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# Tetraethylene Glycol - Based Electrolytes for High Temperature Electrodeposition of Compound Semiconductors

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## Abstract

We report an investigation of tetraethylene glycol (TEG) solutions of chloride salts ( $\text{CdCl}_2$ ,  $\text{TeCl}_4$ , and  $\text{HgCl}_2$ ) for electrodeposition of films of CdTe and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ , leading II-VI semiconductors. The high boiling point ( $314^\circ\text{C}$ ), below-room temperature ( $T$ ) ( $-6^\circ\text{C}$ ) melting point, adequate metal chloride solubilities, and low toxicity of TEG make it a good candidate for electrodeposition at  $T > 200^\circ\text{C}$ . Such temperatures tend to activate growth of larger crystallites than with aqueous electrolytes at  $T < 100^\circ\text{C}$ , as are advantageous in optoelectronic applications.

Initial results do, indeed, indicate a dramatic increase in crystallinity with deposition temperature, especially for the CdTe films which are nearly amorphous when grown at room temperature.  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  films ( $x < 0.5$ ) are marginally polycrystalline when grown at room temperature but also improve in crystallinity at higher growth temperatures. There appears to be a strong decrease in film adherence and uniformity as growth temperature increases for both materials probably because the greatly increased carrier concentrations at higher temperatures increase film conductivity which, in turn, supports easy electroplating of protruding loose dendritic and/or columnar crystallites, instead of the monolayer-by-monolayer growth of lower conductivity material as occurs at lower temperatures, especially in the higher bandgap/lower conductivity CdTe. The same increase in film conductivity with temperature is responsible for the decrease in the relative photosensitivity of both the CdTe and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  with temperature. At all temperatures, the inferior adherence, uniformity, and photosensitivity as well as the superior crystallinity of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  over that of the CdTe are also explained by its lower bandgap and higher conductivity. On balance, however, the initial results prove the utility of high temperature TEG electrolytes for electrodepositing CdTe and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  films with much better crystallinity than for those grown at lower temperatures, notably in aqueous baths.

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## Introduction

Electrodeposition is a potentially advantageous method for producing materials used in solar cells and other optoelectronic devices. However, there are problems with electrodeposition that must be solved before it can be applied to optoelectronic device manufacturing. One is that electrodeposition tends to produce films that are amorphous or have relatively poor crystallinity. The research described herein is an effort to investigate one method to address this problem as a follow up to previous research on metal chalcogenide electrodeposition.

This work has focused on the growth of binary and ternary metal telluride semiconductor compounds at temperatures up to  $200^\circ\text{C}$  in organic solutions of tetraethylene glycol (TEG) (b.p. =  $314^\circ\text{C}$ ). The compounds investigated thus far are CdTe and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . It is hoped that growth of these at high temperatures (in principle up to the boiling point) will produce films with much larger grain (crystallite) sizes than in those grown at room temperature. More crystalline films should exhibit better per-

formance in subsequent devices. Other attributes of high temperature growth include higher current densities which yield increased deposition rates and more complete diffusion of and reaction between the elements in the film (e.g., Cd, Hg, and Te) to produce a more homogeneous and stoichiometric compound phase. Since both diffusion and reactivity are temperature dependent (proportional to  $\exp[-E_A/RT]$ ), moderate temperature increases could have dramatic effects.

Results thus far have indicated success in achieving the objective of enhanced crystallinity. CdTe films grown at elevated temperatures have exhibited much better crystallinity than those grown at room temperature, and the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  films follow the same trend but not as dramatically.

## Review of Literature

There has been much recent work on the electrodeposition of various semiconductor materials, including

CdTe (Takahasi et al., 1984; Darkowski and Cocivera, 1985; Engelken and Van Doren, 1985), CuInSe<sub>2</sub> (Pern, Goral, et al., 1988; Pern and Noufi, 1988), CdS (Baranski et al., 1981), SnS (Mishra et al., 1989), SnSe (Engelken et al., 1986), Cu<sub>2-x</sub>S (Engelken and McCloud, 1985), WSe<sub>x</sub> (Engelken et al., 1985), and GaAs (Yang et al., 1992). Electrodeposition has even recently been applied to high temperature superconductors (Weston et al., 1992).

