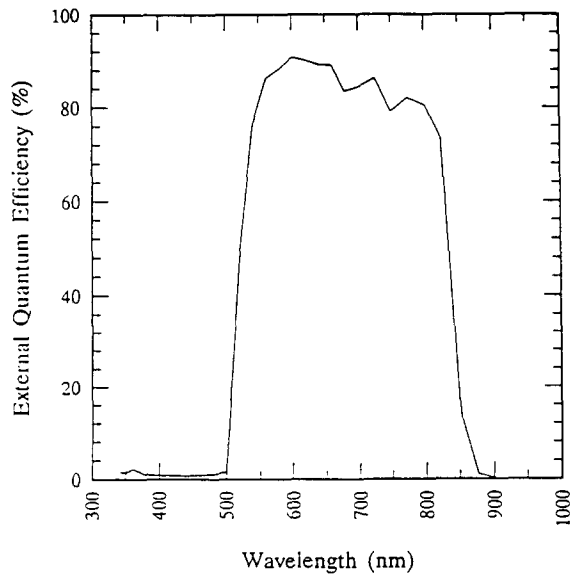


Fig. 4. Quantum efficiency versus wavelength of CdS/CdTe/ZnTe:Cu Cell #40691.231-1, measured at zero volts with 11.4 mA/cm² light bias.

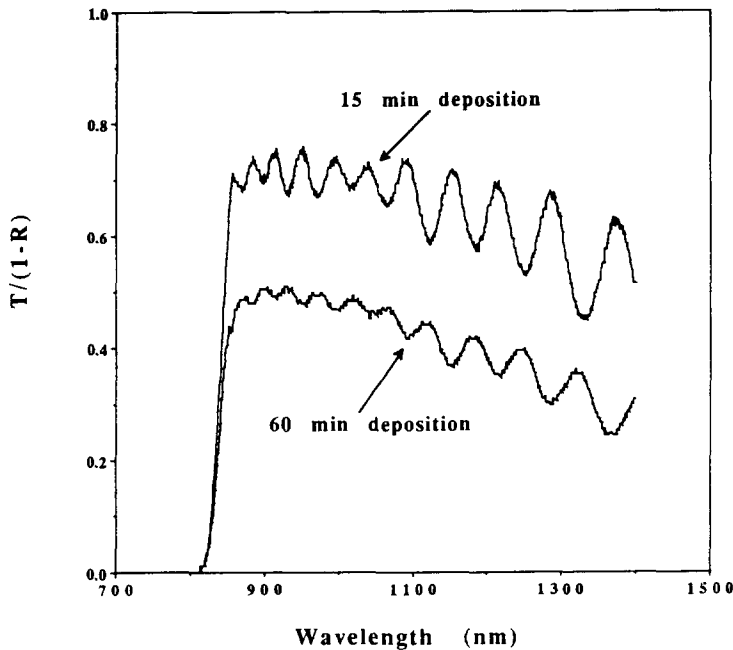


Fig. 5. Normalized transmission, $T/(1-R)$, spectrum of 7059/ITO/CdS/CdTe/ZnTe:Cu for two ZnTe:Cu deposition times.

that no additional Cu is required to optimize the device. The I - V behavior of several ITO/CdS/CdTe/ZnTe:Cu cells with Cu/Au contacts were measured under AM1.5 illumination at 25°C at the Solar Energy Research Institute (SERI). Fig. 3 shows the light I - V curve for a cell with $V_{oc} = 705$ mV, $J_{sc} = 18.8$ mA/cm², FF = 65.7%, and efficiency = 8.7%. This device had a series resistance of only 4 Ω cm² which implies low contact resistance. Fig. 4 shows the quantum efficiency for this device measured at 0 V with 11.4 mA/cm² light bias.

To evaluate the cells for tandem cell application, the total transmission and reflection was measured for different deposition times, hence, thicknesses. The normalized transmission, $T/(1-R)$, is shown in fig. 5 for cells with the ZnTe:Cu grown for 15 min and 60 min deposition times under the following conditions: 0.1 M ZnCl₂, 10⁻⁴ M TeO₂, 10⁻⁴ M CuSO₄ in TEA, pH \approx 3.2, $T \approx$ 60°C. The ZnTe thickness for the 15 min and 60 min depositions was estimated to be 80 nm and 180 nm, respectively. From fig. 5, the cell with the ZnTe:Cu grown for 15 min has $T/(1-R) \approx$ 70% at 900 nm. This can be compared to the results reported by Meyers et al. [3] where the maximum $T/(1-R)$ was \approx 30% for a cell with \approx 100 nm thick ZnTe. Thus, the electrodeposited ZnTe:Cu has higher transmission than the evaporated ZnTe:Cu demonstrating the advantage of the very thin electrodeposited films. The ZnTe:Cu thickness and the Cu doping level need to be optimized to further reduce absorption.

4. Conclusions

Cu-doped ZnTe films, < 100 nm thick, were deposited by an electrochemical method for the first time. A CdTe/CdS/ITO/glass substrate was externally short circuited to a zinc counter electrode in an aqueous bath consisting of ZnCl_2 and TeO_2 to complete an electrochemical cell. Control of both pH and TeO_2 concentration was necessary to deposit single phase ZnTe films. A copper complex added to the bath allowed controllable p-type doping of the ZnTe films. CdTe/CdS solar cells using the ZnTe:Cu as the primary contact to the CdTe achieved efficiencies of 8.7% with low contact resistance. The optical transmission of cells using ZnTe:Cu made in this manner is higher than on cells using evaporated ZnTe:Cu, making this an attractive contacting method for tandem cells and for use of optical back surface reflection enhancement techniques in conjunction with thin CdTe.

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References

- [1] P.V. Meyers, Sol. Cells 23 (1988) 59.
- [2] J.F. Jordan and S.P. Albright, Sol. Cells 23 (1988) 107.
- [3] P.V. Meyers, C.H. Liu, L. Russell, V. Ramanathan, R.W. Birkmire, B.E. McCandless and J.E. Phillips, Proc. 20th IEEE PVSC (1988) 1448.
- [4] R.N. Bhattacharya, K. Rajeshwar and R.N. Noufi, J. Electrochem. Soc. 131 (1984) 939.
- [5] K.R. Murali, I. Radhakrishna, K.N. Rao and V.K. Venkatesan, J. Mater. Sci. 25 (1990) 3521.
- [6] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions (Pergamon Press, New York, 1966).
- [7] M.P.R. Panicker, M. Knaster and F.A. Kroger, J. Electrochem. Soc. 25 (1978) 566.
- [8] B.E. McCandless and R.W. Birkmire, Sol. Cells 31 (1991) 527.