Electrodeposition of Zinc Telluride from a Zinc Chloride-1-Ethyl-3-methylimidazolium Chloride Molten Salt

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The electrodeposition of tellurium and zinc telluride was investigated on a nickel electrode in the 40-60 mol % zinc chloride-1-ethyl-3-methylimidazolium chloride molten salt containing propylene carbonate as a cosolvent at 40°C. Tellurium(IV) can be electrochemically reduced to tellurium in this solution. Addition of 8-quinoledimine (oxine) to the solution shifts the reduction of Te(IV) to more negative potential. Deposits of Zn-Te can be obtained through the underpotential deposition of zinc on tellurium which occurs at a potential near −0.1 V. At potentials more negative than ca. −0.5 V, tellurium can be further reduced to tellurium(II) species which can react with zinc(II) to form Zn-Te. Energy-dispersive spectroscopy data indicate that the composition of the Zn-Te deposits is dependent upon the deposition potential and the Te(IV) concentration in the plating solution. Characteristic X-ray diffraction patterns of cubic ZnTe are observed for the electrodeposited Zn-Te samples that have been annealed at temperatures ranging from 250 to 400°C. The flatband potential of the Zn-Te electrodeposits was determined by photocurrent and impedance (Mott-Schottky plot) experiments. The optical bandgap of the ZnTe deposits determined by optical absorption spectrometry is 2.3 V, which agrees well with the literature values.

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Room-temperature molten salts1,2 can be obtained from the combination of certain quaternary ammonium chloride melts, such as 1-ethyl-3-methylimidazolium chloride (EMIC) and 1-n-butyl-3-methylimidazolium chloride (BMIC), and metal chlorides such as AlCl3 and GaCl3. These ionic liquids have been shown to be useful electrolyte for various electrochemical applications such as electrodeposition and batteries. This is because these molten salts exhibit several attractive properties including good ionic conductivity, wide electrochemical window, and negligible vapor pressure. Many examples of electrodeposition of pure metals3-9 and aluminum alloys10-17 from chloroaluminate melts can be found in the literature. On the other hand, the use of room temperature molten salts for electrodeposition of semiconductor materials is less explored.8-21

ZnTe, one of the II-VI semiconductors, has found a wide range of applications in switching devices and solar cells.22,23 These applications make ZnTe a material worthy of study. Among the various techniques, electrodeposition provides a simple, low-cost means for fabrication of thin-film semiconductors. Extensive work has been conducted for the electrodeposition of ZnTe from aqueous24-28 and nonaqueous media,29-32 but no work has been performed in low-temperature molten salts. Thus, it is of interest to explore the possibility of using a molten salt bath for ZnTe electrodeposition. Previous studies revealed that zinc metal could be electrodeposited from acidic AlCl3-EMIC melts31 or from a mixture of 50-50 mol % AlCl3-EMIC and 50-50 mol % ZnCl2-EMIC melts.30 The electrodeposition of zinc is not expected from basic AlCl3-EMIC melt because the zinc(II) probably exists as ZnCl4− in this melt, and its reduction potential is beyond the cathodic limit of the melt. The electrochemistry of tellurium was studied in basic AlCl3-EMIC melts, and it was found that Te deposits could be obtained from the reduction of Te(IV), and the resulting Te deposits could be further reduced to Te(II).31 The electrodeposition of Te from acidic AlCl3-EMIC melt was complicated, however, by the formation of tellurium clusters. In view of the fact that zinc cannot be electrodeposited from basic AlCl3-EMIC melt, while tellurium electrodeposits cannot be obtained from acidic AlCl3-EMIC, it would be difficult, though not impossible, to use the AlCl3-EMIC melt system for the electrodeposition of ZnTe.

Similar to the AlCl3-EMIC melt system, the combination of ZnCl2 and EMIC produces low-temperature molten salts.32 Because zinc chloride is a Lewis acid, the Lewis acidity of the ZnCl2-EMIC melts can be adjusted by varying the molar ratio of ZnCl2 to EMIC in the melt. It has been shown that zinc metal can be electrodeposited from ZnCl2-EMIC melts that contain more than 33 mol % ZnCl2. Previous investigations indicate that it is possible to electrodeposit Cu-Zn and Co-Zn alloys from these melts.33,34 To further explore the potential utility of ZnCl2-EMIC melt as an electrolyte for electrodeposition, this work reports the electrochemistry of tellurium and the electrodeposition of ZnTe in this melt system.