Various industrial groups have researched commercialization of solar cells that have involved one or more electrodeposition steps in their fabrication. Rockwell (Ogden and Tench, 1981), Monosolar (Rod et al., 1980), and AMETEK (Fulop et al., 1982) all investigated the electrodeposition of CdTe. The National Science Foundation has funded considerable work in this area, including that of one of the authors (Rajeshwar and Engelken, 1990). The U.S. Department of Energy and the Solar Energy Research Institute (SERI), now the National Renewable Energy Laboratory (NREL), conducted and/or sponsored investigation of electrodeposition of CdTe and CuInSe<sub>2</sub> (CIS) (Basol and Kapur, 1990; Kapur et al., 1987).

If fundamental problems with film (1) crystallinity (2) uniformity/adherence, and (3) stoichiometry/native doping can be effectively solved, electrodeposition can serve as an extremely convenient and low cost method for producing thin film-based optoelectronic devices.

### Material and Methods

The apparatuses used in these experiments included an IBM EC 225 Voltammetric Analyzer, a Hewlett Packard 7046-B x-y-t recorder, a 300 ml Pyrex beaker, and a Teflon beaker cover with the appropriate holes. The anode was made of Poco pyrolyzed graphite and its submerged area was approximately 6 cm<sup>2</sup>. The reference electrode was a Fisher Ag/AgCl reference electrode for measurements below 110°C or a piece of Poco pyrolyzed graphite for those above 110°C. The cathode clamp was constructed of Poco graphite and Teflon bolts and nuts, and the cathode substrates were Balzers 50 ohms/square ITO glass with approximately three cm<sup>2</sup> submerged. Other items included a Fisher Hg-filled thermometer and a Teflon coated stir bar.

Supplies and reagents used included Fluka tetraethylene glycol, and Johnson-Matthey CdCl<sub>2</sub>, TeCl<sub>4</sub>, HgCl<sub>2</sub>, and ultra-pure NaCl.

A Rigaku D-MAX x-ray diffractometer was used to characterize crystallinity. A Perkin-Elmer Lambda 19 UV/VIS/NIR spectrophotometer was used for optical absorbance spectroscopy.

The ITO glass substrates were prepared by washing with Comet cleanser and tap water, followed by thorough rinsing in distilled water and drying with a hot air blower.

The solutions contained 100 ml of tetraethylene glycol, with 10<sup>-3</sup> M TeCl<sub>4</sub> and 0.05 M CdCl<sub>2</sub> for CdTe deposition, or 10<sup>-3</sup> M HgCl<sub>2</sub>, 2.10<sup>-3</sup> M TeCl<sub>4</sub>, and 0.05 M CdCl<sub>2</sub> for Hg<sub>1-x</sub>Cd<sub>x</sub>Te deposition. The salts generally took overnight to dissolve completely in the viscous organic solutions.

The films were grown at cathode voltages ranging from -0.6 to -0.8 V referenced to the Ag/AgCl electrode. The deposition voltage was determined by analyzing photovoltammograms to find the region exhibiting the largest photocurrents which indicate semiconducting behavior. Deposition temperatures ranged from room temperature (21°C) to 170°C. The deposition times required to obtain reasonably thick films ranged from approximately 24 hours at room temperature (current densities less than 100 μA/cm<sup>2</sup>) to 2-3 hours at the highest temperatures (current densities close to 1mA/cm<sup>2</sup>). This was due to the standard increase in current density versus temperature at a given voltage. The solutions were slowly stirred to help improve the uniformity of the films. During film growth, the substrate was occasionally illuminated with white light to monitor the photosensitivity of the film versus time and thickness. Films were rinsed in a tetraethylene glycol bath at the same temperature as the deposition bath and were allowed to cool slowly to room temperature in that bath to prevent cracking and flaking. The films were then rinsed in pure distilled water and were allowed to dry in the hood air stream. The films were stored in either ziplock bags or plastic Petri dishes.

