Novel Ways of Depositing ZnTe Films by a Solution Growth Technique

Final Subcontract Report
1 January 1990 - 1 January 1992

R. W. Birkmire, B. E. McCandless,
T. A. Yokimcus, A. Mondal
Institute of Energy Conversion
University of Delaware
Newark, Delaware

NREL technical monitor: T. S. Basso

❖NREL

MASTER

On September 16, 1991 the Solar Energy Institute was designated a national laboratory, and its name was changed to the National Renewable Energy Laboratory.

NOTICE

PREFACE

ZnTe and other II-VI compounds were deposited by an electrochemical method for use as contacts and window layers for CdTe and CuInSe$_2$ solar cells. The work was performed at the Institute of Energy Conversion under the general direction of Robert Birkmire by Brian McCandless, Anup Mondal, Tracey Yokimcus and Laurie Adkins.

SUMMARY

A. Objectives

The objective of this research was to develop novel processes for the deposition of thin (<500Å) ZnTe layers suitable as transparent ohmic contacts for CdS/CdTe solar cells. The processes developed for ZnTe deposition were also applied to deposition of other II-VI semiconductor layers for polycrystalline thin film solar cells.

B. Discussions

The Institute of Energy Conversion (IEC) investigated three processes for the deposition of ZnTe - surface exchange with CdTe where Cd is replaced by Zn from an aqueous bath to form a ZnTe layer, solution growth, and galvanic deposition from an aqueous bath. The galvanic deposition technique proved to be the only method in which ZnTe films were successfully and reproducibly formed.

Galvanic cells were constructed in solution with Zn foil used as an anode and a glass/ITO/CdS/CdTe substrate acting as a cathode. These electrodes were externally short-circuited, and their potential difference was the driving force for the electrochemical reaction. The optimal solution in which ZnTe was formed consisted of 0.1 M Cd salt and 10^{-4} M TeO_2; a Cu salt in the range of 10^{-4} to 10^{-5} M and triethanolamine were added for the formation of Cu-doped ZnTe films. Both temperature and pH were controlled, and deposition times of 10 to 30 minutes resulted in film thicknesses of 30 to 150 nm. The effects of agitation, temperature, and Cu doping on the ZnTe films were determined. Structural, optical and electrical film properties were characterized and CdS/CdTe/ZnTe devices were fabricated and evaluated.

The formation of ZnSe and CdS films using this galvanic deposition method was attempted, and encouraging results were achieved for the formation of CdS films on SnO_2/glass substrates. Electrochemical deposition processes for ZnSe film formation on $CuInSe_2$/Mo/glass substrates proved to be problematic in terms of film uniformity.

Conclusions

An electrochemical process has been successfully developed for the reproducible deposition of ZnTe and copper-doped ZnTe films suitable as transparent ohmic contacts for CdS/CdTe solar cells. The development of this method and optimization of key processing steps in the fabrication of CdS/CdTe/ZnTe:Cu devices has allowed IEC to achieve cell performance results of FF>70% and η ~10%. Preliminary efforts have indicated that the deposition methods investigated are potentially feasible for the formation of other II-VI compounds for use in polycrystalline thin film solar devices and should be the focus of future work.

LIST OF CONTRIBUTORS

Robert W. Birkmire

Brian E. McCandless

Tracey A. Yokimcus

Anup Mondal

Laurie Adkins

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SECTION 1.0
INTRODUCTION

1.1 BACKGROUND

CdTe/CdS thin film solar cells have been shown to be a promising candidate for photovoltaic power modules (1,2). Small area devices 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. One approach uses a 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). Further, CdTe based cells are candidate wide bandgap cells for tandem structures using $CuInSe_2$ based cells (3). However, in the n-i-p CdTe cells, the 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. It is thus necessary to prepare ZnTe having the required electronic properties but which are continuous and thin (<500Å) to minimize the absorption. This approach has the additional advantage of permitting alternative CdTe device designs which incorporate optical enhancement. It is not possible to deposit continuous thin ZnTe films by vacuum evaporation. Thus, there is a need to develop an alternative deposition process to deposit thin ZnTe films which can improve device performance, and possibly be more cost effective for commercial applications. The objective of the research described in this report is to develop novel processes for deposition of semiconductor window/contact layers for thin film polycrystalline solar cells, specifically a method of depositing thin semitransparent ZnTe films for CdTe solar cells.

1.2 TECHNICAL APPROACH

In order to achieve the objectives, the Institute of Energy Conversion (IEC) carried out a program of investigation and analysis to deposit ZnTe and ZnSe films according to the following research tasks:

a. IEC investigated methods for depositing II-VI films using solution growth and electrochemical techniques. The processes investigated included direct ZnTe film formation on the CdTe surface and an exchange reaction with CdTe surface forming a ZnTe layer where Cd is replaced by Zn. Doping of the ZnTe film with Cu to control the resistivity was an integral part of the process.

b. IEC characterized the structural, optical and electrical properties of the ZnTe films using established techniques of x-ray diffraction and total reflection and transmission

measurements. Emphasis was placed on obtaining single phase films and on minimizing sub bandgap absorption.

c.   IEC fabricated superstrate CdS/CdTe/ZnTe solar cells to characterize the contact properties of the ZnTe films on a working device. The properties of the devices using the ZnTe contact were compared to devices using Au or Cu/ITO as the CdTe contact. Emphasis was placed on total transmission through the device and resistivity losses due to the contact.

d.   IEC investigated different processes for depositing ZnSe films onto Mo/glass and CuInSe$_2$/Mo/glass substrates. The processes investigated were solution growth, electrodeposition, and galvanic deposition. The primary difficulty encountered with the solution growth method was promoting reaction of Zn and Se on the substrate; reproducible deposits could not be achieved. Both electrochemical and galvanic techniques met with limited success owing to the wide difference in deposition potentials of Zn and Se.

e.   IEC deposited CdS and CdTe films by the galvanic technique to investigate the application of the deposition technology to other II-VI compounds and to demonstrate the feasibility of an all-galvanically deposited device.

1.3 REPORT OUTLINE

The report is divided into two major sections which describe the work completed on ZnTe:Cu (Section 2) and ZnSe (Section 3). The extension of the galvanic process to other compounds is briefly discussed in Section 4. There are three Appendices. Appendix A is a paper presented at the 22nd IEEE Photovoltaic Specialists Conference in Las Vegas, 1991, on the deposition of ZnTe:Cu films. Appendix B is a manuscript of follow-up investigation of ZnTe:Cu deposition accepted for publication by Solar Energy Materials. Appendix C is a report written to the University of Delaware Honors Program for work on ZnSe deposition, carried out under their Research Scholar Program.

2.1 BACKGROUND

At the outset of this project, several pathways to formation of
ZnTe directly on CdTe/CdS substrates were considered. The pathways
investigated and their significant results are summarized in the
following three sections for: 1) surface exchange reactions; 2)
solution growth; and 3) galvanic deposition.

2.1.1 Exchange Reactions

Three exchange reaction paths were investigated, according to the
generalized reaction:

$$(CdTe)solid + (ZnLn)aq \longrightarrow (ZnTe)solid + (CdLn)aq,$$
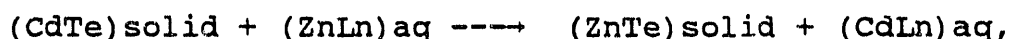
where Ln is an appropriate ligand. Table 1 lists the reaction
routes explored and their standard free energies. Although the
overall reaction free energies are negative, indicating that the
reactions are indeed possible, their magnitudes are relatively
small.

The following growth conditions were varied: solution temperature
from 25 to 80°C, concentration from 0.03 to 3 molar, pH from 2.3 to
8.5 (basic solution only used for $ZnCl_2$ reactions), and reaction
time from 5 to 10 minutes. In addition, the CdTe surface was
etched in hydrazine for 5 minutes prior to reaction. The hydrazine
etch produces a Te excess at the CdTe surface. None of the
experiments resulted in measurable ZnTe film formation.

Table 1. Reaction routes and standard free energies for CdTe to
ZnTe surface exchange.

Ligand	Reaction (Free Energy (Kcal/mole))	Overall Standard Free Energy (Kcal/mole) at 25°C
Cyanide:	$CdTe + Zn(CN)^{-2} \longrightarrow ZnTe + Cd(CN)^{-2}$ (-25.6) (-22.92) (-28.05) (-25.78)	-5.31
Chloride:	$CdTe + ZnCl_2 \longrightarrow ZnTe + CdCl_2$ (-25.6) (-0.84) (-28.05) (-3.43)	-5.04
Acetate:	$CdTe + Zn(C_2H_3O_2)_2 \longrightarrow ZnTe + Cd(C_2H_3O_2)_2$ (-25.6) (-2.06) (-28.05) (-2.06)	-2.45

2.1.2 Solution Growth

Two chemistries were explored to attempt to form ZnTe by solution growth:

1. A solution of Na_2Te was prepared from Te powder, NaOH, and $Na_2S_2O_4$ as a source of Te^{-2} ions. $Zn(C_2H_3O_2)_2$ was added as the source of Zn with NH_3 as a complexing agent. A small quantity of Te precipitated out of the solution, but no ZnTe formed.

2. Zn dust was added gradually to a solution of TeO_2 and NaOH. The solution had a reddish color which suggested the presence of Te^{-2} ions rather than the Te^{-2} ions needed for the reaction: $TeO_2 + 2\ e^- \longrightarrow Te^{-2}$, where the electrons are supplied by the oxidation of Zn dust as it is added to the bath. The precipitates formed were found to contain ZnO and Te.

2.1.3 Galvanic Deposition

ZnTe films were deposited galvanically, a special case of electrochemical deposition, from an unstirred aqueous bath containing 0.1 M $ZnCl_2$ or $ZnSO_4$ and about 10^{-4} M TeO_2. The TeO_2 was first dissolved with NaOH and then pH was adjusted using HCl. Controlling the bath pH between 3 and 4 and temperature between 50°C and 80°C was necessary to deposit uniform, adherent, single phase ZnTe films. Doping of the ZnTe films was achieved by adding a Cu^{+2} complex to the bath. For this, a few drops of TEA were added to a $CuCl_2$ or $CuSO_4$ solution to form the complex which was then introduced into the main bath. The galvanic cell was then constructed by dipping in the bath a glass/ITO/CdS/CdTe substrate and a zinc foil, which were externally short circuited by a wire. In the solution the zinc, being electro-positive, acts as the anode, while the substrate becomes the cathode. The electrochemical reaction is driven by the potential difference between the electrodes. The zinc acts as both a source of electrons for the cathodic reaction and a source of Zn^{+2} ions. The reactions leading to the formation of ZnTe:Cu are most likely:

Anode Reaction

$Zn \rightarrow Zn^{+2} + 2e^-$, $E^o_{ox} = +0.76V$

Cathode Reaction

$Zn^{+2} + 2e^- \rightarrow Zn^o$, $E^o_{red} = -0.76V$

$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te^o + 2H_2O$, $E^o_{red} = +0.56V$

$Zn^o + Te^o \rightarrow ZnTe$

$Cu(TEA)_n^{+2} + 2e^- \rightarrow Cu^o + nTEA$
$$n = 1, 2, \ldots$$

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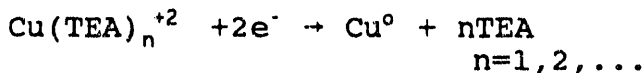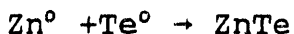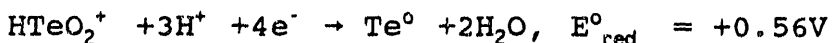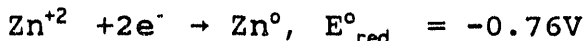
2.2 GALVANIC DEPOSITION OF ZnTe

2.2.1 Bath Chemistry

ZnTe films were deposited galvanically from an unstirred aqueous bath containing $ZnCl_2$ or $ZnSO_4$ and TeO_2. The TeO_2 was brought into solution by dissolving it in a solution of NaOH. The pH of the bath was adjusted to ~3 using dilute HCl. The bath temperature was maintained at 50-60°C during the deposition. A conductive substrate, typically Glass/ITO/CdS/CdTe or Glass/SnO_2/CdS/CdTe, and a zinc electrode were externally short circuited together and were immersed in the bath to form an electrochemical cell. A similar method was reported by Bhattacharya et al. (4) for depositing CdTe and by Murali et al. (5) for depositing CdSe. Cu doping of the ZnTe films was achieved by co-deposition of Cu from either $CuCl_2$ or $CuSO_4$. Figure 1 shows a schematic sketch of the apparatus. Nominal ZnTe:Cu deposition conditions used for this work are summarized below:

▸ Adjustable Parameters:

CdTe Surface Preparation: 0.01% Br_2CH_3OH for 5 seconds

Bath Composition: 0.1 M $ZnCl_2$ or $ZnSO_4$

10^{-4} M TeO_2 brought in via NaOH solution

10^{-5} to 10^{-4} M $CuCl_2$ or $CuSO_4$

pH: 3.0 to 3.2, adjusted with HCl

Temperature: 55°C

Mixing: Unstirred bath

Anode: Zn, area 2 - 0.1 cm^2

Cathode: CdTe/CdS/ITO, area 4 - 5.5 cm^2

Cathode Lead: Pt wire, bonded with In

Deposition Time:

For device contacts: 10 to 30 minutes (~30 to 150 nm)

For XRD, EDS measurements: 60 to 120 minutes

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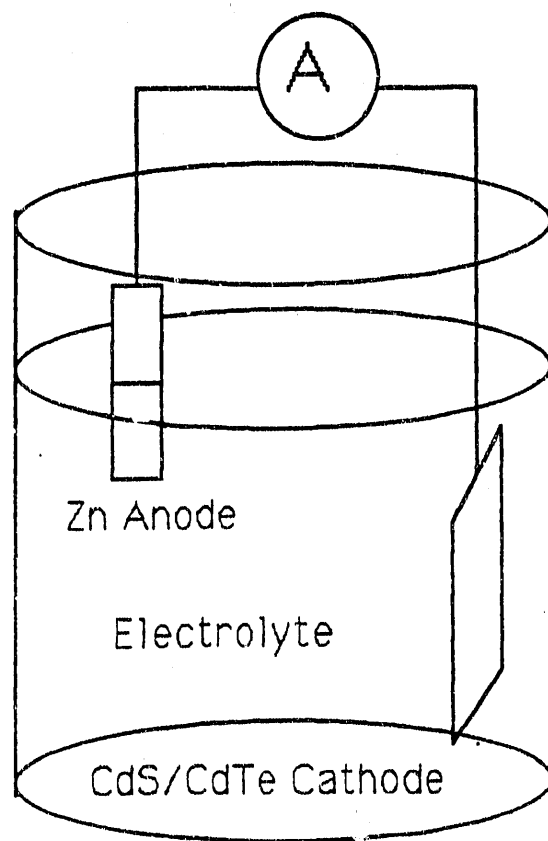
Figure 1. Schematic diagram of galvanic apparatus.

▶ Measured Parameters:

Deposition Current Density

Deposition E.M.F.

Cathode Rest Potential after Deposition with Respect to Ag/AgCl Reference Electrode (SSCE)

Deposition Thickness by Gravimetric Method

pH

Optical Transmission of Device Structure

Gravimetric Thickness Determination

Constants used in the work:

Molecular weight (g/mol)	Zn	65.37
	Te	127.6
	Se	78.96
	ZnTe	192.97
	ZnSe	144.33
	Cu	63.54
	$CuCl_2$	98.99
	$CuSO_4$	159.60
Density (g/cm^3)	Zn	7.13
	Te	6.25
	Se	4.79
	ZnTe	6.0
	ZnSe	5.4

2.2.2 Electron-Mass Balance

To describe the reaction chemistry of the galvanic deposition, coulometric, potential, and pH measurements were made during ZnTe deposition and gravimetric measurements of the cathode and anode were made before and after deposition. These measurements, described below, showed that: 1) while ZnTe was plated onto the cathode, Te plated onto the anode; 2) the cathode gained half the mass expected for the measured current density; and 3) the bath pH increased throughout the run. Thus the deposition proceeded in a different manner than expected for a six electron reaction route, and the reactions considered above (Section 2.1) are not the only reactions occurring during growth.
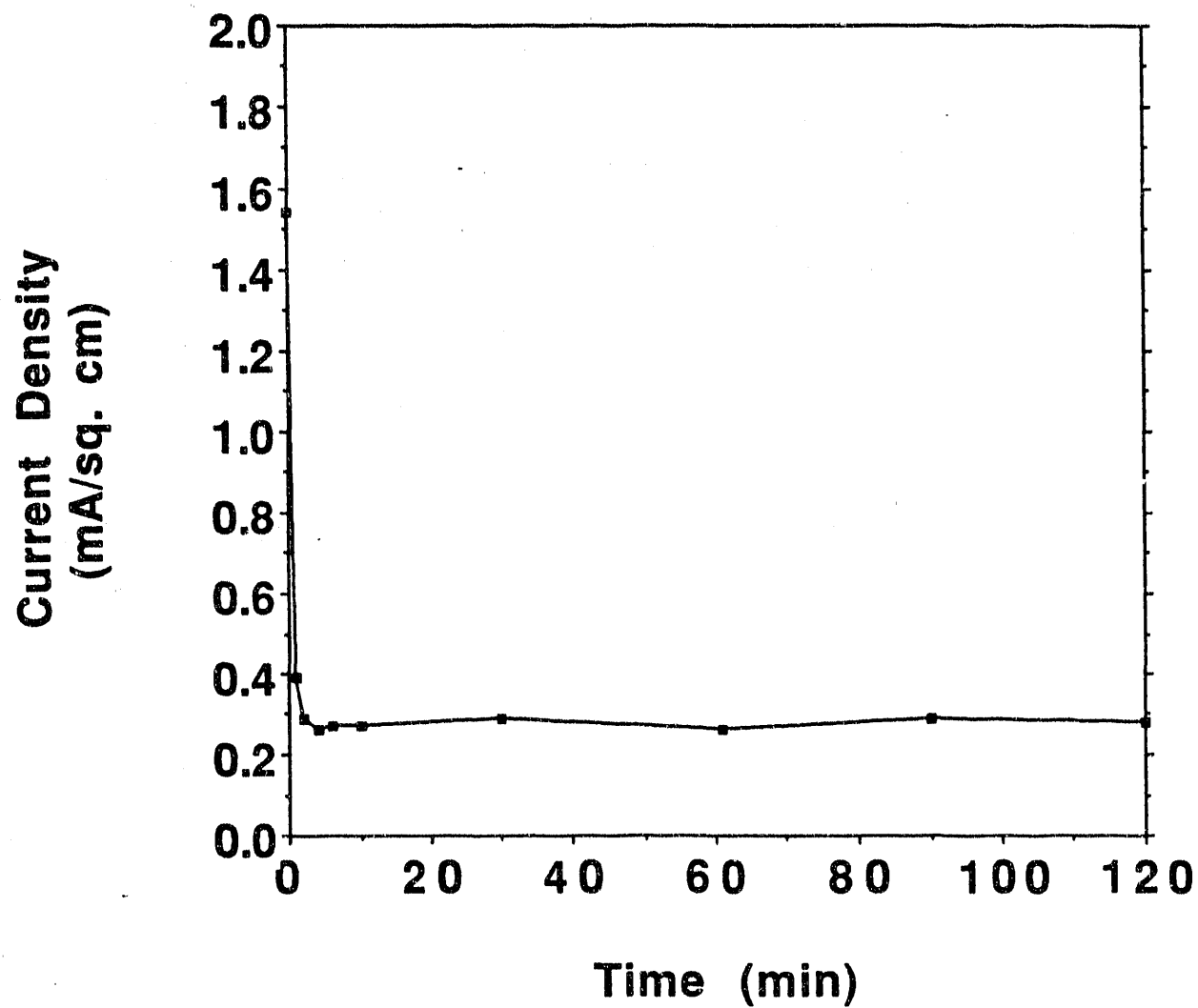
Figure 2. Cathode current density as a function of deposition time for ZnTe bath.