Experimental

Apparatus.—All electrochemical experiments were conducted inside a Vacuum Atmospheres glove box filled with dry nitrogen. The moisture and oxygen level in the box was kept lower than 1 ppm. The electrochemical experiments were accomplished with an EG&G model 273A potentiostat/galvanostat controlled with EG&G model 270 software. A three-electrode electrochemical cell was used for the electrochemical experiments. The nickel working electrode was fabricated by inserting a piece of nickel rod (Stream, geometric area 0.080 cm2) into a Teflon tube. The electrode was polished successively with increasingly finer grades of energy paper followed by silicon carbide grit, and finally to a mirror finish with an aqueous slurry of 0.05 μm alumina, rinsed with distilled water, and dried under vacuum. Bulk electrodeposits were prepared on nickel foils (0.5 × 0.5 cm, Aldrich, 99.99%). For voltammetry, the counter electrode was a zinc spiral (Aldrich, 99.99%) immersed in a pure 50-50 mol % ZnCl2-EMIC melt contained in a fritted glass tube. For electrodeposition experiments, the counter electrode was a piece of tellurium plate directly immersed in the bulk solution. The reference electrode was a zinc wire placed in a separate fritted glass tube containing pure 50-50 mol % ZnCl2-EMIC melt. A Hitachi S-4200 field effect scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS) working at 15 kV was used to examine the surface topography and the elemental compositions of the electrodeposits. A Shimadzu XD-D1 X-ray diffractometer was used to study the crystalline phases of the Zn-Te electrodeposits. Samples for XRD studies were prepared on nickel plates and held in the sample compartment with clay substrate. Optical measurements of Zn-Te samples were carried out with a Hewlett-Packard model 8452A diode array spectrophotometer. Photocurrent experiments of the Zn-Te deposits were carried out in 0.1 N S/S2- solutions prepared by dissolution of Na2S·9H2O and S in deionized water. Impedance measurements for the Mott-Schottky plot were performed with an EG&G model 263A potentiostat connected to an EG&G model 5210 lock-in amplifier operated in a frequency range between 0.05 and

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Figure 1. Staircase cyclic voltammograms of 50 mM Te(IV) in 40-60 mol % ZnCl₂-EMIC melt at nickel electrode at 80°C: (—) before addition of oxine, (—) after addition of 50 mM oxine. Scan rate 50 mV s⁻¹.

5000 Hz using an EG&G model 398 software. For photocurrent experiments, an Ag/AgCl (3 M NaCl俚) reference electrode and a platinum wire counter electrode were used, and the light source was a 50 W halogen lamp.

Chemicals.—The EMIC was prepared and purified according to the method described in the literature.³ The ZnCl₂-EMIC melts were prepared in a glove box by mixing proper amounts of ZnCl₂ (99.99%, Aldrich) and EMIC in breakers followed by heating at 100°C for 2 days. Anhydrous TeCl₄ (99.9%) and anhydrous propylene carbonate (PC, 98%), purchased from Aldrich, were used as received. Standard ZnTe powders was received from Stream. Oxine (8-quinolinol) was obtained from Reidel-de-Haen and used as received.

Results and Discussion

Voltammetric studies.—Initially the 50-50 mol % ZnCl₂-EMIC melt was chosen for this study because of its low melting temperature which is near room temperature. However, the solubility of TeCl₄ in this melt was found to be low even when the temperature was raised above 80°C. Other preliminary experiments showed that the solubility of TeCl₄ could be increased by decreasing the melt acidity. Consequently, to have a reasonable Te(IV) concentration in the melt solution, a less acidic (40-60 mol %) ZnCl₂-EMIC melt was employed in this study. The dissolution of TeCl₄ into the 40-60 mol % ZnCl₂-EMIC melt produces yellow solutions. A typical staircase cyclic voltammogram recorded within a potential range from 1.80 to 0.40 V for 50 mM of TeCl₄ in a 40-60 mol % ZnCl₂-EMIC melt at nickel electrode at 80°C: (—) before addition of oxine, (—) after addition of 50 mM oxine. Scan rate 50 mV s⁻¹.

For electrodeposition, complexing agents are frequently added to the electrolyte to improve the quality of the electrodeposits. In this work, the effect of a common ligand, 8-quinolinol (oxine), was studied. A typical cyclic voltammogram for 50 mM of TeCl₄ in the 40-60 mol % ZnCl₂-EMIC melt containing oxine at a nickel electrode is also shown in Fig. 1. It was observed that the introducing of oxine into the solution led to a decrease in the peak height of wave c₁, whereas a new reduction wave appeared at a potential of about 0.71 V. Eventually, wave c₁ disappeared completely when the introduced number of moles of oxine was equal to or more than that of TeCl₄. This indicates that oxine complexed with Te(IV) and rendered the reduction of Te(IV) to shift to a more negative potential.