### Results and Discussion

Photovoltammograms were run for both the CdTe and the Hg<sub>1-x</sub>Cd<sub>x</sub>Te deposition baths in order to determine the voltammetric structure and, thus, the voltage region in which semiconducting CdTe or Hg<sub>1-x</sub>Cd<sub>x</sub>Te (versus nonstoichiometric and/or mixed phase) plating was occurring. Figure 1 shows the voltammetric structure of the CdTe bath at 60°C. The pure, metallic Cd cathodic deposition wave is not seen on this voltammogram because it occurs at a considerably more negative (over 0.3 V) potential in tetraethylene glycol than in water (-0.40 V (SHE)). The elemental tellurium and "Cd<sub>x</sub>Te" waves are apparent as well as anodic stripping peaks associated with electrochemical dissolution of Cd out of the surface of the CdTe and the subsequent dissolution of the remaining Te and CdTe. This voltammogram exhibits conspicuous cathodic photocurrents, indicative of semiconducting material.

Figure 2 shows the voltammetric structure of the CdTe solution at 135°C. The cathodic deposition and anodic stripping waves are much larger in this case, due to the increased current and, hence, amount of material

plated at the higher temperatures. The photocurrents appear to be smaller, but this is primarily due to the higher current scale used versus that of Fig. 1.

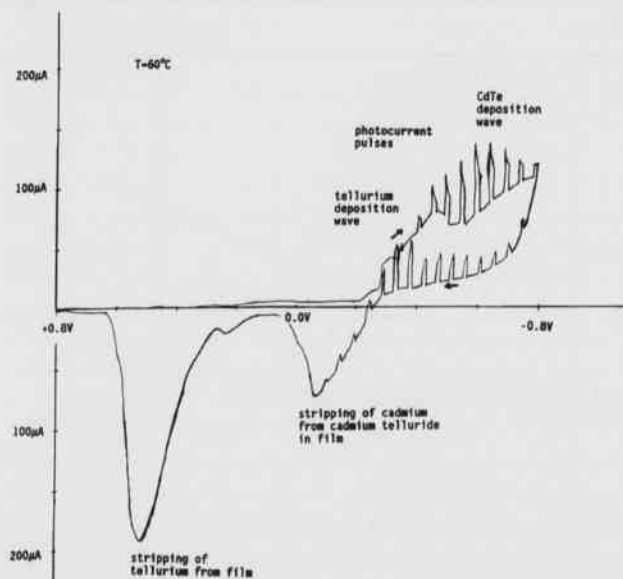


Fig. 1. Cyclic voltammogram (current-voltage curve) for an indium-tin oxide coated glass cathode in a tetraethylene glycol solution of 0.05 M  $\text{CdCl}_2$ ,  $10^{-3}$  M  $\text{TeCl}_4$ , and 0.10 M  $\text{NaCl}$  at  $60^\circ\text{C}$ . The sweep rate was 5 mV/s and the reference electrode was  $\text{Ag}/\text{AgCl}$ . Note the cathodic photocurrent pulses at the more negative voltages, indicative of semiconducting material.

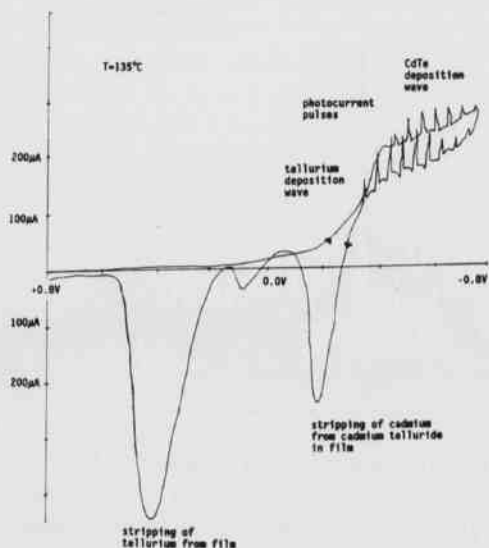


Fig. 2. Cyclic voltammogram as with Fig. 1 except that  $T = 135^\circ\text{C}$  and a graphite strip was used as a reference electrode. Note the increase in the current levels.

Figure 3 shows the voltammetric structure for the  $\text{CdTe}$  solution at  $165^\circ\text{C}$ . Once again, the currents in the deposition and stripping waves have increased with temperature. In this case, there seems to be a true reduction in photocurrent from that at lower temperatures, perhaps due to drastically increased carrier densities and conductivity at this temperature.