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- CATHODE

Figure 2 shows the deposition current density as a function of time for an undoped ZnTe deposition onto CdTe/CdS (#40687.22). The steady state cathodic current, obtained after about 5 minutes of deposition, was 0.670 mA, and the run time was 60 minutes. For a sample area of 4.4 cm^2, the steady state cathodic current density was thus 0.15 mA/cm^2. The cathode accumulated a net mass of 0.39 mg or 2.0×10^{-5} moles of ZnTe. Based on the cathodic current measured and the simple reaction:

2.2.1) $Zn^{+2} + Te^{+4} + 6e^- \longrightarrow$ ZnTe,
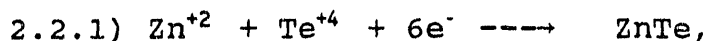
we would have expected a mass increase of 0.80 mg using:

2.2.2) dm/dt = (I x MWprod)/(F x n),

where dm/dt = mass gain per unit time, I = mean current ($\int Qdt$), MW= molecular weight of the products, F = Faraday constant, and n = number of electrons.

From the total mass gained by the cathode the ZnTe contribution to the cathodic current is 0.32 mA, which is 50% of the measured current. The electron efficiency for the galvanic deposition is thus approximately 50%, in contrast with values of 80-90% obtained for CdTe electrodeposition. In the galvanic case, however, the electrons are provided by oxidation of the Zn anode, not an external power source.

- ANODE

The Zn anode blackened during deposition and lost mass. In the example given here, for an anode area of 1.9 cm^2, the mass lost was 1.35 mg. Based on the anode area and the current density in the circuit, we expected the anode to lose 0.82 mg. Despite the presence of the black coating, the anode lost nearly twice the mass expected based on the cathodic current and the oxidation reaction:

2.2.3) $Zn^0 - 2e^- \longrightarrow Zn^{+2}$, $E_{ox} = +0.763V$ SHE
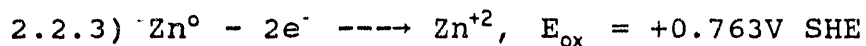
The Zn electrode is highly soluble in acidic solution and is therefore easily oxidized to provide electrons. $HTeO_2^+$, on the other hand, is easily reduced. Thus Te reduction at the Zn electrode must be spontaneous, despite the fact that it is the anode for the deposition of ZnTe. Note that at low pH (1-3), Zn will spontaneously reduce Te from $HTeO_2^+$ solution with no external circuit, demonstrated by immersing a Zn strip in 0.01 M $HTeO_2^+$ at 60°C and pH=2 for 30 minutes.

This was confirmed by EDS and XRD analyses which showed that after the deposition, the anode was coated with a layer of Te. This

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reduction of $HTeO_2^+$ to Te at the anode thus results in additional $HTeO_2^+$ depletion by:

2.2.4) $\quad HTeO_2^+ + 3H^+ + 4e^- \quad \longrightarrow \quad Te^o + 2H_2O$, $\quad E_{red} = +0.559V$ SHE.

Further, it involves additional H^+ ions, which combine with OH^- to form water, resulting in an increase in pH, which reduces the TeO_2 solubility further, as shown in the Pourbaix diagram for $[TeO_2]$ versus pH (Figure 3). All of this has the effect of limiting the rate at which Te, and therefore ZnTe, may deposit.

During the first year of study Zn anodes of a large area (~ 2 cm^2) were used to ensure a high 'throw', which is usually preferred for obtaining uniform electrodeposits. We subsequently found that a few square mm area is sufficient to sustain the deposition current density without significantly depleting the dissolved Te species. The 'throw' is actually a critical factor in cases of very high current density and low bath conductivity.

By shifting to a smaller Zn anode, anodic Te depletion was all but eliminated, and the bath was found to be reusable by merely replenishing the exhausted Te. The bath plating efficiency for electrons is only 50%, but since the electrons are provided by the anode, this is of little consequence. Knowledge of the electron plating efficiency permits calculation of appropriate intervals for Te replenishment and the estimation of film thickness by deposition current measurements. It still remains to determine the reactions responsible for the other 50% of the electrons measured during growth.

- pH CHANGE

During deposition, the pH increases from about 3.2 to 3.6 in a 60 minute run. This corresponds to about 3.8×10^{-4} M or 7.6×10^{-5} Mol of H^+ converting to H_2O in 60 minutes, which works out to 1.3×10^{-6} Mol/min of H^+ being depleted. The increase is due to the dissociation of $HTeO_2^+$ via equation 2.2.4 which requires $3H^+$ for each Te reduced. The 7.6×10^{-5} Mol of H^+ is thus expected to produce 2.5×10^{-5} Mol of ZnTe. From the cathode mass gain we measured 2.0×10^{-5} Mol ZnTe, leaving an excess of 0.5×10^{-5} Mol of Te, which was deposited on the anode. A makeup buret with dilute HCl can be used to compensate for this effect, allowing more $HTeO_2^+$ to remain in solution during the run and stabilizing the deposition rate.

2.2.3 Half Cell Behavior

At several points during a deposition we measured the individual cathode and anode rest potentials and the difference (the E.M.F.) or driving force of the deposition. By definition, it should equal the difference between the half-cell reactions of the cathode and anode, and this was verified (Table 2).

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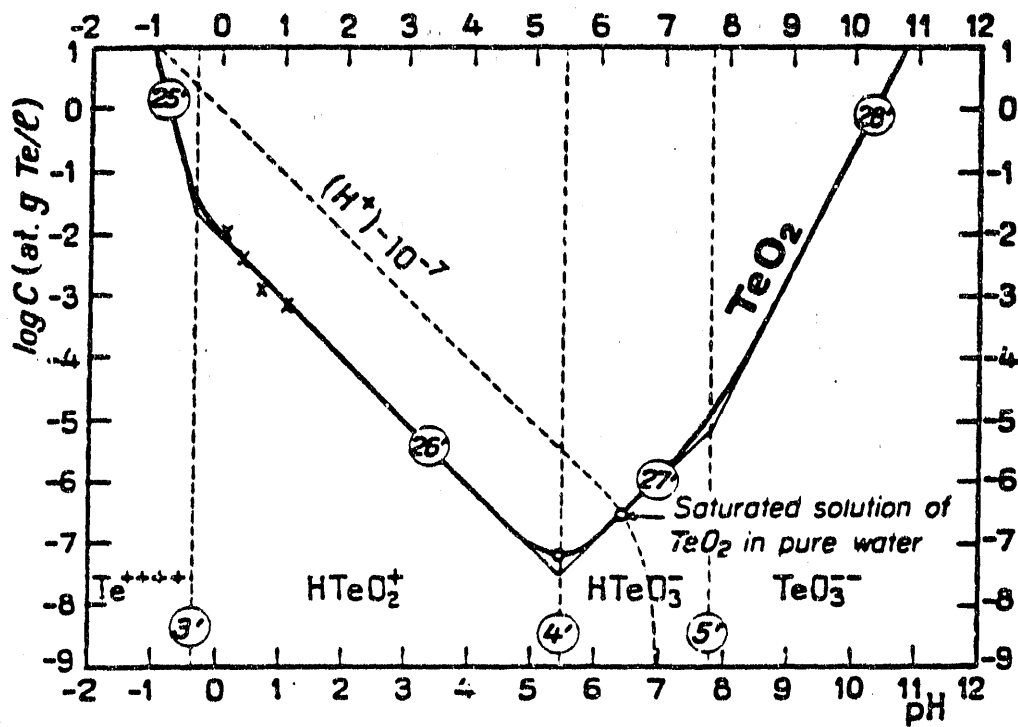
Figure 3. Pourbaix curve for [TeO₂]-pH (6).

Table 2. Cathode, anode, and difference in potentials (volts) during ZnTe deposition. Cathode and anode values measured with respect to SSCE, and all values measured at pH = 3.2 and T = 55°C.

	Start	End
Cathode Potential	-0.32 unstable	-0.60 stable
Anode Potential	+0.99 stable	+1.01 stable
Difference	-	+0.41
Measured Difference	+0.37 stable	+0.37 stable

The various components of the bath, taken separately, were further analyzed to identify possible sources of poor ZnTe:Cu deposition control. The half-cell potentials of the bath constituents were measured as a function of concentration in aqueous solutions at pH values near those used for ZnTe:Cu deposition. Since the half-cell potential of metals and their ions in solution are related by the Nernst Equation, the potential is a measure of the activity, taken as the concentration, of the ionic species in solution. The activity of the free metal is taken as 1. The half-cell measurements were made using high purity Zn, Te, and Cu electrodes, referenced to a Ag/AgCl$_2$ standard (SSCE). Although deionized water was used, no attempt was made to remove dissolved oxygen from the water, therefore, a small offset was expected in the absolute values of the potentials. As Table 3 shows, we observed reasonable values for the ZnCl$_2$/Zn, ZnSO$_4$/Zn, and for the TeO$_2$/Te solutions but obtained a large discrepancy for the CuCl$_2$/Cu solution.

Table 3. Half-cell reduction potentials (E) for Zn, Te, and Cu as a function of ion concentration. A.C.S. grade reactants, room temperature measurements.

[Ion] (M)	Calculated E(SHE)	E(SSCE)	Observed E(SSCE)	O-C (V)
ZnCl$_2$/Zn				
1	-0.76	-0.98	-1.00	+0.02
ZnSO$_4$/Zn				
1	-0.76	-0.98	-0.98	0.00
TeO$_2$/Te				
10^{-4}	+0.47	+0.25	+0.25	0.00
10^{-5}	+0.45	+0.24	+0.24	0.00
CuCl$_2$/Cu				
10^{-2}	+0.28	+0.06	-0.29	-0.35
10^{-3}	+0.25	+0.03	-0.32	-0.35
10^{-4}	+0.22	+0.00	-0.34	-0.34

For Cu, the offset between observed and calculated potentials was negative, indicating that the activity of the dissolved Cu species was lower than desired, making it harder to deposit. This is expected to produce lower Cu levels in the films. The magnitude of the offset in the Cu values suggested contaminated stock solution, so we tested other solutions from higher purity $CuCl_2$ (Cu^{+2}) made immediately (fresh) and 3 months previously (old), from purified CuCl (Cu^{+1}), and from $CuSO_4$ (Cu^{+2}). Only the sulfate solution yielded the half-cell potentials expected, as shown by the zero difference in the O-C column of Table 4. The variable potentials obtained with the chloride solutions for the same Cu concentration would translate to variable Cu cathode exchange currents, hence variable Cu deposition rate and incorporation into the ZnTe film.

Table 4. Half-cell reduction potentials (E) for Cu ion to pure Cu wire as a function of ion concentration for various starting chemicals. Room temperature measurements. All values of E are in volts.

Cu Compound	Valence	[Cu] (M)	Calculated E(SHE)	Calculated E(SSCE)	Observed E(SSCE)	O-C (V)
CuCl	+1	10^{-2}	+0.22	+0.00	+0.04	-0.18
CuCl	+1	10^{-4}	+0.10	-0.12	-0.03	+0.09
$CuCl_2$ (old)	+2	10^{-2}	+0.28	+0.06	-0.24	-0.30
$CuCl_2$ (fresh)	+2	10^{-2}	+0.28	+0.06	+0.01	-0.05
$CuSO_4$	+2	10^{-2}	+0.28	+0.06	+0.06	0.00
$CuSO_4$	+2	10^{-4}	+0.22	+0.00	0.00	0.00

We did not determine why the chloride solutions behaved as observed, but instead decided to proceed using the sulfate solution. For the deposition of Cu-doped ZnTe, the Cu is brought into solution by first complexing the Cu salt with triethanolamine (TEA), which reduces the activity of the Cu^{+2} for deposition.

This is a controlled way of limiting the Cu species for effective concentrations below about 10^{-5}. We measured the half-cell potential for $CuSO_4$ solution with increasing amounts of TEA to determine the activity, a, of complexed Cu^{+2} for a starting concentration of 10^{-4} M. In the typical ZnTe:Cu deposition, 10 drops of TEA was used. As TEA was added, $CuSO_4$ solution turned blue and the pH increased. For this experiment HCl was added to maintain the pH at 3.2 (see Table 5).

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Table 5. Half-cell measurements and activity determinations for Cu^{+2} complexed with TEA. $[Cu]=10^{-4}$ M; pH=3.2; and T=21°C.

[TEA] (dr)	E(SSCE) (V)	E(SHE) (V)	a (M)
0	-0.006	+0.214	5×10^{-5}
2	-0.038	+0.182	4×10^{-6}
5	-0.048	+0.172	2×10^{-6}
10	-0.071	+0.149	3×10^{-7}

The TEA complexing, which shifts the activity of the Cu species, can be used to tailor the optical absorption of the ZnTe:Cu film. Depositions with no Cu but with TEA added to the bath showed no effect on the deposition rate or optical properties of the ZnTe.

2.2.4 External Effects on the Deposition

- Thermal and Mixing Effects on Deposition Rate

The effects of two control variables - temperature and mixing (stirring) on the deposition current were measured. Figure 4 shows the effect of temperature on the cathode current density and growth rate from room temperature to about 85°C for a bath containing 1×10^{-4} M CuSO$_4$. The cathode current - temperature dependence was found to be essentially linear in this temperature range.

Figure 5 shows the influence of stirring the solution with a magnetic stirrer during the deposition of ZnTe:Cu with 1×10^{-4} M CuSO$_4$ in the bath. For this, a 2 minute pre-deposition in unstirred solution was performed to place the time frame of the experiment outside the steep transient period of reaction at the start of a run. The stir rate (in r.p.m.) was measured using an optical tachometer. In addition to the monotonically increasing growth rate, stirring greatly reduces the oscillatory cathode current experienced during a run. This leads to the conclusion that the oscillations in unstirred baths are caused by variations in the cathode exchange current due to the changing width of the depletion region over the substrate as the $HTeO_2^+$ (the limiting ionic species) is consumed and replenished. In the unstirred bath, the replenishment is driven by diffusion and thermal convection; in the stirred bath, the diffusion limitation is overcome by mechanical convection.
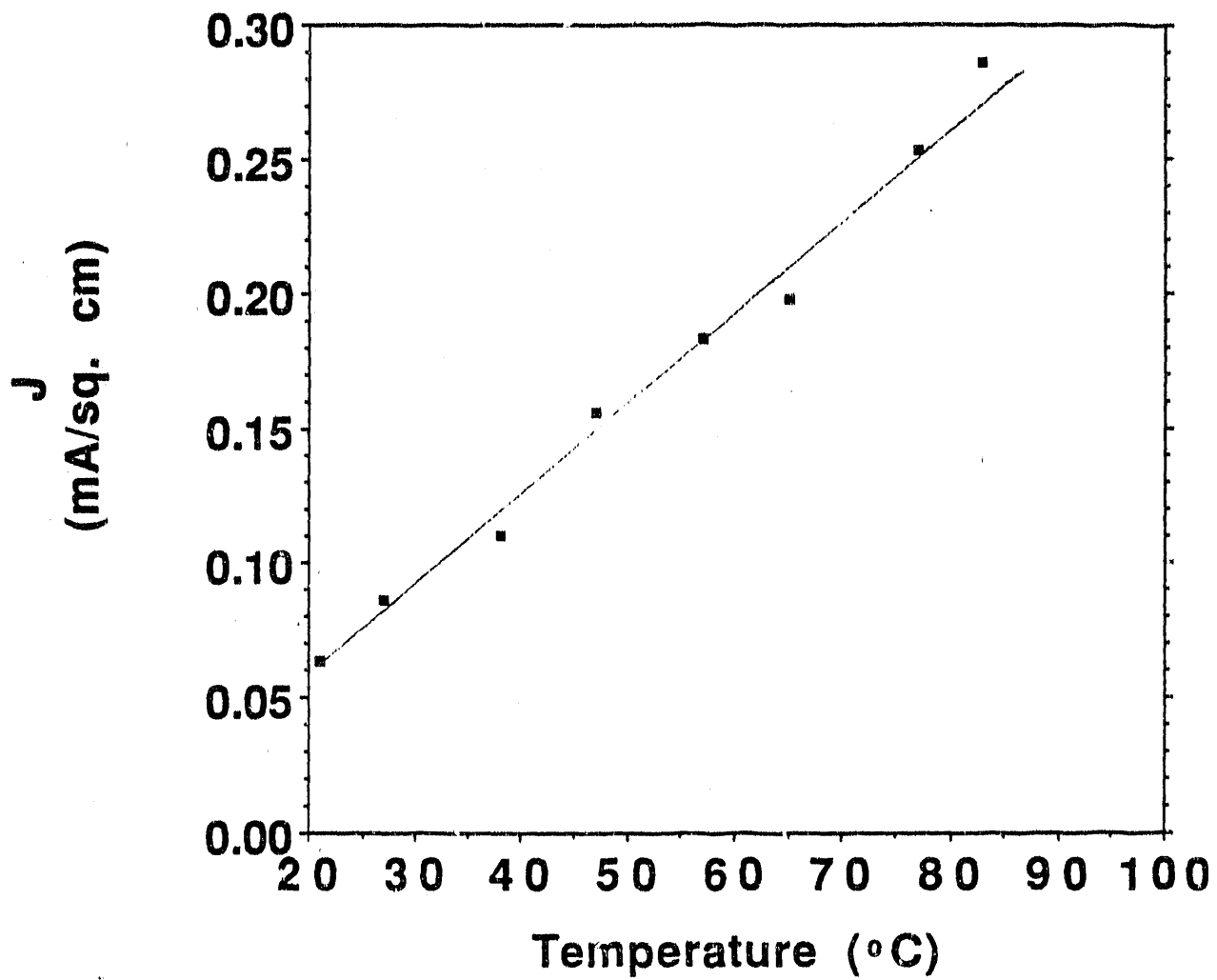
Figure 4. Cathode current density as a function of temperature.
The sample area = 5.25 cm^2, the pH = 3.2, and the solution was
unstirred.

