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Molten Salt Electrolytes for Electrodeposition of CdTe Films

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Abstract

We report preliminary investigation of several molten salt electrolytes containing CdCl_2 and TeCl_4 for the electrodeposition of CdTe films at temperatures well above ($>250^\circ\text{C}$) those used with aqueous and organic electrolytes. These high temperatures have potential to dramatically increase the crystallite size (Poole, Engelken, et al., 1994), as is important for optoelectronic device applications of CdTe, a leading II-VI semiconductor. This paper will survey the results obtained with electrolytes such as $\text{B}_2\text{O}_3/\text{HBO}_2$ (m.p. $\approx 230^\circ\text{C}$), NaCH_3COO (m.p. $\approx 324^\circ\text{C}$), ZnCl_2 (m.p. $\approx 283^\circ\text{C}$), and LiCl/KCl (m.p. $\approx 350^\circ\text{C}$), with an emphasis on the latter two. Key material to be presented includes 1) voltammetric data for the solutions, 2) x-ray diffractometry data for deposited films, 3) a discussion of the numerous practical problems associated with high temperature electrochemistry, especially in corrosive, volatile systems, and 4) emphasis of the value of an operationally feasible high temperature plating system to the commercial viability of electrodeposited semiconductor films.

Introduction

Cadmium telluride, a leading II-VI semiconductor, is used in optoelectronic devices such as photovoltaic and photoconductive cells. Its direct bandgap of 1.44 eV makes it a nearly ideal candidate for solar energy conversion. CdTe films have been electrodeposited from aqueous solutions at low temperatures ($< 100^\circ\text{C}$), but such films tend to be amorphous or have poor crystallinity. Electrodeposition of CdTe from a molten solution should dramatically increase crystallite size due to the much greater thermal energy available to activate diffusion and reaction of plated atoms. Such films, deposited at temperatures above 250°C , have shown a remarkable increase in crystallinity, as reported herein.

This work focused on selection of a suitable electrolyte not only stable at the operating temperature, but also supporting cadmium and telluride electrochemistry and growth of CdTe films. This required extensive research wherein ZnCl_2 , NaCH_3COO , $\text{B}_2\text{O}_3/\text{H}_3\text{BO}_3$, and LiCl/KCl , each containing dissolved CdCl_2 and TeCl_4 , were analyzed. The results obtained so far with LiCl/KCl solutions have indicated success in achieving the objective of enhanced crystallinity.

Materials and Methods

Significant research has been performed within the last twenty years on the electrodeposition of semiconductor materials (including CdTe) at temperatures below

250°C (Takhashi et al., 1984; Darkowski and Cocivera, 1985; Engelken and Van Doren, 1985; Poole et al., 1994), but little work has been performed on electrodeposition of semiconductors at elevated temperatures ($>250^\circ\text{C}$). LiCl/KCl solutions have been used previously for electrodeposition of CdSe (Minoura et al., 1985) and metals such as Mo (Gabriel et al., 1994). Electrodeposition at high temperatures has also recently been applied to superconductors (Weston et al., 1992).

The apparatus used in the experiments consisted of an EG&G Princeton Applied Research Model 362 scanning potentiostat, a Hewlett Packard 7046-B x-y-t recorder, a Munsey M88 oven, Pyrex/quartz beakers, and a graphite beaker cover with appropriate holes for the insertion of electrodes. Two inch long cylindrical pieces were cut from a ceramic tube and wedged into the holes to insulate the graphite electrodes from the beaker cover. For voltammetric analysis, 6.15 mm (dia.) x 150 mm (before cutting to 100 mm for use) graphite rods were used as anode, cathode, and reference electrodes. The graphite cathode was replaced by 0.0127 cm thick molybdenum foil when films were being deposited. Initially, all experiments were performed without the graphite reference electrode, but subsequently, three electrodes were used for the detailed analysis of LiCl/KCl solutions. Very small electrode areas ($\approx 2\text{ cm}^2$) were immersed in the solutions. Steel clamps with steel nuts and bolts were used to hold the electrodes securely above the beaker cover. An Omega thermocouple and temperature controller were used to measure and control the temperature.