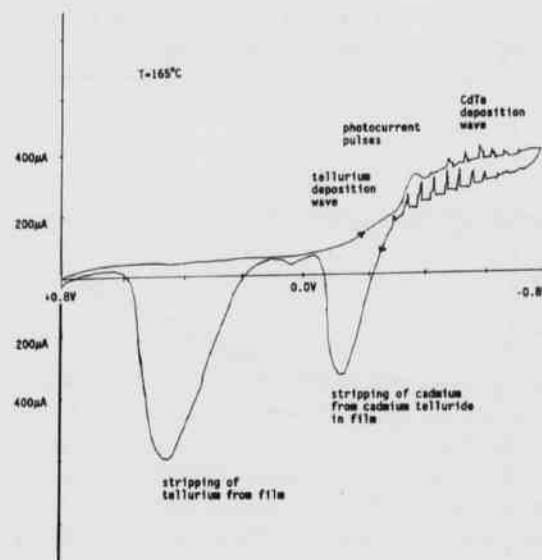


Fig. 3. Cyclic voltammogram as with Fig. 2 except that  $T = 165^\circ\text{C}$ . Note the increase in the current with temperature and an apparent decrease in the relative photocurrent.

The voltammetric structure for the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  bath at room temperature is shown in Fig. 4. The currents and the photocurrent pulses in this case are small. Also, the separate deposition and stripping waves are not as distinct as in the  $\text{CdTe}$  solution probably due to the mutual underpotential deposition of both  $\text{Hg}$  and  $\text{Te}$  into  $\text{HgTe}$  in one broad wave/reaction. The small but distinct photocurrent is indicative of semiconducting  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  rather than "metallic"  $\text{HgTe}$  (no bandgap). Fig. 5 shows the voltammetric structure of the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  solution at  $100^\circ\text{C}$ . In this case, the currents are much larger, but no photocurrents can be seen, probably because at this temperature, the low bandgap material has itself been driven nearly "metallic" (huge carrier concentrations).

Figure 6 shows the x-ray diffractometer (XRD) ( $\text{Cu-K}\alpha$ ) plot of intensity versus goniometer angle ( $2\theta$ ) for a  $\text{CdTe}$  film grown at room temperature. The peaks seen in this plot correspond directly with the indium tin oxide (ITO) substrate coating. The vertical lines on the plot indicate where the peaks for  $\text{CdTe}$  should lie (i.e., the "standard"

powder diffraction file date). The absence of peaks other than those from ITO indicates that the material on the substrate was amorphous. Figure 7 shows the XRD plot from a CdTe film grown at 90°C. This plot shows very large CdTe peaks, indicating much better crystallinity for this film. Figure 8 shows the XRD plot for a CdTe film grown at 170°C. This plot also shows large peaks, although not as large as before. The reason for the smaller peaks in this latter case is probably not decreased crystallinity, but a much smaller film thickness which reduced the strength of the diffracted X-ray signal.

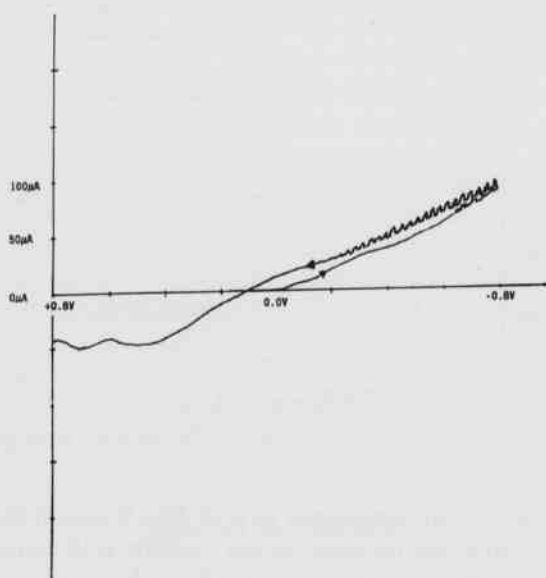


Fig. 4. Cyclic voltammogram (5 mV/s) for a ITO-coated glass cathode in a TEG bath  $10^{-3}$  M in  $\text{HgCl}_2$ ,  $2 \cdot 10^{-3}$  M in  $\text{TeCl}_4$ , and 0.05 M in  $\text{CdCl}_2$ . Note the single, broad cathodic wave starting near 0 V (Ag/AgCl), probably indicative of mutual underpotential deposition of Hg and Te into  $\text{HgTe}$ . The subsequent appearance of cathodic photocurrent is indicative of incorporation of Cd into the film and deposition of semiconducting  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  at the more negative voltages.