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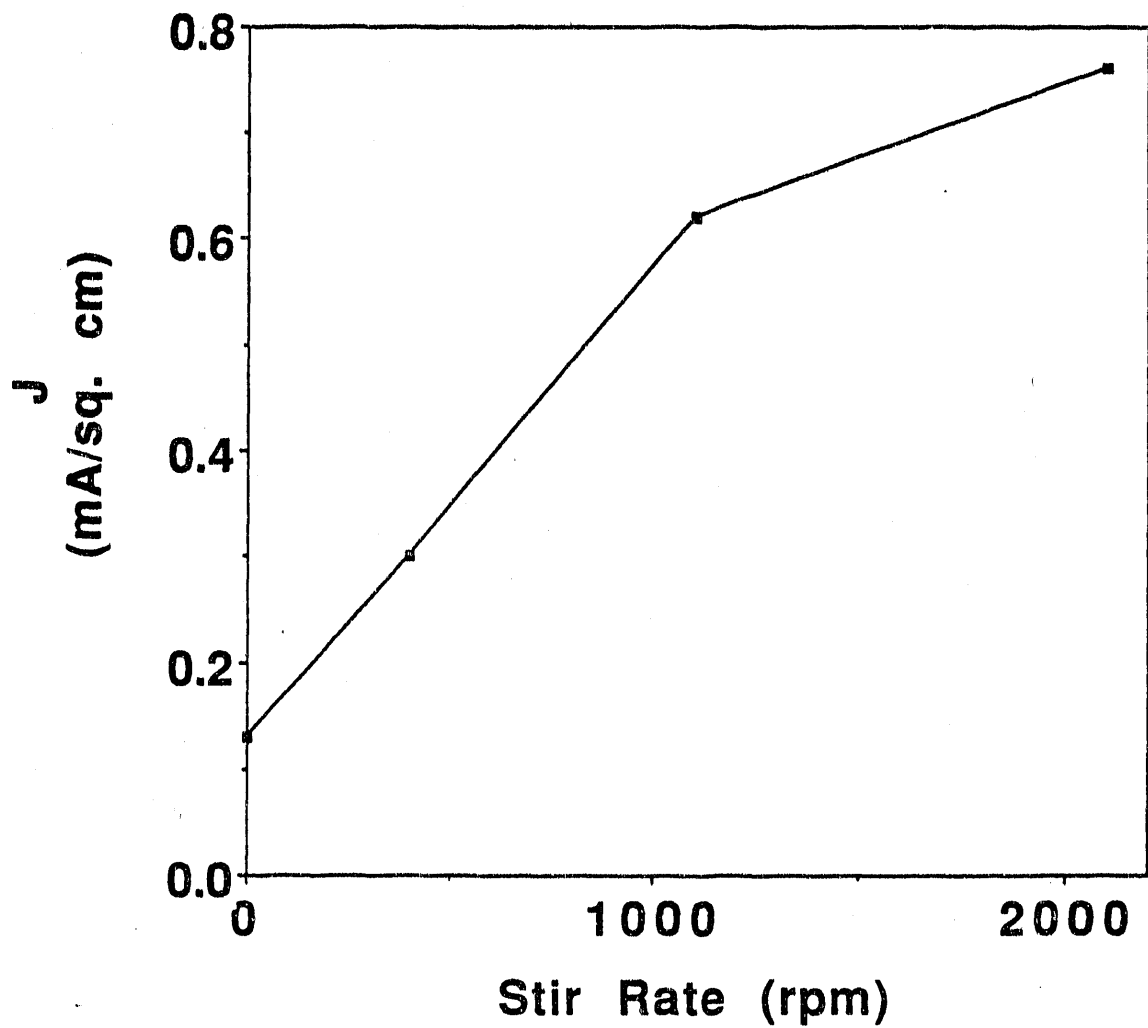
Figure 5. Cathode rrent density versus stir rate.

- Electrical Connection to CdTe/CdS Substrate

To reproducibly obtain visually uniform CdTe/CdS substrates, we improved the electrical connection of the Pt wire substrate. This was accomplished by soldering the wire with In to the ITO along opposite edges of the 1" x 1" substrate. A gain in uniform deposition area was achieved by suspending the samples horizontally in the bath. In this case, the entire 1" x 1" can be utilized and thermal and surface concentration effects are minimized.

The final galvanic cell arrangement adopted for reproducibly depositing uniform ZnTe:Cu films onto CdS/CdTe substrates is depicted in Figure 6. The bath is heated in a water jacket, the anode size is reduced to minimize Te depletion, and the electrical connection circumscribes the substrate.

2.3 ZnTe:Cu FILM PROPERTIES

2.3.1 Structural

Structural properties and composition of ZnTe:Cu films were measured on selected samples by x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS). To obtain sufficient signal strength with these techniques, thicker films were deposited by increasing the deposition time. We are aware that the conclusions drawn from the thicker films may not totally apply to the films used for devices, however gross differences between samples deposited under different bath conditions may be expected to apply to thinner films in a relative sense.

In all films where ZnTe was detected by XRD, the (111) reflection of the cubic phase was observed (7). Single phase films were obtained under the following range of conditions: Sulfate or chloride bath, pH from 3 to 4, temperature from 50°C to 80°C, $[Cu^{+2}]$ from 0 to 10^{-4} M. Figure 7 shows XRD patterns for undoped films deposited at pH of 3.2 and 2, showing the presence of ZnTe or Te for the respective cases. At lower pH, Te films were preferentially deposited. At very high Cu concentration, Cu_2Te was preferentially deposited.

2.3.2 Optical Properties

Optical transmission and reflection of films in the device structure were measured using a Perkin Elmer spectrophotometer over the wavelength range 400 to 1400 nm. The transmission in the CdTe sub-bandgap wavelength range (greater than 850 nm), normalized for front surface reflection, provided a relative measure of the ZnTe:Cu transparency. No difference was found between films deposited in sulfate or chloride based baths. For fixed Cu bath concentration, the ZnTe:Cu/CdTe/CdS transmission decreased with increasing ZnTe:Cu deposition time, hence thickness, as shown in

17
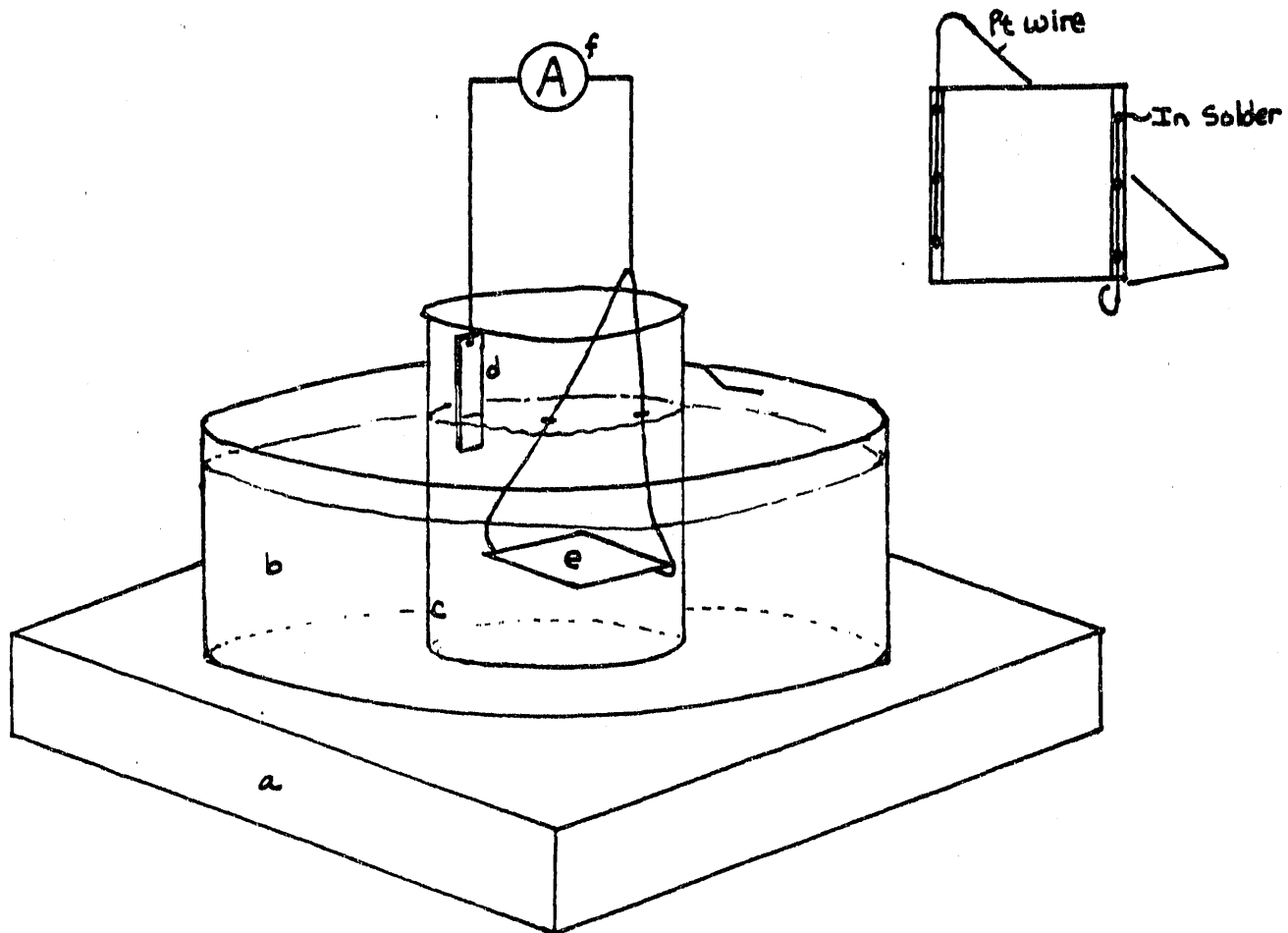
a. Hot Plate
b. Water Jacket
c. 200 ml beaker
d. Zn.Foil
e. CdTe/CdS/SnO₂/Glass Substrate

f. Ammeter

Figure 6. Galvanic cell configuration.

18
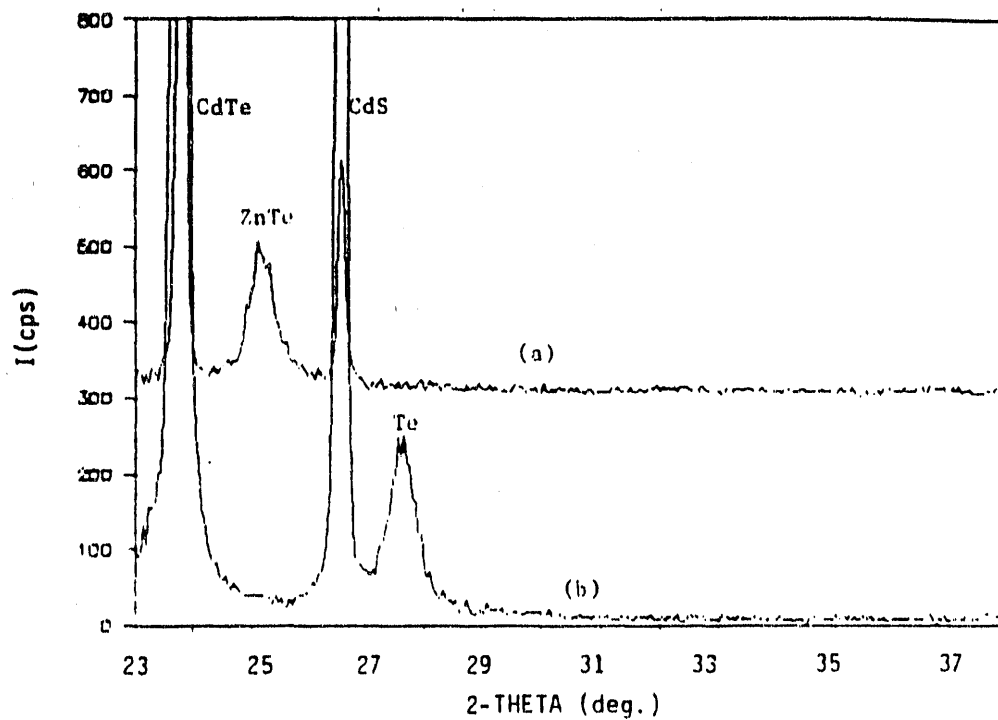
Figure 7. X-ray diffraction for undoped films on CdTe/CdS: a) deposited at pH = 3.2 and b) deposited at pH = 2.

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Figure 8. The only other parameter found to influence transparency was the Cu concentration in the bath, described below in Section 2.3.3.

2.3.3 Influence of [Cu]

The key to the utility of ZnTe:Cu contacts in devices is the copper concentration in the ZnTe:Cu layer, which serves two purposes: 1) to dope the ZnTe p-type and 2) to serve as a diffusion dopant for CdTe in a manner analogous to that in Cu/Au contacts (8). The effect of systematically varying the Cu concentration, [Cu], in the deposition bath was studied over a wide range of bath compositions and for a number of dependent parameters. Addition of Cu to the ZnTe bath increased the deposition rate (Figure 9) and the deposition current density (Figure 10). For films of nominally the same thickness, increasing Cu concentration in the bath decreases the transmission as shown in Figure 11. The effects on deposition current density, device transmission, observed phases, and relative surface EDS results are summarized in Table 6. The device properties obtained for different Cu concentrations are discussed below in Section 2.4.

Table 6. Steady state deposition current density, normalized optical transmission, XRD, and relative EDS results for different [Cu] for nominal film thickness of 150-200 nm, all on CdS/CdTe substrates.