Supplies and reagents used included Aldrich H_3BO_3 (which dehydrated to HBO_2 upon heating), B_2O_3 , LiCl, and KCl, Fluka $NaCH_3COO$, and Alfa/Johnson Matthey $ZnCl_2$, $CdCl_2$, and $TeCl_4$. Distilled water was used to rinse the deposited films.

A Rigaku D-MAX x-ray diffractometer was used to obtain a plot of intensity vs. goniometer angle (2θ). This process gives an indication of the relative crystallinity of the film samples.

The molarity of $CdCl_2$ and $TeCl_4$ was maintained near 0.01 M and 0.002 M, respectively. The total volume of the solution was kept between 10 ml and 15 ml. The voltammetric sweeps were usually run from 1.0 V to -1.5 V (cathode-anode, and cathode-reference voltages for the two and three electrode configurations, respectively). This range was found to be suitable to exhibit all required cathodic and anodic structures. Films were deposited by setting the initial sweep voltage at the desired deposition value. This voltage was then applied to the solution for the required deposition time.

The beaker containing the electrolyte was placed in the oven and heated until the electrolyte melted. The B_2O_3/HBO_2 mixture (in the ratio 1:5 by weight) had a melting point of approximately 220°C. $NaCH_3COO$ melted near 325°C. $ZnCl_2$ had a melting point of 283°C. Although both LiCl and KCl have melting points above 550°C, their mixture (in the ratio 1:1 by mass) melted at 350°C if the temperature was maintained for a prolonged period of time. The mixture melted much more rapidly if the temperature was allowed to rise further. Usually, the operating temperature was maintained 20°C above the melting point. When the electrolyte had melted completely, $CdCl_2$, $TeCl_4$, or a mixture of the two was added to the solution. These dissolved readily in all solutions except B_2O_3/HBO_2 . The beaker cover, holding the electrodes, was placed over the beaker. Wires with woven ceramic insulation were connected to the graphite electrodes. This entire assembly was clamped securely to provide good electrical connection between the wire and electrode. These wires protruded through an orifice in the oven.

Results and Discussion

Current vs. voltage structures obtained from voltammograms enable one to deduce the regions in which different elements and/or compounds are being deposited. On the forward sweep, cathodic deposition waves or peaks are observed while the reverse sweep shows anodic stripping peaks.

The B_2O_3/HBO_2 mixture never melted to a clear liquid. It had a tendency to become extremely viscous, and then form large bubbles if the temperature was raised fur-

ther (beyond 230°C). The $CdCl_2/TeCl_4$ did not dissolve in this mixture but stayed in a powdery form over the surface. Extremely small currents (of the order of a few μA) were observed. No accurate voltammetric data could be collected due to the interference caused by low frequency electrical noise from the heating element relative to such low currents.

$NaCH_3COO$ did not work well as an electrolyte either, probably due to its strong reducing characteristics at the high operating temperature (330°C). The solution turned greenish black after addition of $TeCl_4$, probably due to formation of elemental Te. A voltammogram obtained for $NaCH_3COO$ is shown in Fig. 1. Two distinct cathodic deposition peaks can be seen, one at -0.5 V, (cathode to anode) (possibly elemental Te) and the other at -1.1 V (cathode to anode) (elemental Cd), but only one anodic stripping peak is seen, corresponding to cadmium. The appearance of only one weak tellurium plating wave/peak and a poorly defined-to-nonexistent tellurium stripping peak is also consistent with the reduction of Te (IV) to Te (0) by the acetate ion and, hence, decrease in Te ion concentration. The currents seen in the voltammogram were of the order of tens of mA, over electrode areas a few tenths of a cm^2 .