Figure 9 shows the XRD plot for an  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  film grown at room temperature. The vertical lines on the plot show the locations of the peaks for a commercial sample of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  ( $x \approx 0.2$ ) donated by Johnson-Matthey. The relatively large intensity of the peaks on this plot indicates very good crystallinity for a film grown at room temperatures. Figure 10 shows the XRD plot for an  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  sample grown at 100°C. This plot shows slightly larger peaks, indicating better crystallinity for the higher deposition temperature (although relatively not as large an increase as for CdTe). The high conductivity of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  leads to much easier growth of dendritic crystal-

lites at low temperature than with much lower conductivity CdTe which tends to grow "layer-by-layer" in an amorphous to small grained manner due to the relatively high resistance of the growing film due to its much higher bandgap.

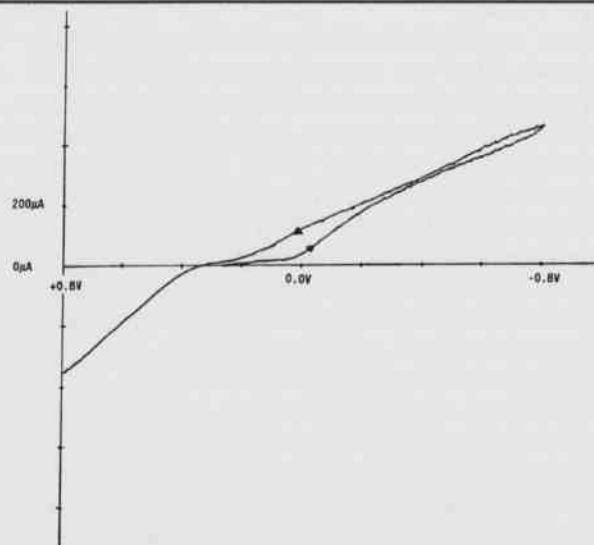


Fig. 5. Cyclic voltammogram as in Fig. 4 except that  $T = 100^\circ\text{C}$ . Note the disappearance of photocurrent pulses, probably because the low bandgap/high conductivity material has been driven nearly "metallic" by the high temperatures.

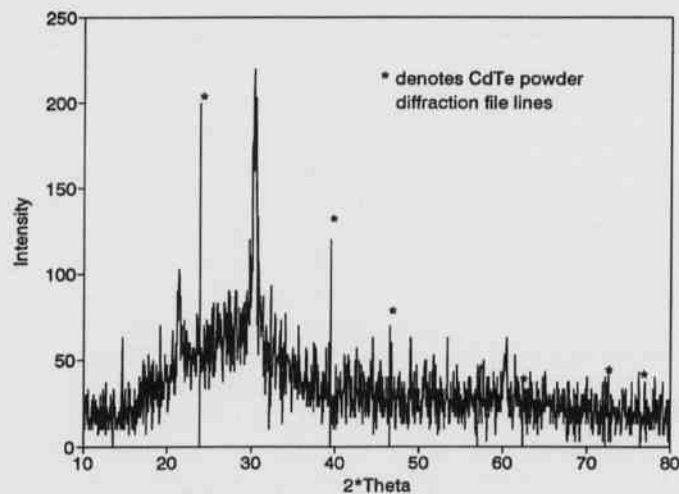


Fig. 6. X-ray diffraction data for a CdTe film electrodeposited onto ITO-coated glass from a bath as described in Fig. 1 and at room temperature. The visible peaks match the indium-tin oxide and there are no large peaks definitely above the noise that match the standard CdTe Powder diffraction file peaks indicated by the vertical lines and stars.