Quantity				
[Cu] (M)	0	10^{-5}	10^{-4}	10^{-3}
Deposition Current Density (mA/cm^2)	0.12	0.25	0.34	0.59
T/(1-R) @ 900 nm (%)	80	75	45	26
XRD	CdTe ZnTe	CdTe ZnTe	CdTe ZnTe	CdTe Cu$_2$Te

Relative Composition by EDS(%):

Cd	30	37	40	25
Te	59	51	50	44
Zn	11	10	3	0
Cu	0	2	7	31

These results show that the Cu concentration in the deposition bath plays a major role in controlling the growth rate, composition, and properties of the deposit and are summarized:

20
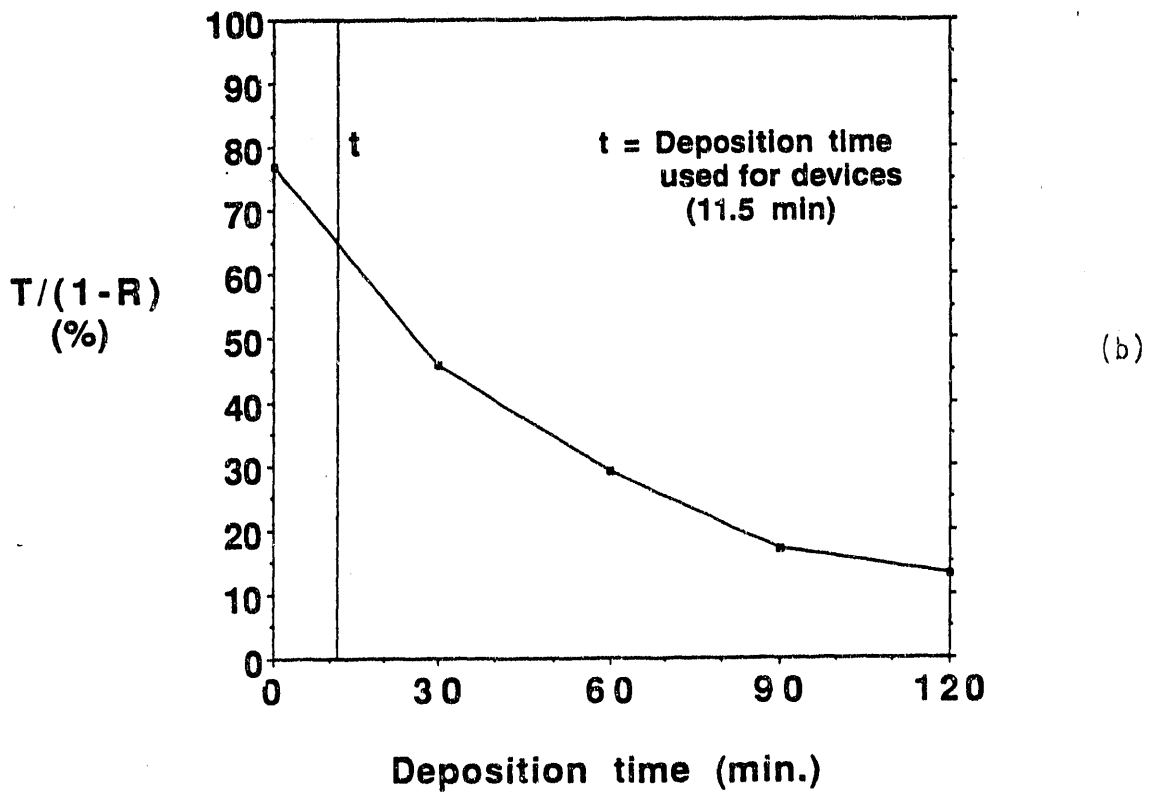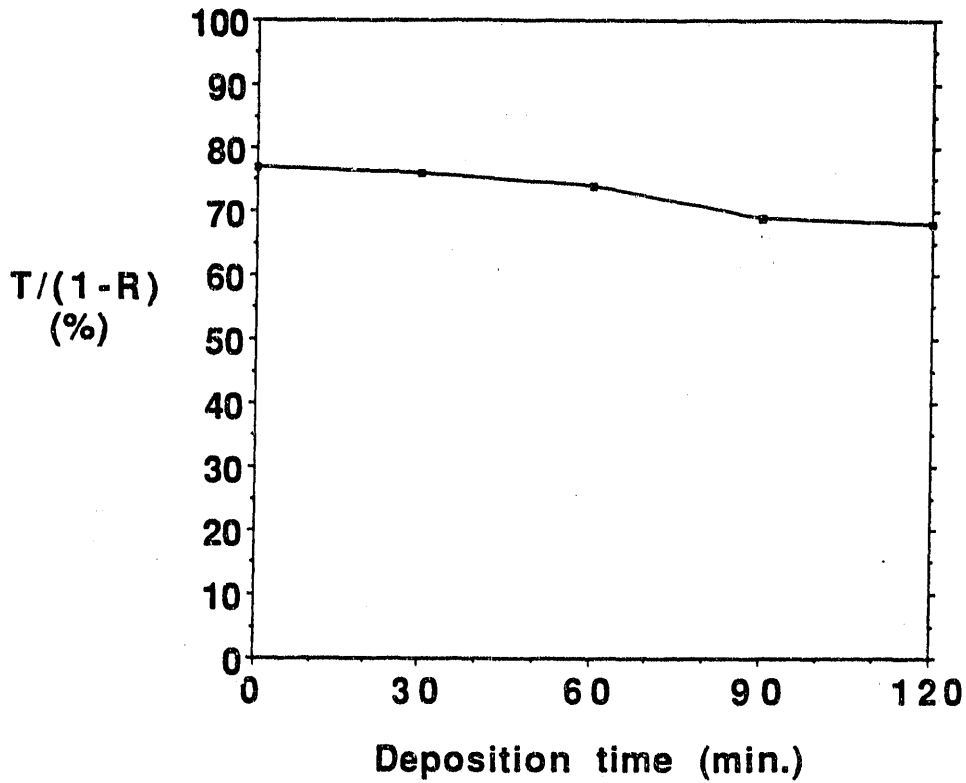
Figure 8. Normalized optical transmission at 900 nm as a function of deposition time for: a) undoped ZnTe on CdTe/CdS and b) ZnTe:Cu on CdTe/CdS with a Cu concentration was 10^{-4} M, the pH was 3.2, and the temperature was 60°C.
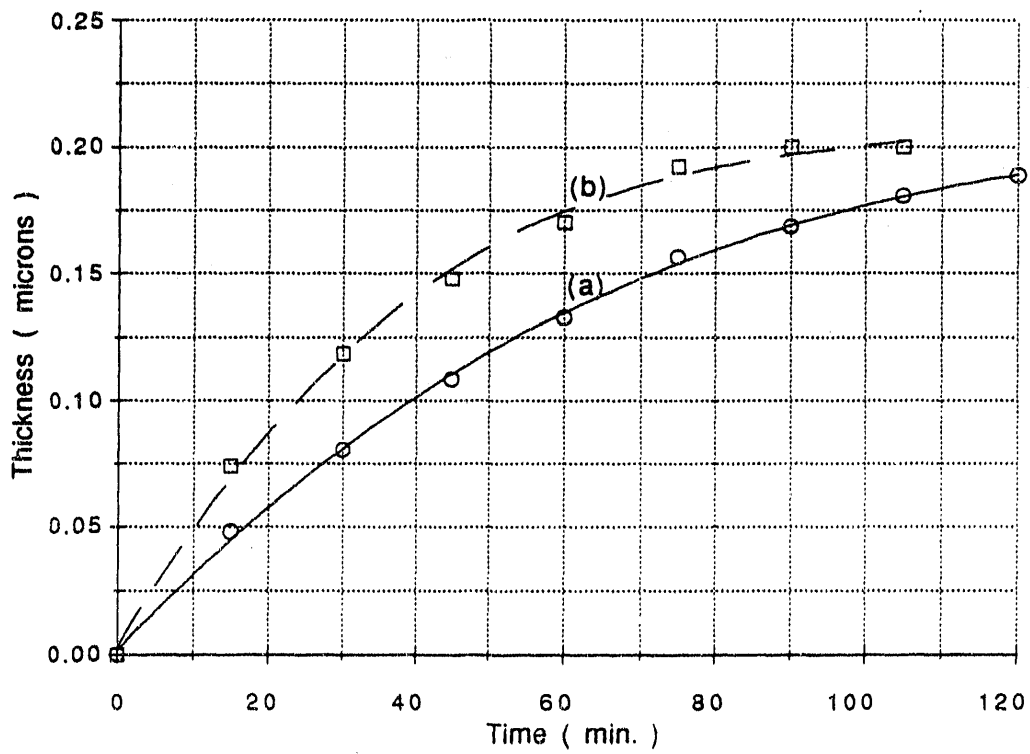
Figure 9. Thickness versus deposition time for: a) ZnTe and b) ZnTe:Cu with [Cu] = 10^{-4} M in the bath.
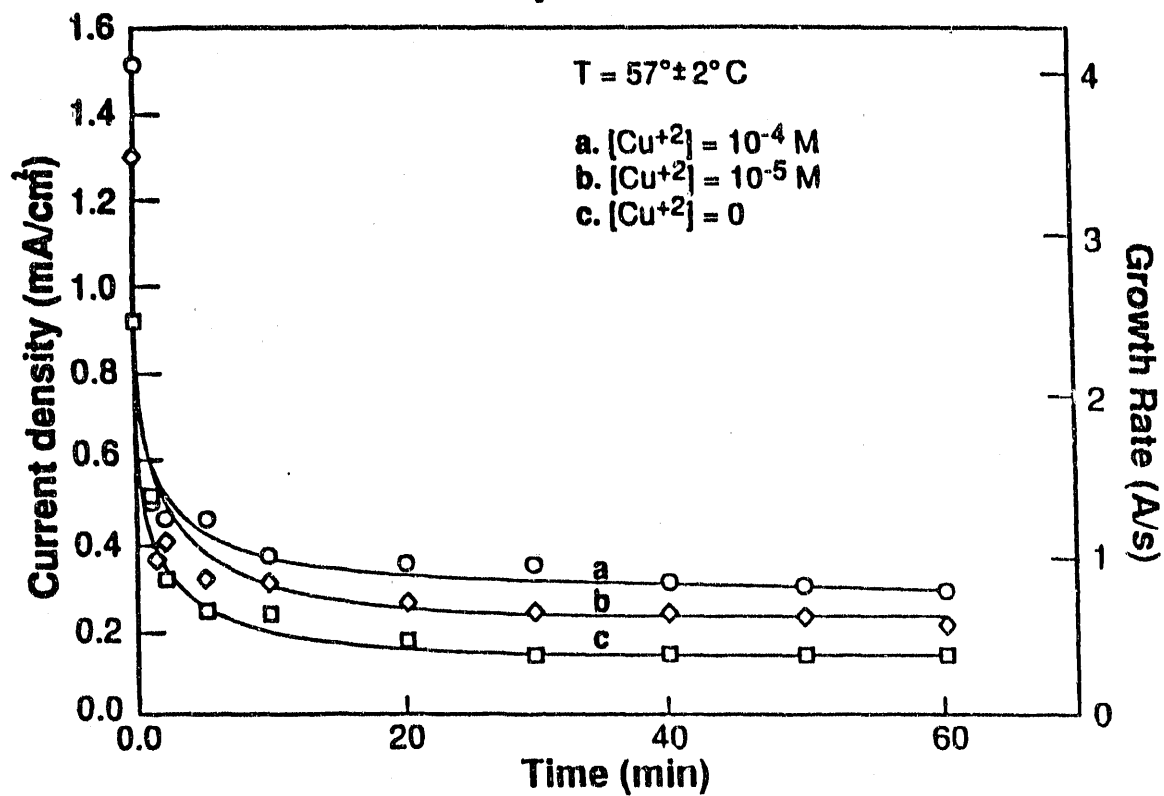
Figure 10. Deposition current density and growth rate versus deposition time: a) $[Cu^{+2}] = 10^{-4}$ M; b) $[Cu^{+2}] = 10^{-5}$ M; c) $[Cu^{+2}]$ = 0.

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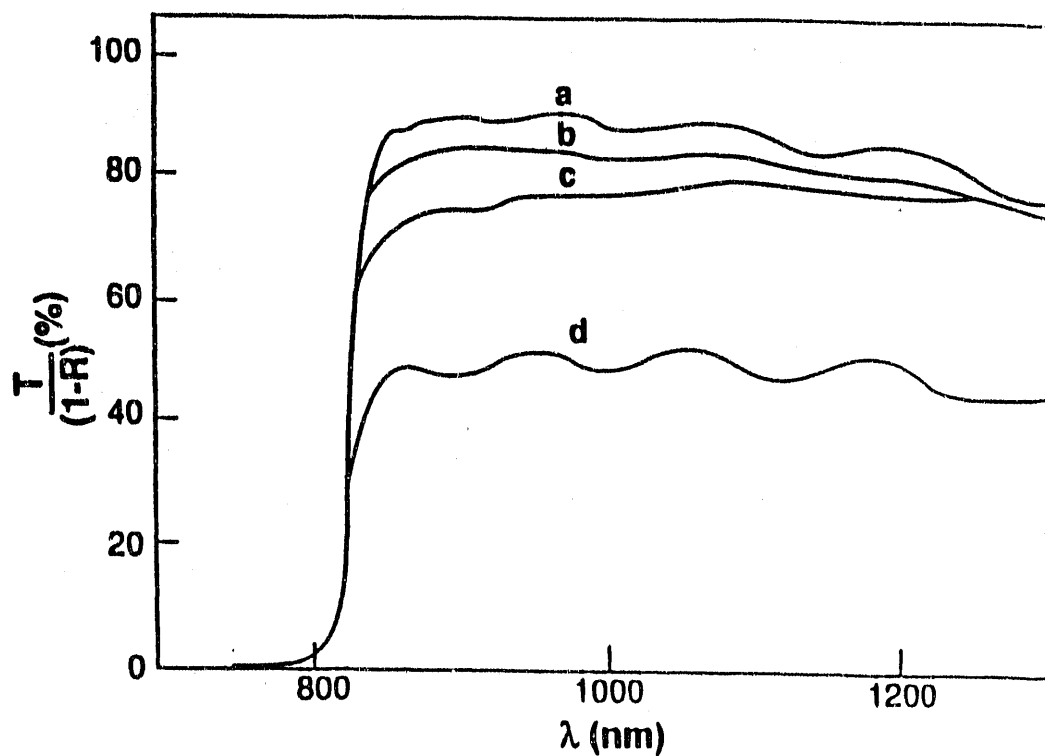
a) Bare CdS/CdTe
b) CdS/CdTe/ZnTe   120 minutes
c) CdS/CdTe/ZnTe:Cu
   (10^{-5} M Cu^{+2} in bath)   120 minutes
d) CdS/CdTe/ZnTe:Cu
   (10^{-4} M Cu^{+2} in bath)   90 minutes

Figure 11. Normalized transmission for 200 nm thick films deposited with different Cu concentrations: a) bare CdTe/CdS; b) undoped ZnTe on CdTe/CdS; c) ZnTe:Cu/CdS for [Cu] = 10^{-5} M; d) ZnTe:Cu/CdTe/CdS for [Cu] = 10^{-4} M in bath.

1) increasing [Cu] increases deposition current density.

2) a bare ITO/CdS/CdTe film has 80% normalized optical transmission at 900 nm. The Cu content in the film reduces this, in proportion to the concentration taken in the bath.

3) at [Cu] greater than 10^{-3}, Cu_2Te is preferentially deposited, with no Zn detected.

4) Relative surface EDS measurements are consistent with XRD and T/(1-R).

2.4 CdS/CdTe DEVICES WITH ZnTe:Cu CONTACTS

2.4.1 Device Uniformity Issues

For solar cell fabrication, the ITO/CdS/CdTe or SnO_2/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, as described elsewhere (8). A mild 0.01% Br_2-CH_3OH etch for 5 seconds was then used to remove any surface residue resulting from the heat treatment. This is an important step in obtaining spatially visually-uniform deposits, as ZnTe did not grow on unetched CdTe surfaces. After the etch, the samples were rinsed in deionized water. Normally, after the etch, the water was observed to bead up, not wet, the CdTe surface.

A Cu-doped ZnTe film, from 50 to 100 nm thick, was then galvanically deposited. A robust contact, either Cu/Au, Au, Ni, or ITO, was deposited onto the ZnTe:Cu to complete the solar cells. The cell performance was optimized by air heat treatments at 150°C to 180°C. The performance of cells with different contacts to ZnTe:Cu, optimized for 60 minutes at 150°C are shown in Table 7. The cells with low FF have large slope at V_{oc}, dV/dJ, which is indicative of a high series resistance, possibly due to slightly more resistive ZnTe:Cu.

Table 7. Device parameters for CdS/CdTe/ZnTe:Cu Cells Using ITO/Ni; Cu/Au, and Ni robust contacts measured under ELH illumination, normalized to 100 mW/cm^2 at 32°C.

Sample	Contact	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	dV/dJ
40694.23	ITO/Ni	766	17.9	54.6	11.2
40691.13		709	16.3	68.3	5.3
40690.232	Cu/Au	754	17.4	60.5	7.7
40690.231		703	16.8	69.0	3.9
40690.221	Ni	616	15.2	74.8	4.0

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While outstanding single parameters were obtained on a few cells, the process in general suffered from non-uniformity and low yield. A high percentage of shunted or shorted devices typically occurred.

A series of depositions were performed on substrates from a single CdTe/CdS deposition to compare the yield, defined as the number of non-shunted devices, and overall performance of devices using ZnTe:Cu with Cu/Au contacts. Three ZnTe:Cu deposition permutations were studied and the results are listed in Table 8: 1) Vertical versus horizontal deposition orientation; 2) ZnTe:Cu deposition time - 10, 20 and 30 minutes (150, 300, and 600 Å thick ZnTe:Cu layers expected); 3) CdTe surface preparation prior to deposition - the standard 0.01% Br_2-CH_3OH treatment versus the same plus a Dichrol dip and 5 minute hydrazine treatment (BDH).

Table 8. Yield, best device parameters achieved, and light-to-dark diode crossover (LDX) for CdS/CdTe/ZnTe:Cu/Cu/Au devices fabricated using the standard processing steps but with variations of the ZnTe:Cu deposition and surface preparation. All samples from 40714 and J_{sc} measured in ELH but normalized to 100 mW/cm^2 at 32°C.

Sample	Prep	Orientation	Depo Time	Yield	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	LDX?
11	H_2O	No ZnTe	-	12/12	667	17.8	62.6	N
12	Br	Vertical	30'	5/9	679	17.7	57.6	Y
21	Br	Horizontal	30'	7/8	569	17.2	55.9	Y
22	Br	Horizontal	20'	8/8	627	16.5	59.2	Y
31	BDH	Horizontal	20'	8/9	644	17.7	59.3	N
23	Br	Horizontal	10'	5/8	607	16.3	56.8	Y

This experiment showed that, with the horizontal orientation and the $CuSO_4$ bath chemistry, the yield was excellent for the 20 minute and 30 minute depositions. All the cells suffered from 'soft' diodes characterized by low V_{oc} and FF, including the control piece, which had no ZnTe.

A key process modification improved the uniformity and yield. In other work (9) we have shown that CdTe cell performance is sensitive to moisture exposure during processing. Since the ZnTe contact is deposited in aqueous solution, we implemented a drying step prior to metallization in H_2-Ar at 180°C for 60 minutes. The results were dramatic as shown in Table 9 for devices with 0.5 μm thick CdS.

Table 9. Effect of heat treatment on CdS/CdTe/ZnTe:Cu/Cu/Au cells. Tested under ELH illumination, normalized to 100 mW/cm^2 at 32°C.

Piece	180°C, H$_2$-Ar HT	Yield	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
40724.13	after Cu/Au	4/8	645	17.1	54	6.0
40724.21	before Cu/Au	8/8	771	17.0	67	8.8

The V_{oc} of the 8 cells on the .21 piece, receiving the drying heat treatment prior to Cu/Au metallization, were very tightly distributed, ranging from 761 to 771 mV. The FF on this piece ranged from 60% to 67%. Efficiencies of 10% would have been achieved with thinner CdS due to higher J_{sc}.

Using pieces from the same CdS/CdTe deposition we revisited the choice of robust contact metal and compared Ni and Au to the standard Cu/Au we have employed throughout the work. The sample was dried as above prior to metallization. Table 10 lists the results for the best device on each piece, both after initial testing and after an air heat treatment for 30 minutes at 190°C.