$ZnCl_2$ proved to be a somewhat better electrolyte than B_2O_3/HBO_2 and $NaCH_3COO$. Currents of the order of a few mA were obtained over comparable areas near 330°C. Figure 2 shows the voltammetric structure for the solution. Three anodic deposition peaks and three cathodic stripping peaks are observed. From left to right, the peaks are those of elemental Te, CdTe, and elemental Cd. These peaks corresponded to 0.6 V, -0.2 V, and -1.1 V (all cathode to anode voltages). Although the results obtained are significantly better than with the two previously mentioned electrolytes, the electrochemical reduction of $CdCl_2$ and $TeCl_4$ was still sluggish, as can be seen from the voltammetric peaks which are small in comparison to the background current. Several attempts were made to deposit a CdTe film from the molten $ZnCl_2$ bath but they all proved unsuccessful.

The results obtained from LiCl/KCl solutions were far more encouraging than the previous results. High currents were observed at the elevated temperatures (350 - 380°C). Currents were as large as a few tenths of an ampere for cathodic Cd peaks. With the presence of only $CdCl_2$ in solution, Cd plated out of the solution at -1.2 V vs. a graphite reference electrode. The plating voltage varied slightly with a change in concentration of the plating species and the presence of additional plating species in the solution. Similarly, the deposition voltage for Te was found to be near -0.8 V vs. graphite. When both $CdCl_2$ and $TeCl_4$ are present in solution, three cathodic and anodic peaks are observed, as is shown in Fig. 3. The CdTe peak appears between the Te and Cd peaks at a