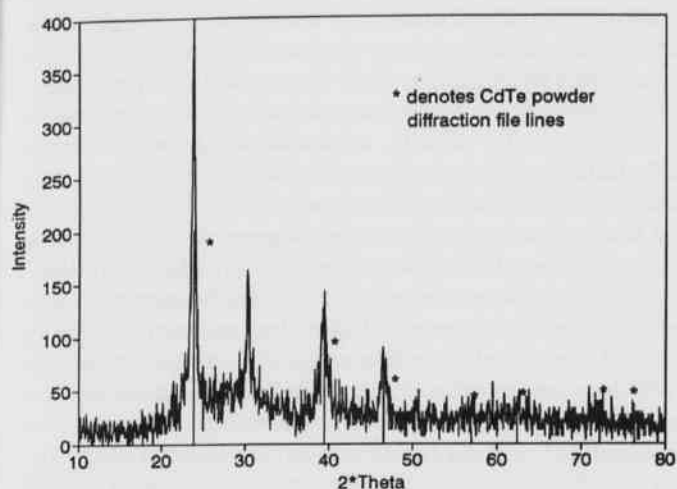


Fig. 7. XRD data as in Fig. 6 but for a film grown at 90°C. Note the appearance of significantly larger peaks matching the CdTe file data and indicating relatively large grain CdTe.

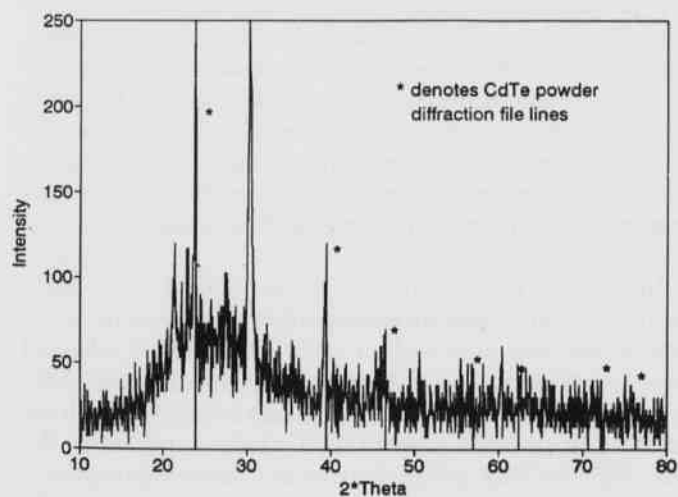


Fig. 8. XRD data as in Figs. 6 and 7 but for a CdTe film grown at 170°C. Again, note the large CdTe peaks. However, they are less intense than in Fig. 7 primarily because of the thinness of this last sample.

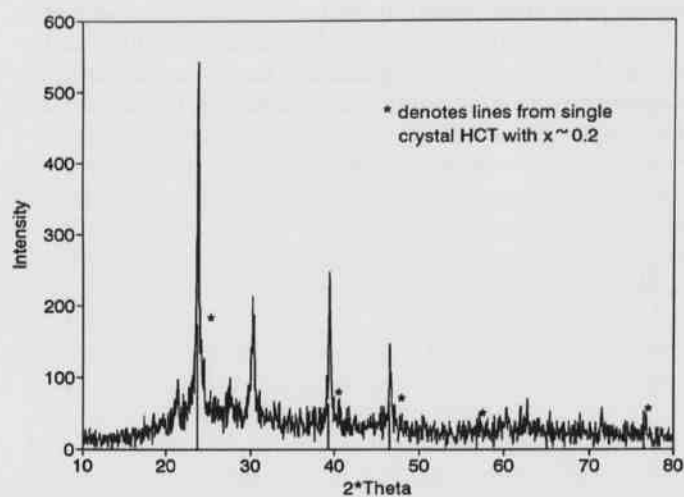


Fig. 9. XRD data for a  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  film electrodeposited on ITO at room temperature. Note the good alignment with the lines representing peak centroid for a single crystal  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  ( $x=0.2$ ) sample. However, the slight mismatch probably represents a somewhat smaller value of  $x$  than 0.2 (i.e., the film peaks are shifted slightly toward those of  $\text{HgTe}$ ). It is significant that the film exhibits good polycrystallinity even when grown at room temperature; this is probably a result of the much greater conductivity of the low bandgap  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  over that of CdTe.