Table 10. Device parameters for CdS/CdTe Cells using ZnTe:Cu/Ni, ZnTe:Cu/Au, and Cu/Au robust contacts with drying heat treatment prior to metallization. Measured under ELH illumination, normalized to 100 mW/cm^2 at 32°C.

Piece	ZnTe:Cu	Metal	Yield	Test	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
40724.31	YES	Ni	6/8	Init	717	16.6	70	8.3
				HT	676	16.6	67	7.5
40724.32	YES	Au	6/8	Init	565	16.7	57	5.4
				HT	770	16.8	68	8.8
40724.11	NO	Cu/Au	8/8	Init	726	17.5	71	9.1
				HT	775	17.0	67	8.8

The results of Tables 9 and 10 show that FF of near 70% are possible with ZnTe:Cu and Ni, Au, or Cu/Au and that samples with different robust contacts respond differently to post contacting heat treatment, unlike the bare Cu/Au contact which always improves with the post contacting heat treatment.

Processing steps found to influence spatial appearance of the ZnTe layer and device performance uniformity are summarized below:

1. Surface preparation prior to ZnTe:Cu deposition, including $CdCl_2$ heat treatment of CdTe and etching of CdTe surface.

2. CdS/CdTe orientation and electrical contact geometry used during ZnTe:Cu deposition.

3. Use of $CuSO_4$ rather than $CuCl_2$ (see Section 2.2.3).

4. Drying of CdS/CdTe/ZnTe:Cu structure prior to metallization.

Other processing parameters were evaluated with regard to deposition chemistry and uniformity but produced minor differences:

1. Stirring of the bath during ZnTe:Cu deposition increased the deposition current but produced visually non-uniform deposits.

2. All-sulfate bath chemistry produced more visually uniform deposits than those made in $ZnCl_2$ with $CuSO_4$. Very high device yield and performance (FF > 70% and V_{oc} > 700 mV) has been obtained on devices having ZnTe:Cu deposited in all-sulfate bath and mixed chloride-sulfate bath.

3. Choice of temperature from 50°C to 90°C had a slight influence on deposition current. XRD spectra of one film deposited at 90°C showed sharper peaks, indicative of larger grain size. No comparison was made of devices with ZnTe:Cu deposited at temperatures other than 60°C.

2.4.2 Contact Property Issues

We identified two issues which influence the contact behavior of the ZnTe:Cu in devices: CdTe surface preparation and Cu content in the ZnTe film. Because both issues involve interaction with CdTe, they were studied in device configurations.

Most of the devices discussed above exhibited varying degrees of blocking behavior in the forward bias portion of their light I-V curves and crossover between light and dark curves. Figures 12 and 13 show the I-V curves for samples with and without light-to-dark diode crossover. The sample without the crossover had BDH etching of the CdTe prior to ZnTe:Cu deposition. The sample with crossover had the standard Br_2CH_3OH etch. A simila comparison on cells with Cu/Au contacts resulted in higher FF (lower R_{voc}) on cells with the BDH treatment.

We also considered the dual role of the ZnTe:Cu as a source of Cu doping for CdTe and as a low resistance contact material. This was studied by depositing ZnTe:Cu films from baths containing different quantities of Cu ions. The nominal Cu concentration used, based on our first year of study, was 10^{-4} M. This was chosen based on a comparison of devices made using Cu concentrations of 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} M. Devices having ZnTe:Cu with [Cu] = 10^{-3} M were

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cell 40714 - 23 - 7 area .2

date	$\frac{mA}{in}$	pen	Int.	temp	comment
JUN 15	2	X	97.5	32°C	init

CURRENT

VOLTAGE

-1.6   -1.2   -0.8   -0.4   0.4   0.8
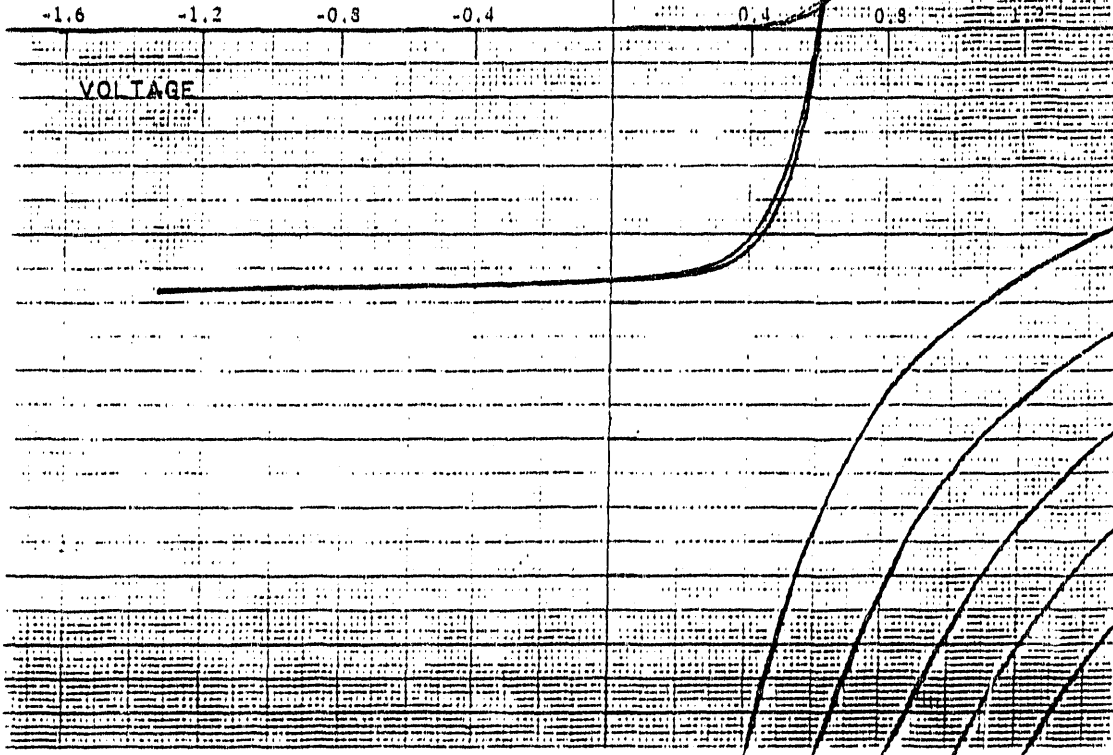
Figure 12. I-V curve for 40714.22 showing light-to-dark crossover. The sample had the standard Br_2-CH_3OH etch prior to ZnTe deposition.

Institute of Energy Conversion

cell 40714 - 31 - 8   area 2

date	$\frac{mA}{in}$	pen	Int.	temp	comment
JUN 21	2	X	87.5	32°C	init

CURRENT

VOLTAGE

-1.6   -1.2   -0.8   -0.4   0.4   0.8
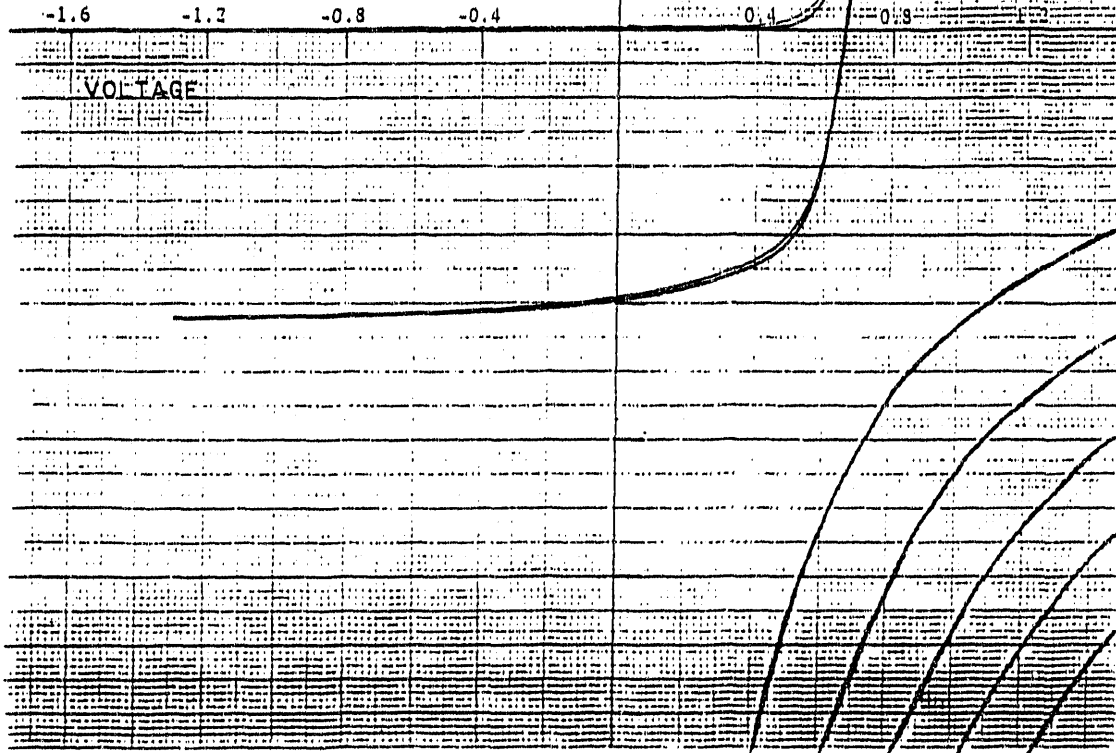
Figure 13.   I-V curve for 40714.31 showing no pronounced light-to-dark crossover.   The sample received a BDH treatment prior to ZnTe.

severely shunted, while devices with ZnTe:Cu with [Cu] = 10^{-5} and 10^{-6} M had low FF and high series resistance. A narrower range, namely 1,2,3, and 4×10^{-4} M of Cu in the ZnTe:Cu bath was investigated to identify an optimum concentration. Table 11 lists the best result obtained at various Cu concentrations. For these samples, the current was monitored and the deposition time was adjusted to give the same total charge through the galvanic cell, resulting in ZnTe:Cu deposits ~500 Å thick. This is to compensate for the increased deposition rate caused by the addition of Cu (see Table 6). Figure 14 shows the efficiency versus the Cu concentration used.

High efficiency was obtained for ZnTe:Cu baths with Cu concentrations around 2×10^{-4} M. In the figure we identify four regions of cell behavior. The rapid fall-off beyond 3×10^{-4} M is due to severe shunting, which may be due to formation of Cu_2Te, which we believe forms along grain boundaries and produces the shorting behavior. This was previously encountered when we deliberately formed Cu_2Te contacts to CdTe as part of other work (10).

The similarity of J-V behavior for cells with high Cu^{+2} concentration to that obtained with devices having Cu_2Te contacts studied previously implies that Cu^{+2} concentrations which give sufficient levels in ZnTe films to dope CdTe and to form low resistance contacts also result in formation of Cu_2Te. Thus the deposition of ZnTe:Cu occurs in competition with the Cu_2Te exchange reaction near the CdTe surface. At Cu^{+2} concentration of $>3\times10^{-4}$ M, the Cu_2Te reaction is favored over formation of ZnTe:Cu.

The device results obtained for 40730.21, having [Cu] = 2×10^{-4} M, are the best we have obtained using the galvanically deposited ZnTe:Cu contact. Future work should examine depositions with [Cu] in the range from 1 to 2×10^{-4} M to determine an optimum value. Also, the deposition method could be altered to restrict formation of Cu_2Te by depositing a thin undoped ZnTe layer onto CdTe, followed by a doped layer to provide Cu for CdTe doping and to minimize contact resistance.

2.5 SUMMARY AND FUTURE WORK

A process for the deposition of thin (<50 nm) ZnTe and Cu-doped ZnTe films suitable as transparent ohmic contacts for CdS/CdTe solar cells was developed. CdTe devices with FF>70% and η ~ 10% have been made using the ZnTe contact. Future work should focus on alternative methods of incorporating Cu into the ZnTe film to eliminate the possible formation of Cu_2Te during film growth.

Table 11. Best cell performance obtained as a function of [Cu] in ZnTe:Cu deposition. The devices had a drying heat treatment prior to metallization. Measured under ELH illumination, normalized to 100 mW/cm^2 at 32°C.

Device	[Cu] (M)	Depo Time (min)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
40719.22	10^{-6}	20.0	633	16.7	60.2	6.4
40719.21	10^{-5}	15.0	653	16.7	56.7	6.2
40725.31	1×10^{-4}	11.5	741	19.2	67.2	9.6
40730.21	2×10^{-4}	11.5	754	19.4	70.6	10.3
40730.22	3×10^{-4}	11.5	655	18.7	37.4	4.6*
40730.13	4×10^{-4}	10.0	347	17.7	32.8	2.0*

* J-V traces unstable
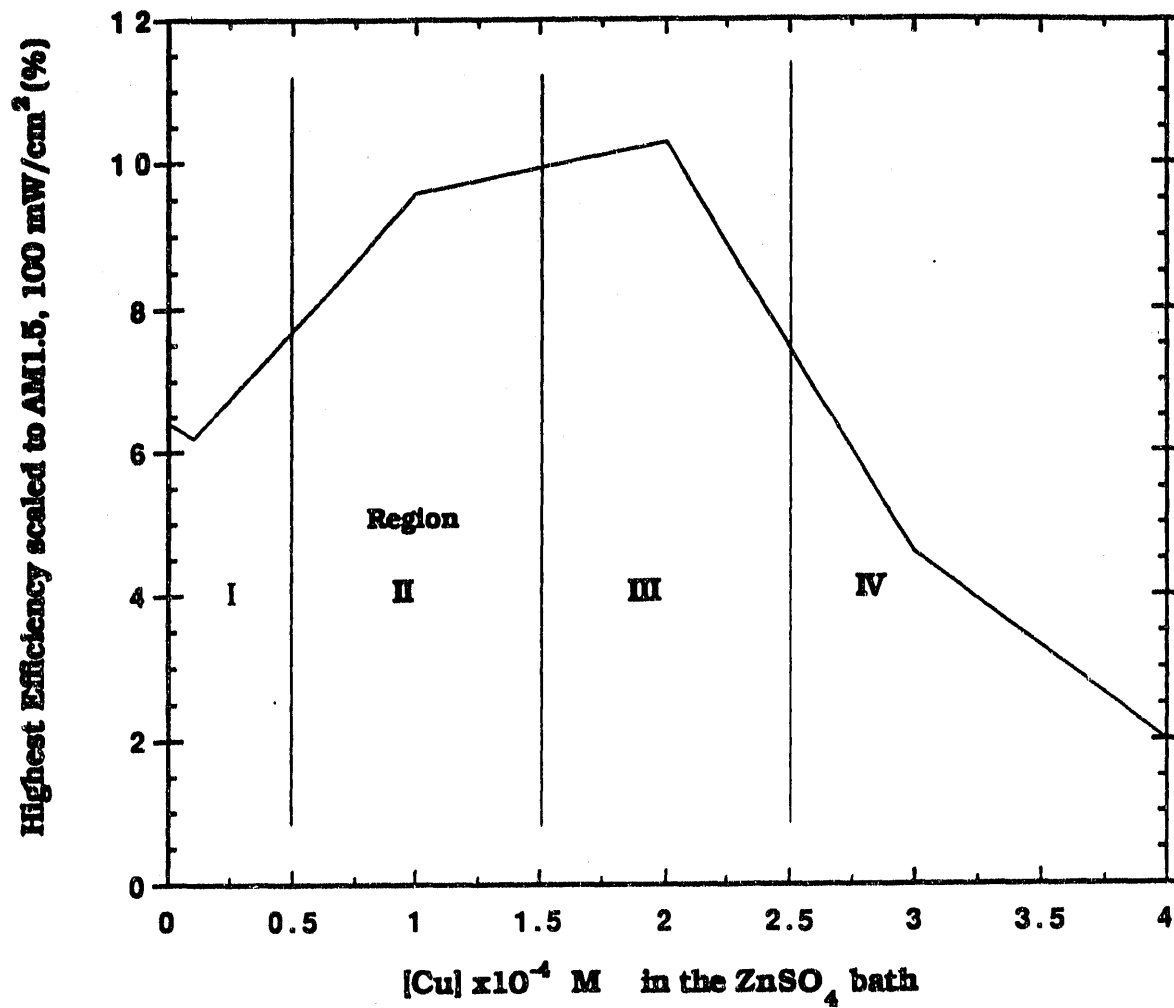
Figure 14. CdS/CdTe/ZnTe:Cu efficiency versus [Cu].

SECTION 3.0
GROWTH OF ZnSe AS A WINDOW LAYER FOR CuInSe$_2$

3.1 BACKGROUND

ZnSe is an alternative window layer material suitable for use in CuInSe$_2$ based solar cells. Like Cd$_{0.85}$Zn$_{0.15}$S films presently in use for some CuInSe$_2$ cells (11), it has a bandgap of ~2.7 eV, making it well-suited for transmission of the solar output to the CuInSe$_2$ layer. It also allows for the possibility of a Cd-free polycrystalline thin film solar cell. The primary difficulty associated with using ZnSe in thin film devices has been obtaining high conductivity films at low temperature on polycrystalline or amorphous substrates. We considered the deposition of ZnSe by solution growth and by electrochemical methods onto a variety of substrates, including CuInSe$_2$/Mo/glass.

3.2 RESULTS OF SOLUTION GROWTH EXPERIMENTS

Depositions were carried out in aqueous solutions of sodium seleno-sulfite and zinc chloride in a manner analogous to that described by Pramanik and Biswas (12). Variations in bath chemistry, temperature, pH and reaction time were investigated on either 7059 glass or CuInSe$_2$/Mo/glass substrates. This work is fully described in Appendix C. While ZnSe films were obtained in some cases, the methods explored were not reproducible. In particular, interactions between the CuInSe$_2$ and Mo with the solution need to be quantified.