Pure 40-60 mol % ZnCl₂-EMIC ionic liquid exhibits a melting temperature higher than room temperature and has to be used at a temperature near or higher than 80°C so that the viscosity of the melt is low enough. It has been shown² that the addition of propylene carbonate (PC) as a cosolvent to this melt can produce a mixture that is liquid at room temperature. The viscosity of this mixture is also lower than the pure melt. In this study, a melt/PC mixture containing 50% (w/w) PC and sufficient amounts of oxine was employed, and the electrochemistry and electrodeposition experiments were performed at 40°C.

Figure 2A shows the typical staircase cyclic voltammograms recorded at a nickel electrode for a melt/PC solution containing 30 mM Te(IV). This figure shows that in addition to waves c₁ and a₁ that are due to the deposition and stripping of tellurium, another
reduction wave, \( c_2 \), at a peak potential of about \(-0.10\) V appears when the cathodic potential scan is extended to \(-0.2\) V. Associated with this wave are an anodic wave, \( a_2 \), at about 0.70 V and a wave, \( a'_2 \), overlapping with wave \( a_2 \). Results from EDS analysis of the electrodeposits that were obtained by constant potential electrolysis at potentials right after wave \( c_2 \) revealed that the deposits contained both zinc and tellurium, indicating that zinc is also deposited at this wave. Because wave \( c_2 \) occurs at potentials more positive than the potential for bulk deposition of zinc, wave \( c_2 \) may arise from the underpotential deposition (UPD) of zinc on tellurium

\[
\text{Zn}^{2+} + \text{Te} + 2e^- \rightarrow \text{Zn} + \text{Te}
\]

[2]

Because UPD of zinc can also occur at nickel substrate, it is possible that wave \( c_2 \) may result from the UPD of zinc on nickel instead of tellurium. In order to verify that the UPD of zinc on tellurium does occur at wave \( c_2 \), cyclic voltammograms for the same solution as in Fig. 2A were also recorded on a glassy carbon electrode (GCE). It has been reported that UPD of zinc did not occur on the GCE. One of the typical cyclic voltammograms recorded on the GCE is shown in Fig. 2B. As shown in this figure, wave \( c_2 \) also occurs on the GCE at the same potential as that observed at the nickel electrode.

Furthermore, wave \( c_2 \) is also observed in the cyclic voltammogram (inset in Fig. 2) recorded on a solid tellurium electrode (surface area not known) immersed in a 40.0-60.0 mol % ZnCl₄·EMIC melt containing no Te(IV). Taken together, these results suggest that the UPD of Zn on Te does occur at wave \( c_2 \). UPD is expected when the work function, \( \phi \), of the deposited metal is smaller than that of the substrate. Considering the work function of these two elements, the UPD of zinc (\( \phi_{\text{Zn}} = 4.33 \) eV) on tellurium (\( \phi_{\text{Te}} = 4.95 \) eV) is not unexpected. Electrodeposition of Zn-Tl thin film through UPD of Zn on Te has also been reported in aqueous bath.

Figure 2A shows that when the cathodic potential scan is extended to \(-0.6\) V, an additional reduction wave, \( c_1 \), which increases in magnitude with increasing Te(IV) concentration of the solution, appears at about \(-0.5\) V before the onset of bulk electrodeposition of zinc. This reduction wave can be ascribed to the further reduction of the Te deposit layer to Te²⁻. In a separate experiment, cyclic voltammograms were recorded on a Te-coated GCE that was immersed in a Te(IV)-free 33-67 mol % ZnCl₂·EMIC melt [in which Zn(II) exists as ZnCl₄²⁻ which is not reducible within the electrochemical window of the melt]. These cyclic voltammograms (not shown) revealed a cathodic stripping peak close to the potential of wave \( c_1 \). Upon addition of ZnCl₂ to this melt after all the Te deposits were stripped off from the electrode, black precipitates were obtained. EDS and XRD analysis of these precipitates indicated that they contained both Zn and Te. These results suggest that the Te²⁻ species produced at wave \( c_1 \) can react with Zn²⁺ to form Zn₉Te or Te and Zn, respectively.

\[
\text{Te} + 2e^- \rightarrow \text{Te}^{2-}
\]

[3]

\[
p\text{Te}^{2-} + p\text{Zn}^{2+} \rightarrow q\text{ZnTe} + (p - q)\text{Zn} + (p - q)\text{Te}
\]

[4]

The reduction of Te to Te²⁻ species is well documented in previous investigations performed in aqueous baths and has been observed also in basic AlCl₃·EMIC room-temperature molten salts.