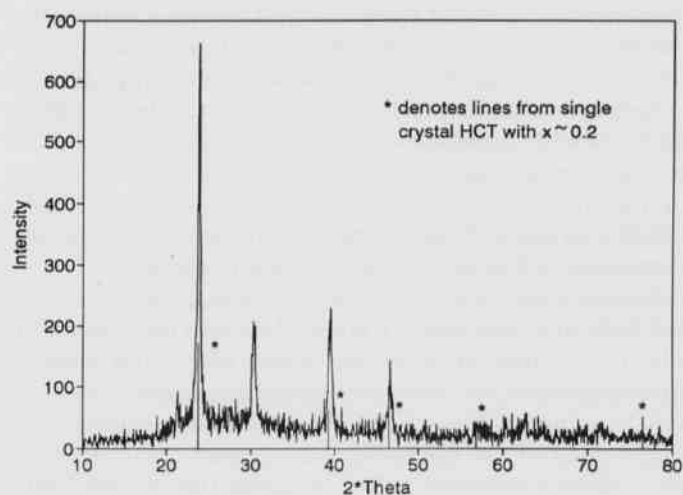


Fig. 10. XRD data as in Fig. 9 except that the deposition temperature was 100°C. Note the slight increase in crystallinity in this case (i.e., peak intensities) over that of the room temperature-grown and comparably thick film in Fig. 9.

A plot of optical absorbance vs. wavelength for a CdTe film is shown in Fig. 11. This plot shows an absorption edge at approximately 800 - 850 nm, consistent with CdTe's 1.5 eV direct bandgap. Problems with film uniformity and adherence (i.e., pinholes) have thus far prohibited good absorption data from being obtained for the  $Hg_{1-x}Cd_xTe$  films.

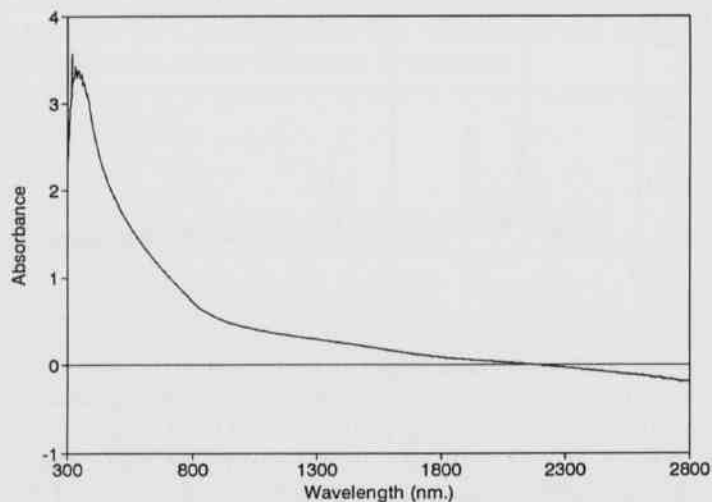


Fig. 11. Optical absorbance vs. wavelength spectrum for a CdTe film electrodeposited from the TEG solution. Note the absorption edge in the 800-850 nm range, consistent with CdTe's 1.5 eV bandgap.

In general, the  $Hg_{1-x}Cd_xTe$  films, although definitely polycrystalline, are not as morphologically uniform or adherent as the CdTe films. Again, the relatively large crystallinity may be due to dendritic type growth that leads to less structurally sound and uniform deposits.

Problems encountered in this work included producing films with good uniformity and adherence. CdTe films grown at high temperatures tended to be more nonuniform than those grown at low temperatures. Also, films grown at high temperatures were much more prone to cracking and flaking upon cooling and rinsing.

An unusual effect was observed in the CdTe deposition bath at temperatures above 135°C. First, the bath took on a cloudy appearance. Then, when film growth was attempted at or above this temperature, copious, dendritic, spongy material was observed growing on the sharp edges of the parallelepiped-shaped cathode. This material was assumed to be cadmium metal but XRD analysis identified elemental tellurium as the only crystalline phase. The actual composition of the material is still under study.