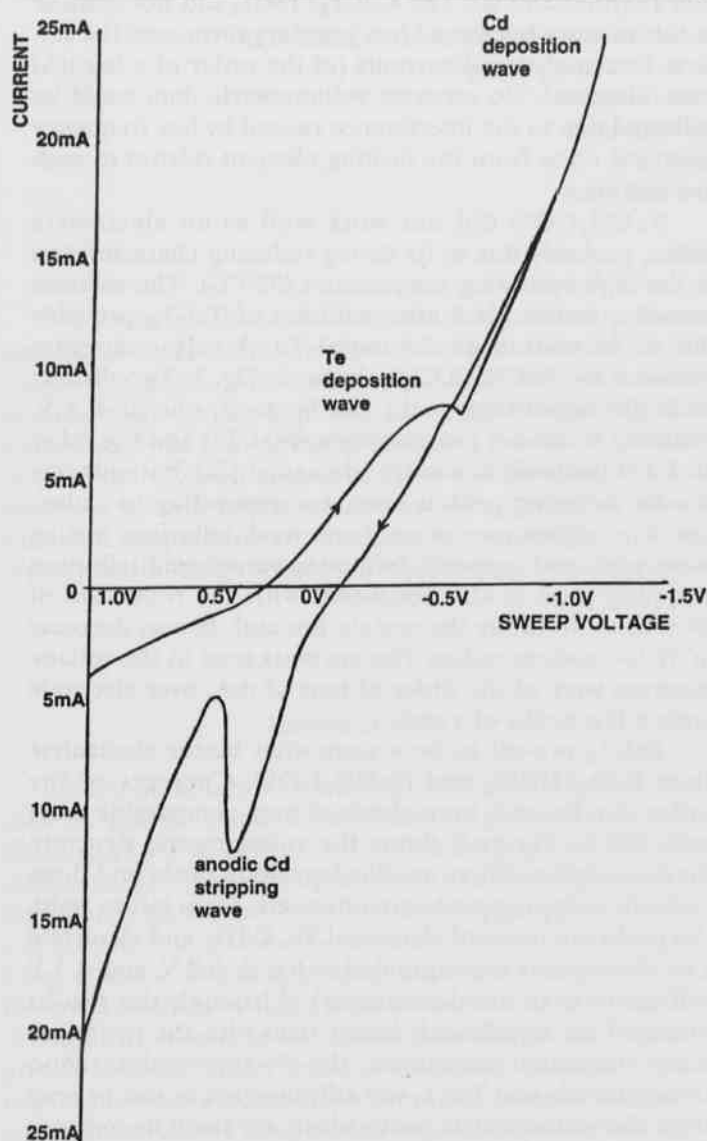


Fig. 1. Cyclic voltammogram (current-voltage curve) for a graphite cathode immersed in a NaCH_3COO solution of 0.01 M CdCl_2 , and 0.002 M TeCl_4 at 330°C . The sweep rate was 10 mV/s . Note that only one well defined anodic stripping peak is present. The voltage was swept from $+1.0 \text{ V}$ to -1.5 V .

voltage near -1.0 V . As before, the three cathodic peaks observed in Fig. 3 (sweeping from a more positive voltage to a more negative voltage; i.e., left to right) are Te, CdTe, and Cd, respectively. The anodic stripping peaks are larger and sharper than the cathodic peaks and appear at less negative values. The voltammetric structures indicate that CdTe can be deposited in the range of -1.0 V and -1.2 V vs. graphite.

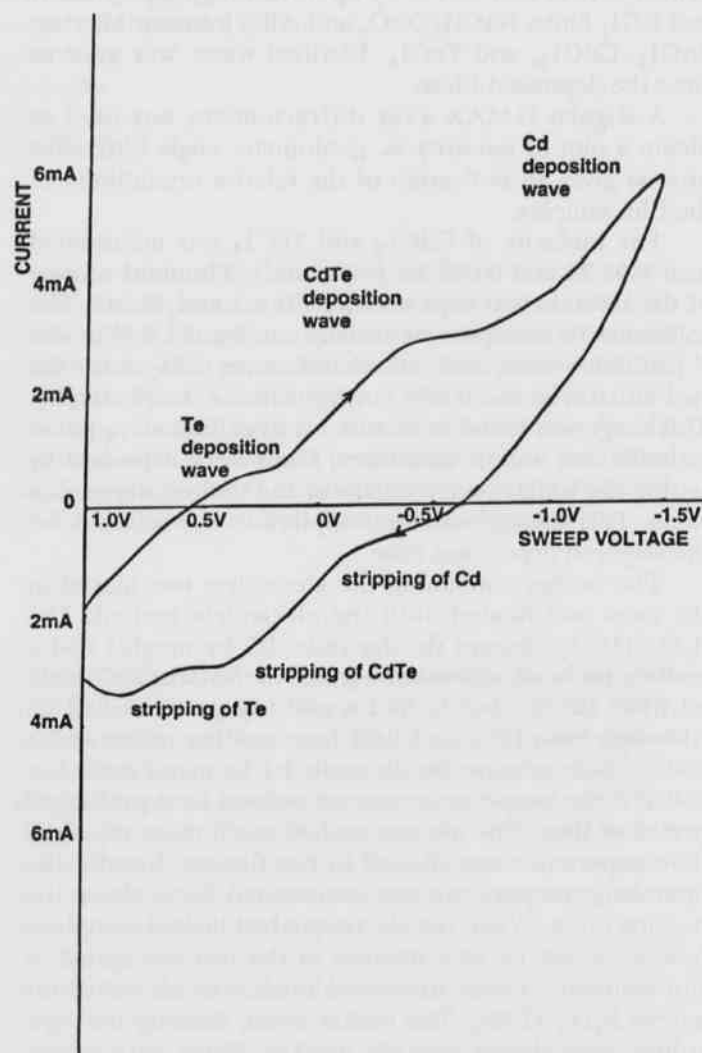


Fig. 2. Cyclic voltammogram for a graphite cathode in a ZnCl_2 solution of 0.01 M CdCl_2 , and 0.002 M TeCl_4 at 350°C . The sweep rate was 2 mV/s and the voltage was swept from 1.0 V to -1.5 V . Note that the peaks (both deposition and stripping) are small with respect to the background "dark" current.