3.3 RESULTS OF GALVANIC AND ELECTROCHEMICAL EXPERIMENTS

Galvanic depositions from an aqueous baths containing ZnCl$_2$ or Zn(C$_2$H$_3$O$_2$)$_2$ and SeO$_2$ were carried out. The pH of the bath was adjusted using dilute HCl. A conductive substrate, in most cases a 7059/Mo/CuInSe$_2$ sample, and a zinc electrode were externally short circuited to form an electrochemical cell. The Zn is electropositive and goes into solution as Zn^{+2} ions:

$$Zn \rightarrow Zn^{+2} + 2e^-$$
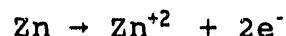
The Zn^{+2} and Se^{+4} ions are reduced at the surface of the sample, resulting in direct formation of ZnSe. The Zn electrode thus acts both as a source of electrons for the cathodic reaction and to replenish Zn^{+2} ions. The experimental parameters and conditions explored were:

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Zn salt	−	$ZnCl_2$, $Zn(C_2H_3O_2)_2$
Se source	−	SeO_2
[Zn salt]	−	0.1 − 1.0 M
[SeO_2]	−	10^{-2} − 10^{-4} M
pH	−	3.5 − 6.3
T_{soln}	−	40 − 80°C
t	−	0.5 − 3.5 hours
anode	−	Zn, Al
substrate	−	400 Å Mo, ITO, $CuInSe_2$

- platinum wire soldered to substrate for better contact to anode
- solution stirred and unstirred during deposition

From XRD measurements we confirmed that ZnSe was formed, however, in most cases elemental Se was present. To grow the ZnSe on $CuInSe_2$, it was necessary 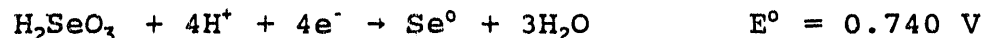to heat treat the $CuInSe_2$ at 200°C in air to reduce the resistivity of the $CuInSe_2$ film. The film growth appears to be limited by potential drops in the $CuInSe_2$ and subsequent growth of the ZnSe film. Films of greater than 50 nm have not been obtained, limiting the use of optical characterization. $CuInSe_2$ devices with the ZnSe/ZnO have been made but have had low voltages, < 300mV, poor FF~ 30% and J_{sc} of ~25 mA. The poor results could be explained by a discontinuous ZnSe film and/or a multi-phase film.

Attempts to empirically determine the optimum bath composition and deposition conditions from the above ranges listed was unsuccessful since continuous, single phase films of ZnSe were not reproducibly obtained.

Electrochemical depositions were thus carried out, since the applied voltage could be independently varied. Initial experimentation involved deposition from baths containing $ZnCl_2$ and H_2SeO_3, which is obtained by dissolving SeO_2 in water. The relevant redox reactions and standard potentials for deposition of Zn and Se are:

$$Zn^{2+} + 2e^- \rightarrow Zn^o \qquad\qquad E^o = -0.763 \text{ V}$$

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se^o + 3H_2O \qquad E^o = 0.740 \text{ V}$$

Since the standard potentials for reduction of Zn^{+2} and H_2SeO_3 differ by more than 1.5 volt, deposition of Se is generally favored.

The best result obtained on ITO/7059 glass by this method was an orange yellow film with an optical absorption edge near that expected for ZnSe. The solution contained 10 ml of 1M $ZnCl_2$ and 2 ml of 10^{-3}M SeO_2. The pH of the solution was 3-4 at 78°C. The applied voltage was −0.75 V with Pt as counter electrode and saturated Ag/AgCl as reference electrode. The solution was stirred during deposition with a magnetic stirrer. Periodic additions of

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1 ml of 10^{-3}M SeO$_2$ solution at 30-45 minute intervals were carried out to replenish Se. An orange yellow film gradually developed with time of deposition. The optical transmission of the film is shown in Figure 15. The absorption edge is located at slightly longer wavelengths than the bandgap of ZnSe (2.7 eV or 460 nm), suggesting that the film may not be stoichiometric ZnSe and contains excess Se.

We next evaluated electrodeposition of ZnSe onto Mo/7059 and CuInSe$_2$/Mo/7059 substrates. Two bath chemistries, based on Na$_2$SeO$_3$ and Na$_2$SeSO$_3$, were selected for study. The electromotive potential for deposition was obtained either in a galvanic cell (two electrode configuration) or in a cell with externally applied voltage (three electrode configuration). The results obtained are summarized below according to bath chemistry.

Sodium Selenite Bath

Ten ml ZnCl$_2$ (1 M) and 2 ml Na$_2$SeO$_3$ (10^{-3} M) solutions were taken in 100 ml total volume at pH = 3.2 and temperatures from 70 to 80°C. For galvanic deposition, a Zn anode was employed. Orange-yellow deposits were obtained on Mo/7059 substrates, but significant gas evolution occurred during deposition, resulting in non-uniform deposits and pitting of the Mo substrate. Different anodes were used to change the deposition potential: Al anodes increased the potential difference, giving enhanced gas evolution while Cd anodes decreased the potential difference, giving lower current densities and non-uniform deposits, probably mostly Se. Consequently, no galvanic depositions were consequently attempted onto CuInSe$_2$/Mo/7059 substrates.

Potentiostatic depositions with this bath were performed using a Pt counter electrode, an Ag/AgCl reference electrode, and Mo/7059 working electrodes. At -0.9 V, gas evolution prevented deposition of uniform films. At -0.75V, however, orange films were obtained after only 20 minutes, at a current density of ~0.1 mA/cm^2. EDS showed these films to be composed of 50% Zn and 50% Se, but depositions for longer periods exhibited slow gas evolution and pitting. At more positive voltages than - 0.75V, the current density was extremely low, and Se was preferentially deposited.

Sodium Seleno-Sulfate Bath

In sequence, 2.5 ml ZnCl$_2$ (1 M), 10 ml TEA (99%), 2.5 ml NaOH (7.5 M, 12 ml NH$_4$OH (30%), 7 ml N$_2$H$_4$ (9.9%), and 1 ml Na$_2$SeSO$_3$ (0.4 M) were taken in 60 ml total volume at pH = 12 to 13 and temperature from 65 to 70°C. This bath chemistry is in accordance with reference (12), for solution growth technique of ZnSe, but in this case the Na$_2$SeSO$_3$ was taken at one sixth the reported concentration. For galvanic deposition, a Zn anode was employed.

Z: ZNSE7ET; absc 1400.0- 400.0; pts 1001; int 1.00; ord 0.4530-80.726; T
inf: 08:27:49   91/05/17 $V_{dep} = -750mV$
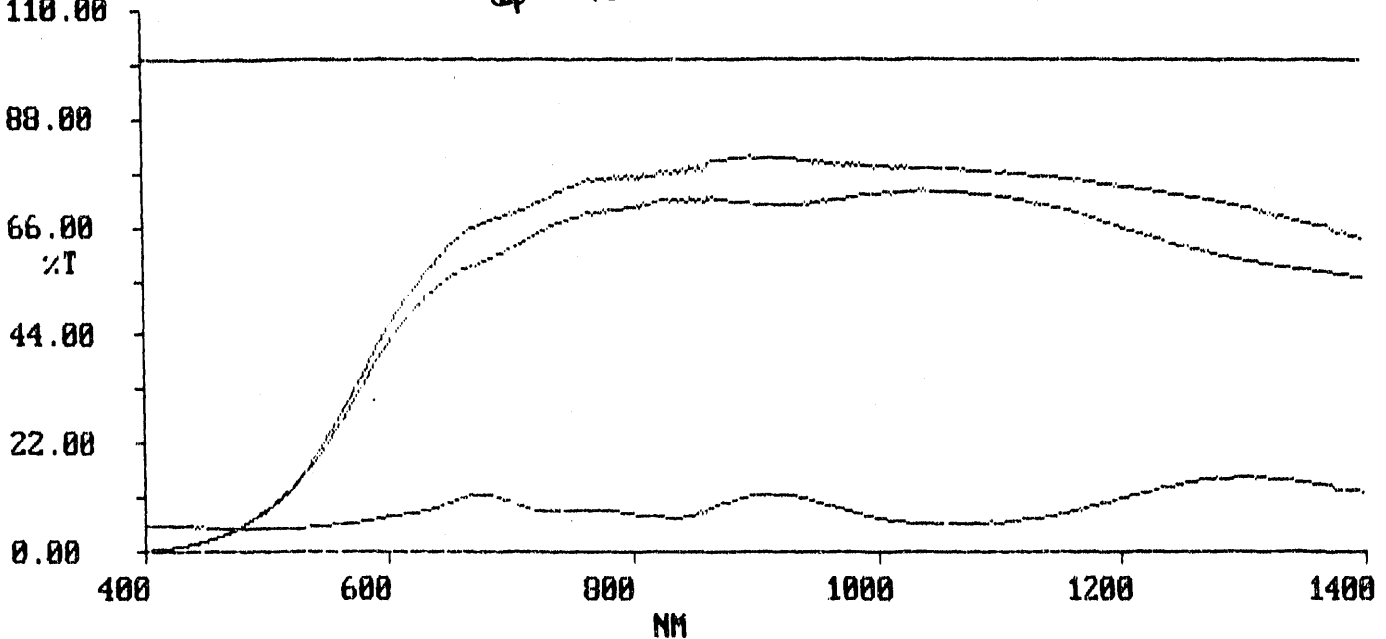
Figure 15. Normalized optical transmission of a Zn,Se deposit obtained on ITO/7059 substrate by electrochemical deposition at -0.75V.

As with the sodium selenite bath, orange-yellow deposits were obtained on Mo/7059 substrates, but significant gas evolution occurred during deposition, again resulting in pitting of the Mo and in non-uniform deposits.

Potentiostatic depositions were carried out as with the sodium selenite bath. This time, however, depositions at -0.9V for about 2 hours yielded yellow films on the Mo/7059 substrates. The current density tended to drop rapidly in the first two to three minutes of deposition, then gradually dropped to a steady state value of about 35 $\mu A/cm^2$. At -0.75 V, the current density was very low and very little deposit was obtained. Depositions were thus carried out on $CuInSe_2$/Mo/7059 substrates at -0.9V. On the $CuInSe_2$ substrates the current density continuously dropped to zero during the deposition with time. Depositions were carried until zero current was reached on each sample.

Devices were completed by sputtering ZnO contacts and Ni bus bars. The best cell obtained so far had low V_{oc} and was slightly shunted: $V_{oc} = 0.113$ V, $J_{sc} = 27.5$ mA/cm^2, and FF = 33.6%. As with previous devices, the poor performance was probably a result of non-uniform electrochemical film growth.

3.4 SUMMARY AND FUTURE WORK

Future study of electro- or galvanic deposition of ZnSe should involve investigation of alternate Se precursors that are expected to narrow the gap between Zn and Se deposition voltages. Preliminary electrochemical considerations indicate that promising seleno-sulfur compounds should be investigated.

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SECTION 4.0
OTHER GALVANIC DEPOSITIONS

Approximately 50 high quality CdS thin films were deposited onto SnO_2 substrates by the galvanic method. The structural and optical properties of the films were characterized and are comparable to films deposited by vacuum evaporation   To demonstrate the potential of films made by this simple technique CdS/CdTe devices were fabricated using evaporated CdTe.

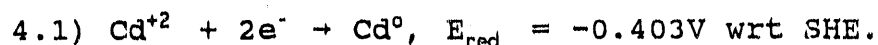The bath chemistry chosen was similar to that of Basol (13) for cathodic deposition of CdS at low pH, using $CdCl_2$ and $Na_2S_2O_3$. The Cd is reduced from Cd^{+2} ions by

4.1) $Cd^{+2} + 2e^- \rightarrow Cd^0$, $E_{red} = -0.403V$ wrt SHE.

An issue with electrochemically describing such a bath was the route by which S is reduced. Acidification of sodium thiosulfate solution produces unstable thiosulfuric acid which spontaneously decomposes into sulfurous acid and sulfur, which precipitates (14).

4.2) $Na_2S_2O_3 + H_2O + 2H^+$ -----→ $2 Na^+ + H_2S_2O_3 + H_2O$

4.3) $H_2S_2O_3$ -----→ $H_2SO_3 + S^0$

The sulfurous acid can also be electrochemically reduced to S (15):

4.4) $SO_3 + 3 H_2O + 4 e^-$ -----→ $S^0 + 6 OH$, $E_{red} = -0.66V$ wrt SHE
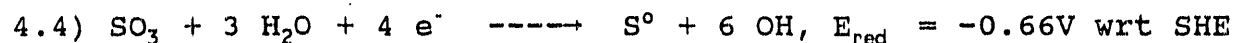
The CdS depositions were carried in an aqueous bath of 0.1 M $CdCl_2$ and 0.01 to 0.05 M of $Na_2S_2O_3$. The pH was adjusted to 3 - 4 with HCl at a temperature of 85°C. The total volume was 200 ml and the beaker was heated in a water jacket on a hot plate. The solution was stirred during deposition using a stirring rod, set to approximately 200 rpm. The SnO_2/glass substrate was soldered to a length of Pt wire which was spot welded to a strip of Cd foil.

Galvanic deposition was initiated by simultaneous immersion of the substrate and foil into the electrolyte, whereupon the substrate and foil become cathode and anode, respectively. Electrochemical information on charge transfer and deposition potential were obtained by measuring the current during the deposition and the voltage between anode and cathode at the start and end of the deposition.

The deposition process was found to be controlled by the reduction rate of Cd. The rate of galvanic deposition was determined primarily by Cd ion concentration and to a lesser degree by temperature and agitation. The deposition rate was constant for films up to 280 nm thick. The galvanically deposited CdS films have similar properties to evaporated CdS films. The quality of

galvanically deposited CdS was demonstrated by fabrication of CdTe/CdS devices with AM 1.5 conversion efficiencies over 8%.

A minor effort was aimed at depositing CdTe by the galvanic method, as had been reported by Bhattacharya, et al. (4). Approximately 20 CdTe films were deposited onto both galvanically and evaporated CdS films. Several devices were processed using galvanically deposited CdTe, achieving limited performance. In one case, an all-galvanic structure was fabricated, consisting of galvanically deposited CdS, CdTe, and ZnTe:Cu. This device had V_{oc} = 500 mV, J_{sc} = 9.6 mA/cm^2, and FF = 40%.

SECTION 5.0
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SECTION 6.0
ABSTRACT

A process for the deposition of thin (<50 nm) ZnTe and Cu-doped ZnTe films suitable as transparent ohmic contacts for CdS/CdTe solar cells was developed. Galvanic cells were constructed in an aqueous solution with Zn foil used as an anode and a glass/ITO/CdS/CdTe substrate acting as a cathode. The anode and cathode were externally short-circuited. The optimal solution in which ZnTe was formed consisted of 0.1 M Cd salt and 10^{-4} M TeO_2; a Cu salt in the range of 10^{-4} to 10^{-5} M and triethanolmaine were added for the formation of Cu-doped ZnTe films. Temperature and pH were controlled, and deposition times of 10 to 30 minutes resulted in film thicknesses of 30 to 150 nm. The effects of agitation, temperature, and Cu doping on the ZnTe films were determined. Structural, optical and electrical film properties were characterized and CdS/CdTe/ZnTe devices were fabricated and evaluated. The development of this method and optimization of key processing steps resulted in devices with FF>70% and $\eta \sim 10\%$. The focus of future work should include the application of the investigated deposition methods to the formation of other II-VI compounds for use in polycrystalline thin film devices.

SECTION 7.0

APPENDIX A

A New Method for Forming ZnTe Contacts for CdTe Cells

A NEW METHOD FOR FORMING ZnTe CONTACTS FOR CdTe CELLS

Anup Mondal, Robert W. Birkmire, Brian E. McCandless

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19716

ABSTRACT

An electrochemical technique (galvanic) has been developed for directly depositing ZnTe films doped with Cu onto evaporated CdTe/CdS/ITO/Glass substrates to form semi-transparent p^+ contact to the CdTe. The CdTe/CdS/ITO/Glass substrates were placed in a solution containing $ZnCl_2$ and dissolved TeO_2 and were short circuited externally to a Zn electrode. Uniform, single phase ZnTe films were obtained for specific pH, temperature and concentration regimes of the reacting ions. Copper doping of the ZnTe films was achieved by adding to the solution appropriate amount of Cu^{+2} ions complexed with triethanolamine (TEA). The results of ZnTe:Cu/CdTe/CdS solar cells fabricated using this method are discussed.

INTRODUCTION

CdTe/CdS thin film solar cells are a viable candidate for commercial power generation applications. Small area devices ($\sim 1cm^2$) have been made by a variety of techniques with efficiencies over 12%, of which several methods are believed to be scalable for large area cell production (1,2). Submodules with efficiencies near 10% have also been reported (2,3). Further, CdTe based cells are candidate wide bandgap cells for tandem cell structures using $CuInSe_2$ based cells. One approach for fabricating CdTe thin film cells uses a n-i-p cell structure (4) which takes advantage of the intrinsic conductivity of CdTe and solves the contact problem to the CdTe by using a p^+ Cu-doped ZnTe layer (ZnTe:Cu) deposited by vacuum evaporation.

In this paper we describe an electrochemical method for depositing thin Cu-doped ZnTe films on CdTe/CdS/ITO substrates. The approach is similar to that used by Bhattacharya et al. (5) and Murali et al. (6) for depositing CdTe

and CdSe films respectively, where the substrate was short circuited externally to an easily oxidizable electrode (e.g. Al or Cd). This method is simple and is carried out without potentiostatic or galvanostatic control. In this paper we describe the process for electrochemical deposition of these ZnTe:Cu films to make p^+ contact to CdTe and report fabrication of solar cells with efficiencies near 10%.
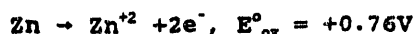
ZnTe FILM GROWTH

ZnTe films were deposited on CdTe/CdS/ITO/glass substrates suitable for solar cells and were prepared as follows: 1) CdS and CdTe were thermally evaporated on to ITO/glass substrates; 2) the samples were coated with $CdCl_2$ and heat treated at 400°C for 30 minutes in air; and 3) the surface of the CdTe was etched for 5 sec in Br_2-CH_3OH solution. The ZnTe:Cu was then deposited as a contact to CdTe. To complete the solar cell a metal contact was deposited on the ZnTe and the cell performance optimized with air heat treatment. A detailed description of the cell fabrication process is presented in reference (7).