There are some distinct bath color changes at temperatures approaching 200°C. First, the baths rather quickly turn a yellow-brown (but still transparent) color whereas

the TEG is clear to just the slightest yellow color at room temperature. Since the yellow color remains after the bath cools, it is likely that it is due to simple oxidation ("charring") in the presence of atmospheric oxygen. We plan on conducting future depositions under an inert atmosphere ( $N_2$ , argon, etc.) to circumvent this problem.

We also observe an additional gray color appearing in the solution at  $T > 200^\circ C$ , accompanied by effervescent gas bubbles in the solution and misty vapor above the solution. This bubbling is not wholesale boiling of the TEG but appear to be due to homogeneous creation of a gaseous product throughout the solution which condenses into a vapor above the solution. This phenomenon also correlates with decreased deposition currents. A likely (but still unproven) mechanism is the reduction of the Te(IV) ions into a gray elemental tellurium suspension by the TEG, itself oxidized into a lower b.p. organic after this occurs, consistent with removal of tellurium ions.

The minute ( $\approx 10^{-3}$  M) concentrations of Hg(II) and Te(IV) required to avoid gross Hg and/or Te richness in the deposits (due to their relatively positive reversible potentials and, thus, the need for their currents to be diffusion-limited) are depleted after several depositions and lead to a continuous decrease in their concentrations that makes exact control of stoichiometry more challenging.

## Conclusions

In this project we have shown the CdTe and  $Hg_{1-x}Cd_xTe$  films electrodeposited at higher temperatures from tetraethylene glycol solutions exhibit better crystallinity than films grown at room temperatures. However, problems exist with high temperature deposition; these include nonuniformity and flaking of the films and chemical changes in the electrolyte. On balance, the preliminary results are encouraging and indicative of the utility of TEG-based electrolytes for electrodeposition of large-grained polycrystalline metal chalcogenide films for optoelectronic applications.

In the future, we plan to investigate other solvents for the deposition baths, including other high boiling point organic solvents and molten salts. The molten salts will allow experimentation at even higher temperatures. Also, we will soon begin electrodeposition of other semiconductor compounds, including  $CuInSe_2$  and from the same high boiling point electrolytes. Inert atmospheres will also be investigated to avoid oxidation of organic phases at high temperature and the deposited films will be characterized in more detail.

### Acknowledgements

The described work is being jointly funded by the NASA JOint VEnture (JOVE), NASA ESPCoR, and NSF/Arkansas Science Information Liaison Office (SILO) Undergraduate Research Fellowship (SURF) Programs as a follow up to an earlier grant from the Arkansas Science and Technology Authority.

Dr. Robert D. Engelken is working with Dr. Frank Szofran of the Electronic and Photonic Materials Branch of the Space Science Laboratory at NASA Marshall Space Flight Center in Huntsville, Alabama under the JOVE Program; the Program is designed to bring together university professors and NASA personnel to work together on mutually interesting projects. R.D.E.'s work involves electrochemical preparation and characterization of compound semiconductors such as  $Hg_{1-x}Cd_xTe$  and  $Hg_{1-x}Zn_xTe$ , both of interest to NASA for both fundamental materials studies (e.g., crystal growth) and device applications. The deposition of high quality films by electrodeposition has emerged as important for producing samples of varying stoichiometry ("x") for subsequent "calibration" of other electrochemical methods being investigated for mapping stoichiometry.

The SILO SURF Program provided additional funding for Chris Poole to continue electrodeposition research through an undergraduate research fellowship. The Program seeks to dramatically increase the involvement of undergraduates in cutting-edge research within Arkansas to improve the technical base and economic competitiveness of the state.

The recently commenced (May, 1994) Arkansas NASA EPSCoR Project includes the Advanced Photovoltaic Materials Research Cluster of which R.D.E. is a participant along with faculty from the University of Arkansas - Fayetteville and University of Arkansas - Little Rock. The Cluster is investigating photovoltaic materials, configurations, and processes, including additional work on electrodeposition of CdTe and  $CuInSe_2$  from nonaqueous electrolytes.

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