Voltammetry was conducted while illuminating the LiCl/KCl baths with 1000 W quartz-tungsten halogen white light through the tempered glass door of the oven. In no case did these "photovoltammograms" exhibit any photocurrent, as normally occurs with photovoltammetry of Cd(II)/Te(IV) solutions in aqueous and organic baths at $T < 150^\circ\text{C}$. The reason is, no doubt, that the high temperatures produced a many order of magnitude increase

in the concentrations of electrons and holes in the deposited CdTe films, thus, driving the material nearly "metallic", and hence, making imperceptible any tiny photomodulated increase in current relative to the large "dark current" values.

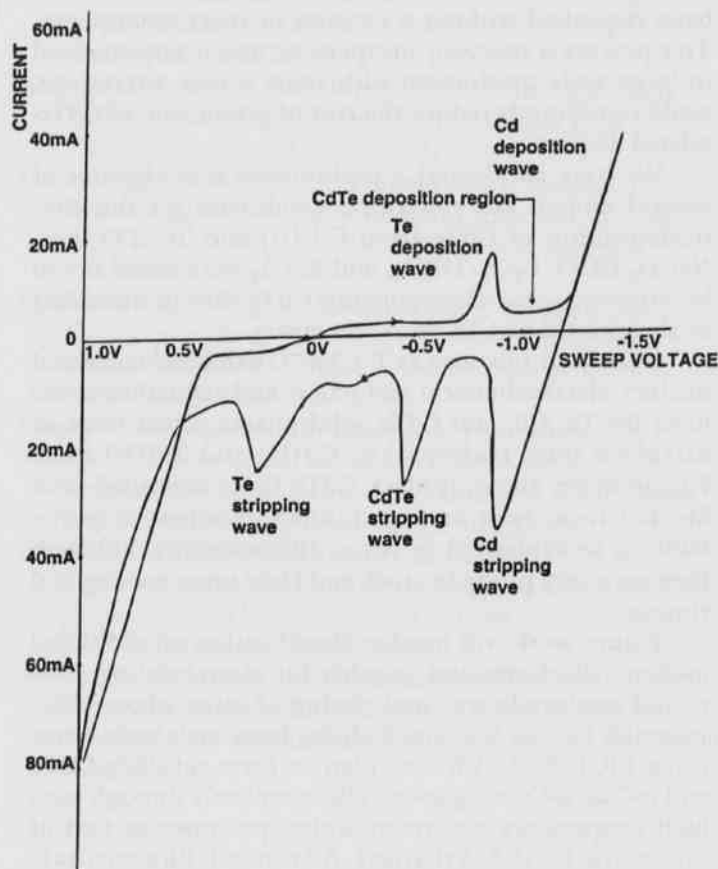


Fig. 3. Cyclic voltammogram for a graphite cathode in a LiCl/KCl solution of 0.01 M CdCl₂, and 0.002 M TeCl₄ at 365°C. The sweep rate was 10 mV/s and the voltage was swept from 1.0 V to -1.4 V. The deposition and stripping peaks were extremely sharp. Larger currents were observed.

Gray-black CdTe films were deposited onto Mo foil. CdTe was found to deposit between -1.1 V and -1.2 V vs. graphite. When the films were allowed to deposit too long (approximately 30 minutes), they were very thick and flaked off when rinsed in distilled water. If the deposition time was too short, no or little crystalline film would grow but a grey discoloration of the Mo foil could be seen.

X-ray diffractometry (XRD) of the thicker films was very encouraging. Large CdTe peaks match perfectly and

reproducibly with standard CdTe powder diffraction file card peaks; best results were obtained when the CdTe film was deposited at -1.125 V. The large peaks indicated a large crystallite size. Figure 4 exhibits XRD plots with standard powder diffraction file data for CdTe films indicated by the vertical lines.