The ZnTe films were deposited galvanically, a special case of electrochemical deposition, from an unstirred aqueous bath containing 0.1 M/l $ZnCl_2$ and about 10^{-4} M/l TeO_2. The TeO_2 was first dissolved with NaOH and then pH was adjusted using HCl. Controlling the bath pH between 3 and 4 and temperature between 50°C and 80°C was necessary to deposit uniform, adherent, single phase ZnTe films. Doping of the ZnTe films was achieved by adding a Cu^{+2} complex to the bath. For this, a few drops of TEA were added to a $CuSO_4$ solution to form the complex which was then introduced into the main bath. The galvanic cell was then constructed by dipping in the bath a glass/ITO/CdS/CdTe substrate and a zinc foil, which were externally short

circuited by a wire. In the solution the zinc, being electro-positive, acts as the anode, while the substrate becomes the cathode. The electrochemical reaction is driven by the potential difference between the electrodes. The zinc acts as both a source of electrons for the cathodic reaction and a source of Zn^{+2} ions. The reactions leading to the formation of ZnTe:Cu are most likely:

Anode Reaction

$$Zn \rightarrow Zn^{+2} + 2e^-, \quad E^{\circ}_{ox} = +0.76V$$

Cathode Reaction

$$Zn^{+2} + 2e^- \rightarrow Zn^{\circ}, \quad E^{\circ}_{red} = -0.76V$$

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te^{\circ} + 2H_2O, \quad E^{\circ}_{red} = +0.56V$$

$$Zn^{\circ} + Te^{\circ} \rightarrow ZnTe$$

$$Cu(TEA)_n^{+2} + 2e^- \rightarrow Cu^{\circ} + nTEA$$
$$n=1,2,...$$
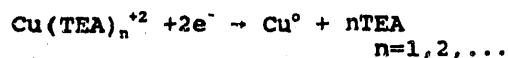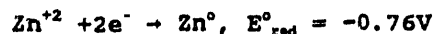
Since Te has a greater positive reduction potential than Zn, it tends to deposit faster from its ions in solution than Zn. Therefore, single phase ZnTe films could only be grown at very low tellurium ion concentration, resulting in a mass transfer controlled reaction. Similar results have been observed for the electrodeposition of CdTe films [8]. The addition of Cu to the ZnTe films also required low Cu ion concentration due to its positive reduction potential ($Cu^{2+} \rightarrow Cu^{\circ}$, $E^{\circ}_{red}=0.337V$). Additionally, the Cu^{+2} ions were complexed with TEA to inhibit the reduction rate.

In Figure 1 we present a plot of ZnTe deposition current density with time, having 1) no Cu, 2) 10^{-5}M/l Cu^{+2} 3) 10^{-4}M/l Cu^{+2} ions in solution. A nearly constant current density is obtained after about 4 minutes which is proportional to the growth rate. The growth rate gradually decreases with the depletion of Te ions in solution. The current and growth rate increase with the addition of Cu^{+2} to the solution. We have also found that the current density and growth rate are dependent on:

1) pH – At pH>4, the solubility of TeO_2 decreases reaching a minimum about pH 5-6 [9], resulting in a precipitation of the TeO_2 from the solution. At pH ≤ 2 elemental Te is preferentially deposited.
2) Temperature – the growth rate increases with the bath temperature.
3) Stirring – the growth rate was

increased by ~6 times the unstirred rate by use of a magnetic stirring rod.
4) Te ion concentration – increasing the Te ion concentration in solution also increases the current density and growth rate. The dissolution of TeO_2 in aqueous solution is itself limited by pH and temperature which has also been observed earlier by Pourbaix [9]. However, increasing the current density or the growth rate does not necessarily yield a better ZnTe film. In fact, non-uniform and loosely adherent deposits occur at higher current densities.

ZnTe:Cu Characterization

From x-ray diffraction (XRD) analysis of ~300 nm thick films, the conditions for single phase films were evaluated. These conditions are: 0.1 M/l $ZnCl_2$, 10^{-4} M/l TeO_2 with a total volume of 100 ml, with the pH adjusted to ~3.1 at $57\pm2^{\circ}C$. Figure 2a is an XRD scan of a film obtained under these conditions. The sharp peak (111) at $2\theta = 25.15^{\circ}$ establishes the formation of a highly oriented cubic phase ZnTe film. Fig. 2b is that of a film grown at pH~2, other conditions remaining same. No ZnTe peaks are detected, however, the peak at $2\theta = 27.63^{\circ}$ indicates the presence of free Te.

The normalized optical transmission of ~200 nm thick ZnTe films deposited on ITO/CdS/CdTe with different amounts of Cu in the bath is shown in Figure 3. Increasing the amount of Cu in the bath reduces the transmission which indicates an increase in the amount of Cu in the ZnTe film, for films of the same thickness. To make high efficiency cells, a Cu concentration of 10^{-4} M/l in the bath is necessary, but the total ZnTe thickness used is only 50-100 nm. In this case the transmission is about 60% at 900 nm. Use of ITO or ZnO in conjunction with the ZnTe:Cu will result in completed devices with 50 to 60% through-film transmission.

CdTe Solar Cells

Solar cells were fabricated by depositing 50-100 nm of ZnTe:Cu (from a bath containing 10^{-4} M/l of Cu^{+2}) and then evaporating a Cu/Au, Ni or ITO contact pad. The cells were then air heat treated at $150^{\circ}C$ for 1 hour [7] to optimize cell performance. Fig. 4 shows the AM 1.5 characteristics of a 7059 glass/ITO/CdS/CdTe/ZnTe:Cu solar cell with a Cu/Au contact. A cell area of 0.08 cm^2 yielded 8.7% efficiency with a 65.7% fill factor. Using ZnTe:Cu

contacts, we have fabricated devices having $V_{oc}>750$ mV, $J_{sc}>20.1$ mA/cm^2, and FF>74%.

CONCLUSION

Cu-doped ZnTe films, 50-300 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. A CdTe/CdS solar cell using the ZnTe:Cu as the primary contact to the CdTe achieved an efficiency of 8.7% with a FF>65%. The optical transmission of cells using ZnTe:Cu made in this manner is higher than for cells using evaporated ZnTe:Cu (10), making this an attractive contacting method for tandem cells and for use of optical back surface reflection enhancement techniques in conjunction with thin CdTe. Currently the properties of the ZnTe:Cu are being optimized for high efficiency solar cells and the stability of the contact is being evaluated.

ACKNOWLEDGEMENTS

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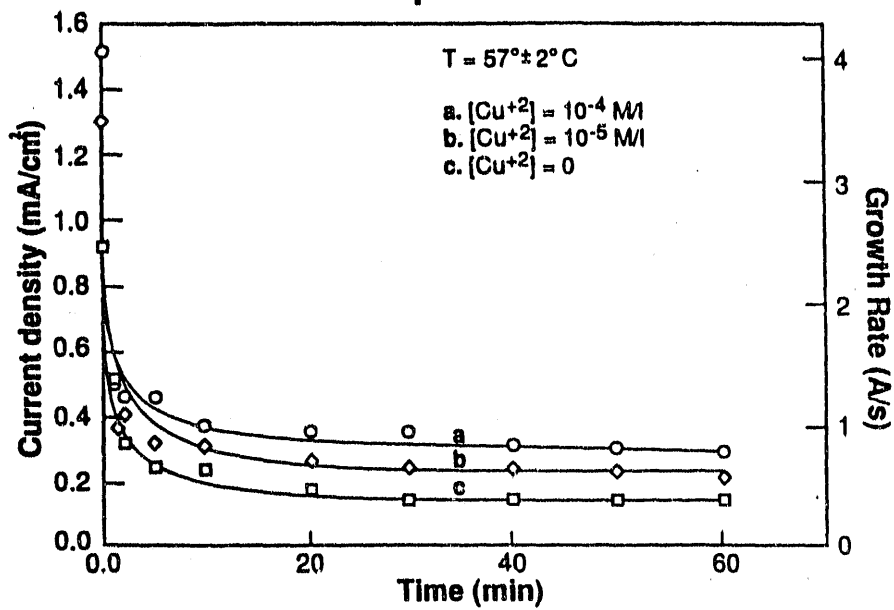
Figure 1. Deposition current density
and growth rate versus deposition time,
a) $[Cu^{+2}]=10^{-4}$ M/l, b) $[Cu^{+2}]=10^{-5}$ M/l, c
$[Cu^{+2}]=0$.
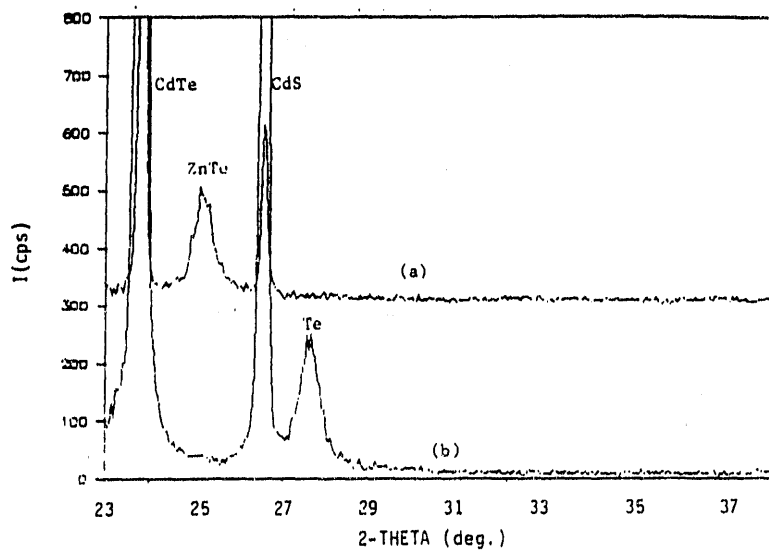
Figure 2. X-ray diffraction for 200-300
nm thick films on CdS/CdTe, a) film
deposited at pH~3.2 b) film deposited
at pH~2.

A-4
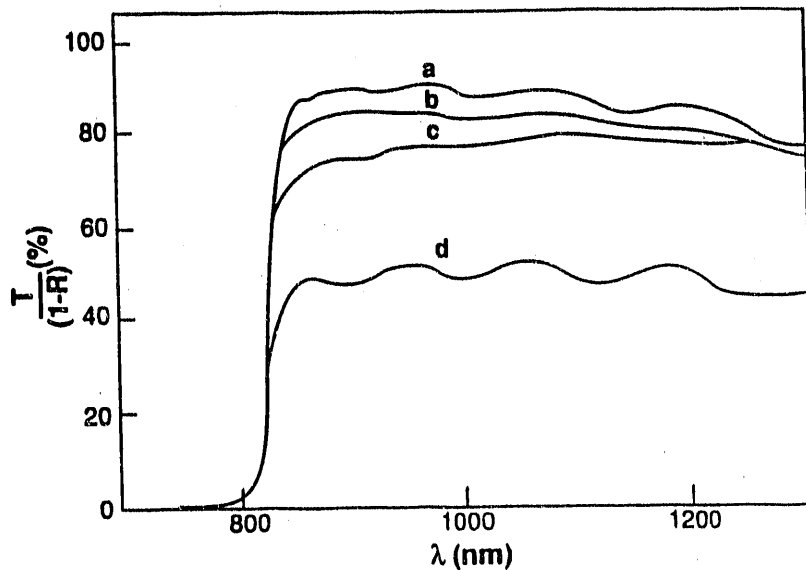
Figure 3. Normalized optical transmission through CdS/CdTe/ZnTe for ~200 nm thick ZnTe films.

ITO/CdS/CdTe/ZnTe:Cu

SERI AM 1.5 at 25C

Cell Area = 0.08 cm^2

V_{oc} = 705 mV

J_{sc} = 18.8 mA/cm^2

FF = 65.7%

Eff = 8.7%

Figure 4. I-V characteristics at AM 1.5 for an ITO/CdS/CdTe/ZnTe:Cu cell measured at SERI. The deposition bath contained $ZnCl_2=10^{-1}$ M/l, $TeO_2 = 10^{-4}$ M/l, $Cu(TEA)_n^{+2} = 10^{-4}$ M/l. The deposited ZnTe:Cu film was 50-100 nm thick.

SECTION 7.0

APPENDIX B

Electrochemical Deposition of Thin ZnTe Films as a Contact

for CdTe Solar Cells

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Electrochemical Deposition of Thin ZnTe Films as a Contact for CdTe Solar Cells

Anup Mondal, Brian E. McCandless, Robert W. Birkmire

Institute of Energy Conversion

University of Delaware

Newark, Delaware 19716-3820

ABSTRACT

ZnTe films doped with Cu were deposited by an electrochemical method for the first time directly onto CdTe/CdS/ITO/Glass subs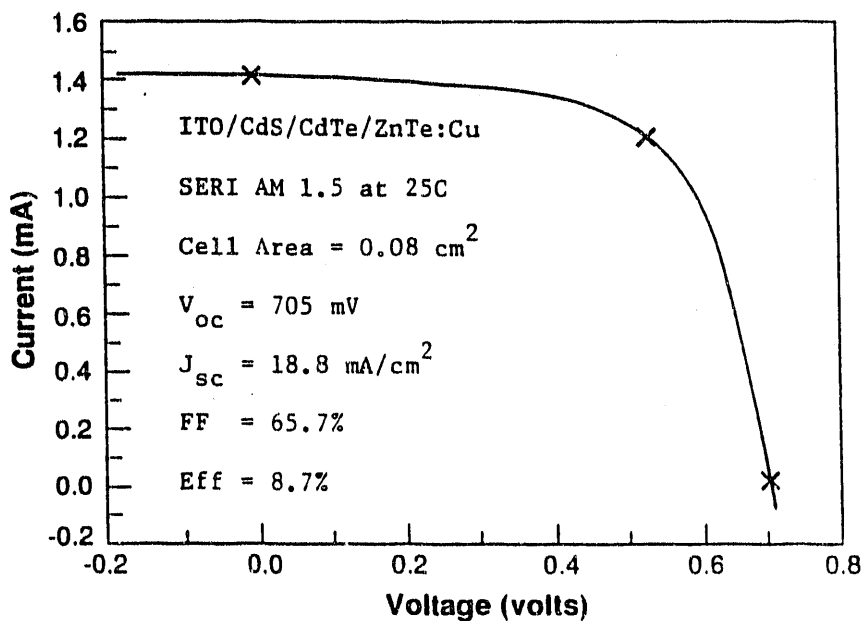trates to form a low resistance contact to CdTe. The depositions were carried out in an aqueous solution of $ZnCl_2$, TeO_2 and $CuCl_2$ or $CuSO_4$ in which the substrate was externally short circuited to a Zn counter electrode to complete an electrochemical cell. Single phase films 50nm to 300nm thick were obtained for specific pH and TeO_2 concentrations and bath temperature. Complexing the Cu^{++} with triethanolamine (TEA) allowed reproducible deposition of p-type ZnTe:Cu films. ZnTe:Cu/CdTe/CdS solar cells fabricated using this method have achieved AM 1.5 efficiencies of 8.7%.

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 (<100nm) 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.

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:

$$Zn \rightarrow Zn^{+2} + 2e^-, \quad E^o_{ox} = 0.76V,$$

where E^o_{ox} 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. Figure 1a shows the time dependence of the ZnTe film deposition onto a 7059/ITO/CdS/CdTe substrate. In this case, the pH was 3.1 to 3.3, the volume was

50 ml, the area of the substrate was -1.9 cm^2, and the Zn electrode area was 1.6 cm^2. A nearly linear growth rate was observed over about 1 hour of deposition after which it tended to saturate, suggesting exhaustion of the Te in the solution. On further addition of TeO_2 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 Figure 1a that a 0.2 μm 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 to 4 and the Te concentration was $10^{-4}M$ or less. To confirm this, 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 Figure 2. The sharp (111) peak at $2\theta=25.20°$ 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 TeO_2. Increasing the Te ion concentration in solution by adding TeO_2 is limited by the solubility of TeO_2 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 the Te in 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. Figure 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 to 3.3, a substrate area of ~2.3 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 in the 50 ml volume used.

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 seconds 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, from 50 to 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 100 mW/cm^2. 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 that no additional Cu is required to optimize the device. The J-V behavior of several ITO/CdS/CdTe/ZnTe:Cu cells with Cu/Au contacts were measured under AM 1.5 illumination at 25°C at the Solar Energy Research Institute (SERI). Figure 3 shows the light I-V curve for a cell with V_{oc}= 705 mV, J_{sc}= 18.8 mA/cm^2, FF = 65.7%, and efficiency = 8.7%. This device had a series resistance of only 4 Ω-cm^2 which implies low contact resistance. Figure 4 shows the quantum efficiency for this device measured at zero volts with 11.4 mA/cm^2 light bias.

To evaluate the cells for tandem cell application, the total transmission and reflection was measured for different deposition

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times, hence, thicknesses. The normalized transmission, T/(1-R),
is shown in Figure 5 for cells with the ZnTe:Cu grown for 15 min
and 60 min deposition times under the following conditions: 0.1M
$ZnCl_2$, 10^{-4} M TeO_2, 10^{-4} M $CuSO_4$ in TEA, pH ~ 3.2, T~60°C. The
ZnTe thickness for the 15 min. and 60 min. depositions was
estimated to be 80 nm and 180 nm, respectively. From Figure 5,
the cell with the ZnTe:Cu grown for 15 min has T/(1-R) ~70% at
900 nm. This can be compared to the results reported by Meyers
et al. [3] where the maximum T/(1-R) was ~30% for a cell with
~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.

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.

ACKNOWLEDGEMENTS

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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

Figure Captions

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

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 In_2O_3
(012) peak from the ITO substrate.

3 Current-voltage measurement of
ITO/CdS/CdTe/ZnTe:Cu/Cu/Au Cell #40691.231-1 at SERI
under SERI AM 1.5 global illumination at 25°C.

4 Quantum efficiency versus wavelength of
CdS/CdTe/ZnTe:Cu Cell #40691.231-1, measured at zero
volts with 11.4 mA/cm^2 light bias.

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

Electrochemical Deposition of Thin ZnTe Films as a Contact for CdTe Solar Cells
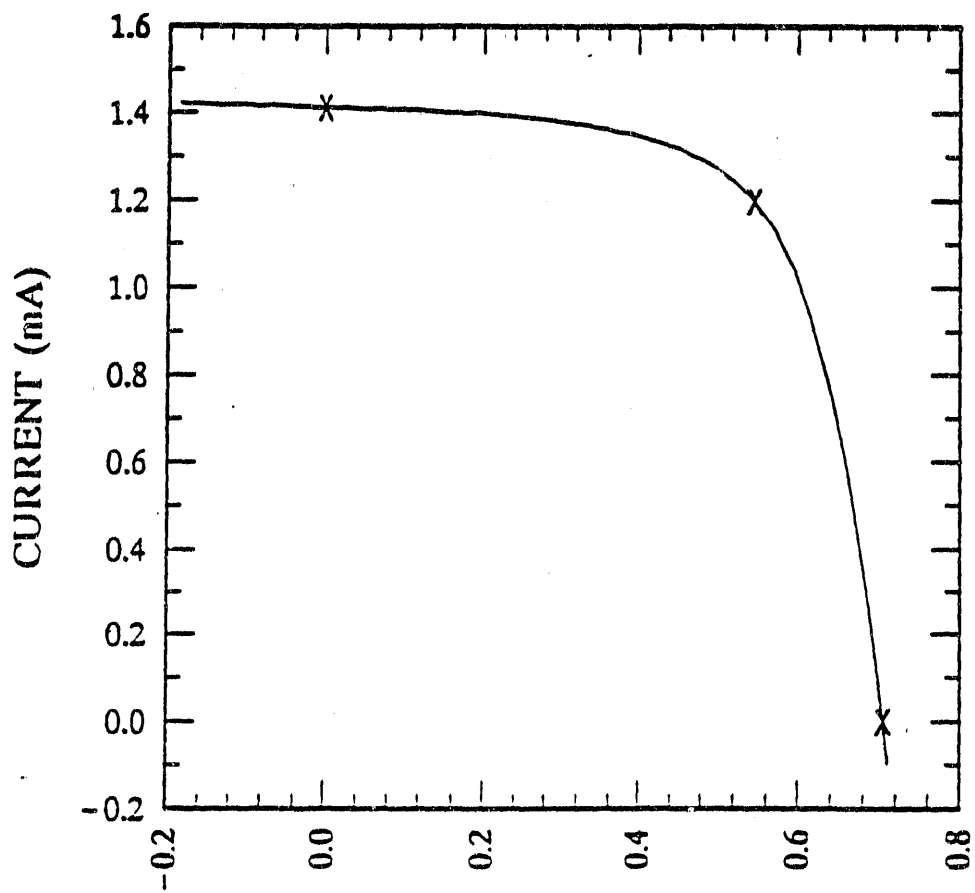**Anup Mondal, Brian E. McCandless, Robert W. Birkmire**
Figure 1
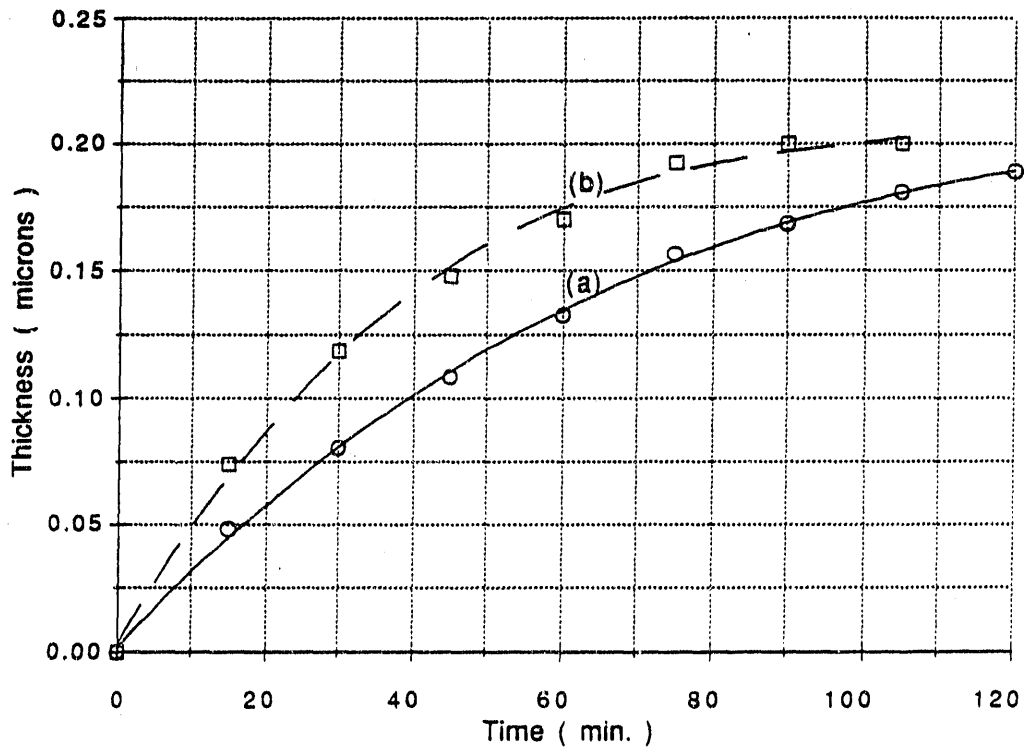
Electrochemical Deposition of Thin ZnTe Films as a
Contact for CdTe Solar Cells
Anup Mondal, Brian E. McCandless, Robert W. Birkmire
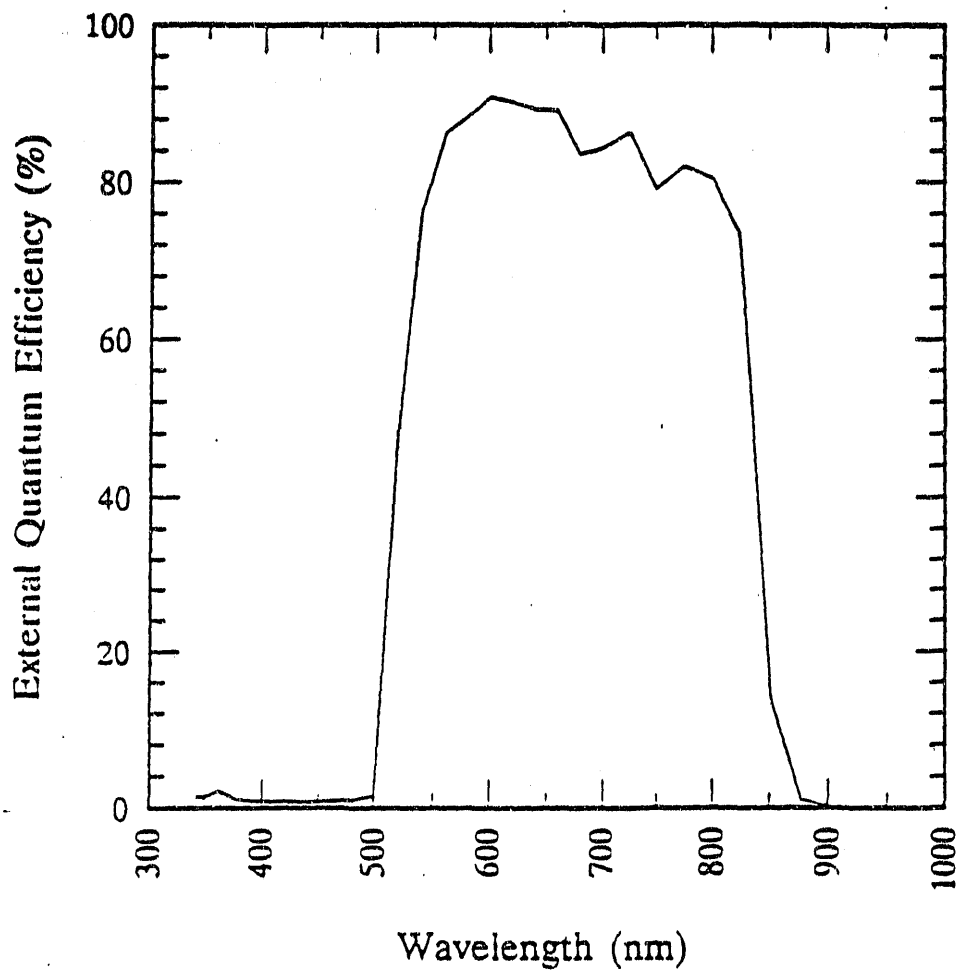**Figure 2**
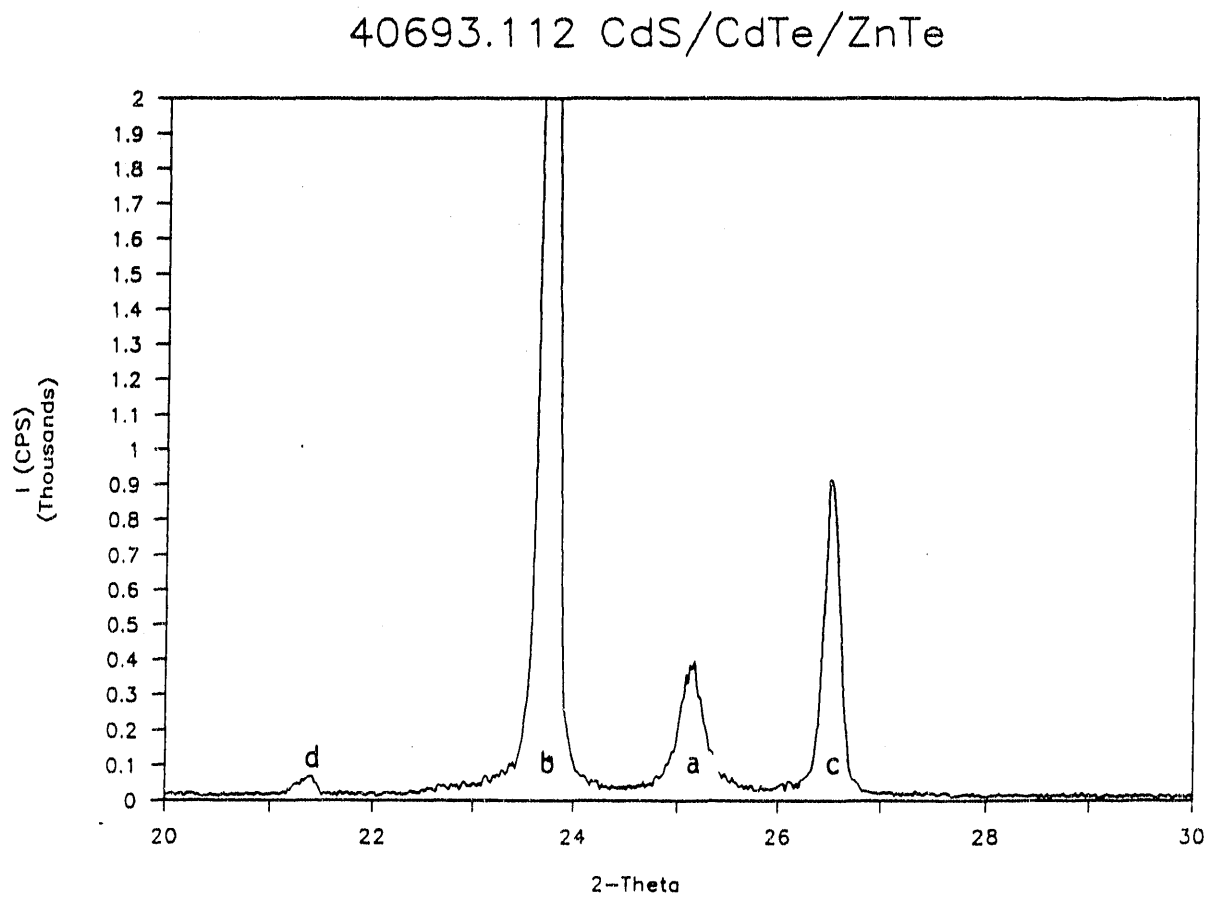
40693.112 CdS/CdTe/ZnTe

Electrochemical Deposition of Thin ZnTe Films as a
Contact for CdTe Solar Cells
Anup Mondal, Brian E. McCandless, Robert W. Birkmire
Figure 3

Electrochemical Deposition of Thin ZnTe Films as a
Contact for CdTe Solar Cells
Anup Mondal, Brian E. McCandless, Robert W. Birkmire
Figure 4

Electrochemical Deposition of Thin ZnTe Films as a
Contact for CdTe Solar Cells
Anup Mondal, Brian E. McCandless, Robert W. Birkmire
Figure 5
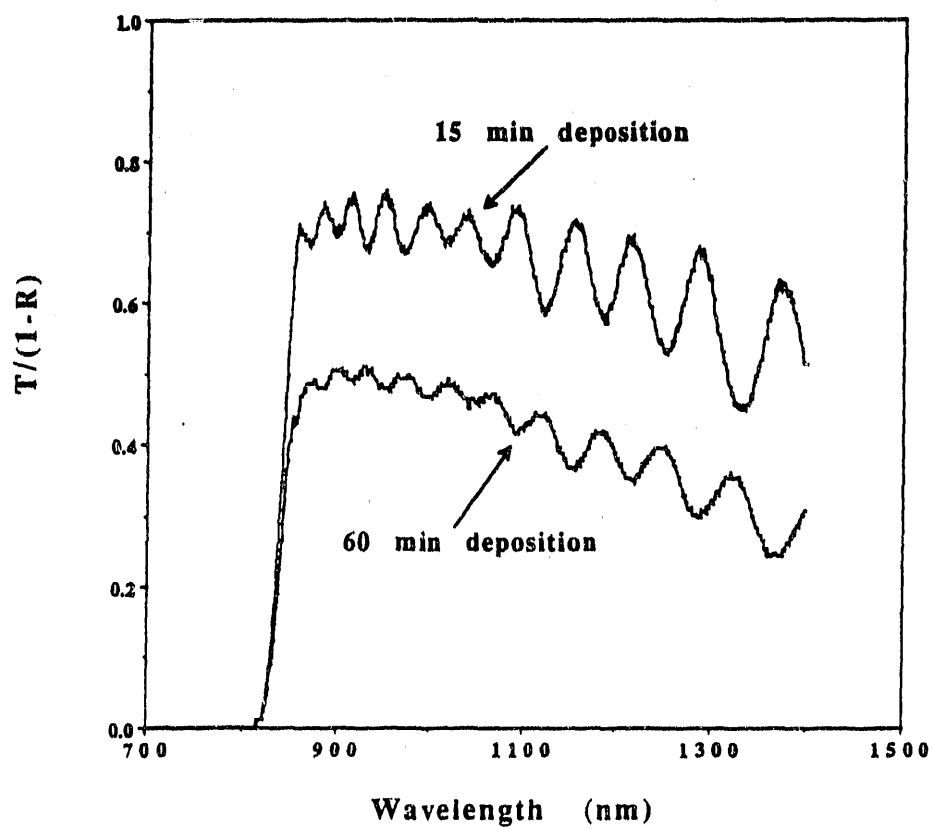
SECTION 7.0

APPENDIX C

Solution Growth Deposition of Zinc Selenide

SOLUTION GROWTH DEPOSITION OF ZINC SELENIDE

Laurie Adkins
Institute of Energy Conversion
University of Delaware

February 8, 1991

ABSTRACT

The solution growth deposition of ZnSe on CuInSe$_2$ substrates is presented. The alkaline bath chemistry used includes sodium selenosulfite with hydrazine reducing agent and zinc chloride with ammonia and TEA complexing agents. Temperature, pH, agitation, and deposition times were varied and results are discussed. CuInSe$_2$ cells were fabricated with chemically deposited ZnSe as window layer. A 3.05% efficient cell is reported with 40.41% fill factor, V$_{oc}$ of 0.2176 V, and J$_{sc}$ of 30.33 mA/cm^2.

Document Control Page	1. NREL Report No. NREL/TP-410-4959	2. NTIS Accession No. DE92010591	3. Recipient's Accession No.

4. Title and Subtitle

Novel Ways of Depositing ZnTe Films by a Solution Growth Technique

5. Publication Date

October 1992

6.

7. Author(s)

R. W. Birkmire, B. E. McCandless, T. A. Yokimous, A. Mondal

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19716-3820

10. Project/Task/Work Unit No.

PV221104

11. Contract (C) or Grant (G) No.

(C) XM-0-18110-1

(G)

12. Sponsoring Organization Name and Address
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

13. Type of Report & Period Covered

Technical Report
1 January 1990 - 1 January 1992

14.

15. Supplementary Notes
NREL technical monitor: T. S. Basso

16. Abstract (Limit: 200 words)

This report describes research to develop novel processes for the deposition of thin (<500Å) ZnTe layers suitable as transparent ohmic contacts for CdS/CdTe solar cells. The processes developed for ZnTe deposition were also applied to the deposition of other II-VI semiconductor layers for polycrystalline thin film solar cells. Three processes for the deposition of ZnTe were investigated: (1) surface exchange with CdTe, where Cd is replaced by Zn from an aqueous bath to form a ZnTe layer; (2) solution growth; and (3) galvanic deposition from an aqueous bath. The galvanic deposition technique proved to be the only method in which ZnTe films were successfully and reproducibly formed. The formation of ZnSe and CdS films using this galvanic deposition method was attempted, and encouraging results were achieved for the formation of CdS films on SnO_x/glass substrates. The development of this method, and the optimization of key processing steps in the fabrication of CdS/CdTe/ZnTe:Cu devices, resulted in cell performance results of > 70% fill factor and ~ 10% efficiency.

17. Document Analysis
a. Descriptors
deposition ; ZnTe ; photovoltaics ; solar cells ; solution growth ; thin films ; polycrystalline

b. Identifiers/Open-Ended Terms

c. UC Categories
273

18. Availability Statement
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

19. No. of Pages

79

20. Price

A08

Form No. 0069E (6-30-87)

END

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11 / 5 / 92