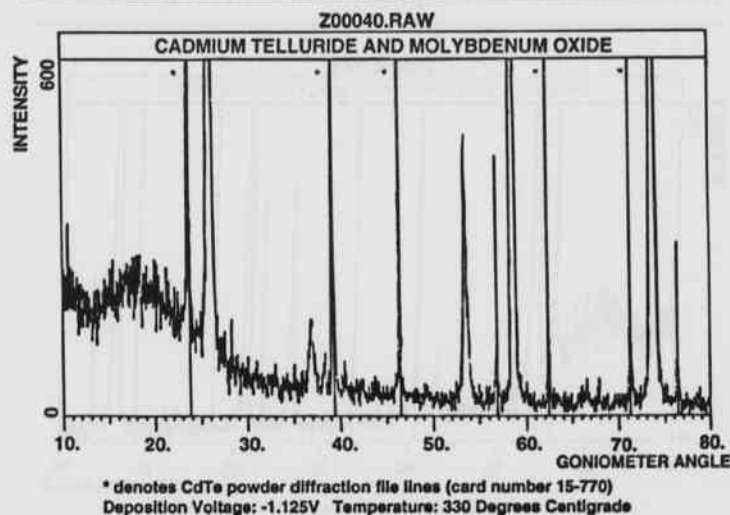


Fig. 4. X-ray diffraction data for a CdTe film electrodeposited onto Mo foil from a LiCl/KCl solution at 380°C. The deposition voltage was maintained at -1.125 V. The large peaks matched the CdTe powder diffraction file peaks. The two peaks at 58° and 74° were Mo substrate peaks.

Certain obstacles were encountered at the high temperatures. Brown fumes were observed on the addition of TeCl₄ to the LiCl/KCl solution. It is possible that HCl gas was evolved as TeCl₄ was hydrolyzed to TeO₂. More likely is the simple evaporation of TeCl₄ (m. p. = 224°C, b. p. = 380°C); a yellow/red coating would slowly accumulate on the beaker and beaker cover over the electrolyte. The fumes emanating from the solution were probably toxic and had to be treated carefully. The graphite anode was also attacked by the solution. Graphite is very unreactive at low temperatures, but it is likely that high temperatures were causing corrosion. The NaCH₃COO solution was unstable at high temperatures. If it was heated beyond the melting point for a prolonged period, it would decompose and form a dark liquid, probably due to the oxidation ("charring") in the air. As mentioned earlier, the B₂O₃/HBO₂ mixture never melted down completely. Thus, the electrodes were never actually immersed in a true liquid, causing low currents that led to uninformative voltammograms.

The major challenge faced while depositing films on Mo foil was the oxidation of Mo to MoO_x. This was indi-

cated by the presence of a blue-gray color above the film on the Mo foil. This is once again attributed to the high operating temperature. XRD analysis confirmed the presence of trace MoO_2 and TeO_2 on some films. Figure 5 and Fig. 6 show XRD data for the same film with standard XRD file data for CdTe and MoO_2 , respectively. The film clearly indicates the presence of both compounds.

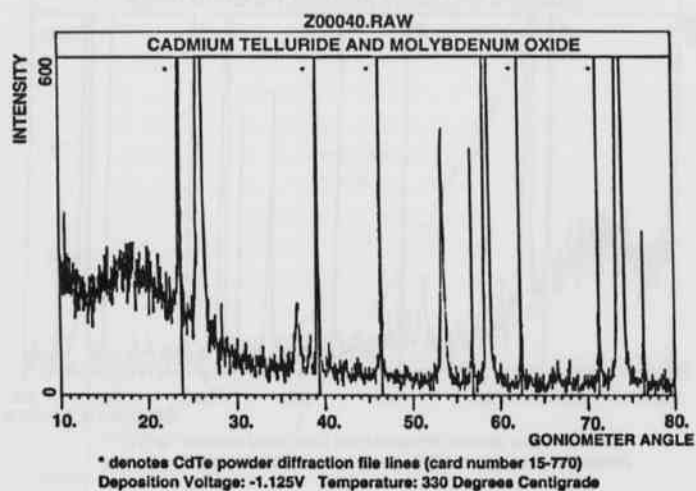


Fig. 5. XRD data as in Fig. 4 but for a film deposited at 330°C. Three large and four small peaks matched perfectly with the CdTe file card. The intensity of the peaks is greater than observed in Fig. 4, primarily due to a significantly longer deposition time and thicker film.

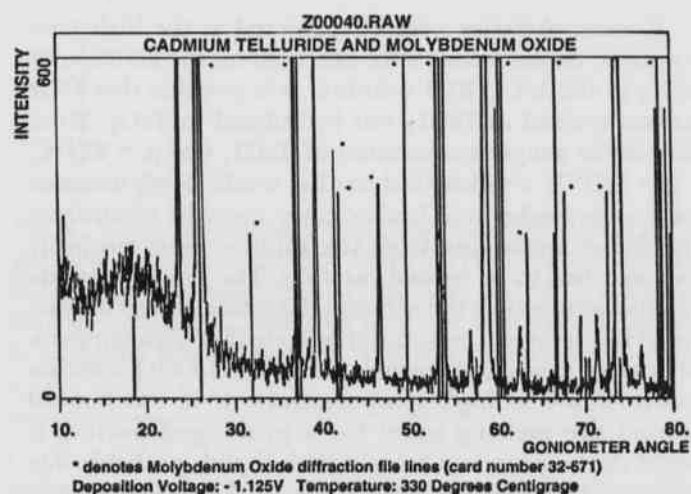


Fig. 6. XRD data as in Fig. 5 for the same film but the matching peaks belong to MoO_2 . Note that all the peaks that had not matched up in Fig. 4 belong to MoO_2 (except the Mo peaks mentioned in Fig. 4). The presence of both CdTe and MoO_2 on the film was clearly indicated by the XRD plots.

CdTe has significant application in optoelectronic devices such as solar cells and light detectors. Hence, it is important that a cost-effective method for electrodeposition of large-grain, device-grade CdTe be developed. The described procedure tentatively meets this criterion, is simple, and is performed in a relatively uncontrolled (ambient) environment. Films with large crystallinity have been deposited without a vacuum or inert atmosphere. This process is relatively inexpensive, and if implemented in large scale production with some minor alterations, could significantly reduce the cost of production of CdTe-related devices.

We have conducted a preliminary investigation of several molten salt electrolyte candidates for the electrodeposition of CdTe from Cd (II) and Te (IV) ions. NaCH_3COO , $\text{B}_2\text{O}_3/\text{HBO}_2$, and ZnCl_2 were found not to be efficacious for electroplating CdTe due to instability or sluggish Cd and Te electrochemistry.

LiCl/KCl mixtures at $T > 350^\circ\text{C}$ exhibited facile and distinct electrochemical reduction and oxidation structures for Te, Cd, and CdTe solid phases plated from or dissolved into, respectively, Cd(II) and Te(IV) ions. Furthermore, the gray-black CdTe films deposited onto Mo foil from such baths exhibited excellent polycrystallinity, as evidenced by X-ray diffractometry, although they were very prone to crack and flake upon cooling and rinsing.

Future work will involve identification of additional molten salt electrolytes suitable for electroplating compound semiconductors and plating of other photovoltaic materials such as CdS and CuInSe_2 from such baths, especially LiCl/KCl . We also plan to form n-CdS/p-CdTe and n-CdS/p-CuInSe₂ solar cells completely through such high temperature electrodeposition processes as part of our work in the Arkansas Advanced Photovoltaic Materials Research Cluster under the AR/NASA EPSCoR program.

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