The last reduction wave, \( c_3 \), shown in Fig. 2A is due to the bulk electrodeposition of zinc which starts at a potential of \(-0.70\) V. The bulk zinc deposits obtained at this wave could be oxidized at wave \( a_2 \). It should be pointed out that the potential at which the bulk zinc deposition occurred in the melt/PC/oxine solution containing Te(IV) is more negative than that in the absence of Te(IV). This is probably because the conductivity of the Te and Zn-Te deposits formed at waves \( c_1, c_2 \), and \( c_3 \) are low and thus, lead to a larger overpotential required for the deposition of bulk zinc.

Figure 3. Variation of the composition of Zn-Te electrodeposits with applied potential in the 40-60 mol % ZnCl₂·EMIC melt containing 50 wt % PC and 50 mM oxine having Te(IV) concentrations of (○) 20 and (●) 50 mM. Deposition temperature 40°C.

Preparation and characterization of Zn-Te electrodeposits. -Zn-Te electrodeposits were prepared at 40°C using constant potential electrolysis on thin nickel foils (0.5 × 0.5 cm) at potentials ranging from \(-0.07 \) to \(-0.8\) V from 40-60 mol % ZnCl₂·EMIC/PC/oxine solutions containing 20 and 50 mM Te(IV), respectively. For all the deposition experiments, the solution was purged (2.4 ccm/min) and the cell was placed in a perfluoralkoxy (PFA) cell jacket immersed in a 50°C bath. The compositions of the Zn-Te electrodeposits analyzed by EDS were plotted as a function of deposition potential shown in Fig. 3. This figure shows that as the applied potential approaches \(-0.2\) V, which is the point at which the UPD of zinc on tellurium starts (i.e., wave \( c_2 \) in Fig. 2), the atomic percentage of zinc in the deposits increases rapidly and becomes relatively independent of the applied potential in the potential region between \(-0.4\) and \(-0.65\) V. Because both Zn and Te are not soluble into the other, the only compound formed should be ZnTe. Any electrodeposits that have composition deviating from 50% will have to be two phases, ZnTe + Zn or ZnTe + Zn. At potentials more negative than \(-0.65\) V the zinc content in the deposits increases again because the bulk deposition of zinc occurs at these potentials. In addition, the zinc content in the electrodeposits obtained between \(-0.4\) and \(-0.65\) V is dependent on the Te(IV) concentration in the plating bath; a lower Te(IV) concentration in the bath results in a higher zinc atomic fraction in the deposits. Because the concentration of Zn(II) ion in large excess over the Te(IV) concentration in the solution, it is expected that the zinc content in the deposits is independent of the Te(IV) concentration and the rate of codeposition of Zn-Te is determined by the mass-transport-limited reduction of Te(IV), similar to those discussed in the codeposition of Al-Ni alloys from acidic AlCl₃-NaCl melts and Al-Cu alloys from acidic AlCl₃-EMIC.
melts. In contrast, the results shown in Fig. 3 indicate that the zinc cannot keep up with the mass-transport-controlled deposition of tellurium. Similar behavior has been reported for the electrodeposition of Al-Ni and Al-Co alloys from acidic AlCl₃-EMIC melts.

As indicated in Fig. 3, it is possible to prepare Zn-Te electrodeposits in the 40-60 mol % ZnCl₂-EMIC/PC/oxine solution with an atomic fraction of zinc approaching 0.5 if the Te concentration is estimated from the intercept of \( I^2 \) on the \( V \) axis. The data shown in the XRD patterns recorded for an electrodeposited Zn-Te sample that has an atomic fraction of zinc of 0.5 is displayed in Fig. 5. The photocurrent of the electrodeposited Zn-Te samples was measured. These measurements were carried out in a dark room using a three-electrode cell, with the ZnTe deposited Ni plate as the working electrode, containing 0.1 N S/S²⁻ as the electrolyte.

The XRD pattern of the as-deposited Zn-Te electrodeposits that are prepared from a 40-60 mol % ZnCl₂-EMIC melt containing 50 wt % PC, 50 mM oxine, and 50 mM Te(IV) before annealing; (c) the Zn-Te electrodeposits that were annealed at 350°C for 2 h, and (d) the ZnTe standard powders. (●) Reflections for ZnTe, (△) reflections for Te, and (S) reflections for clay substrate.

The three-electrode cell was used with the electrodeposits on the nickel substrate as the working electrode. In each experiment, at different applied potentials, \( V \), dark current was measured first, and then photocurrent was measured using a three-electrode cell containing 0.1 N S/S²⁻. The square of the measured photocurrent, \( I^2 \), was plotted as a function of the applied potentials as shown in Fig. 6. According to the equation

\[
I^2 = \text{constant} \cdot (V - V_{FB}) \tag{5}
\]

the flatband potential, \( V_{FB} \), of the Zn-Te electrodeposits can be estimated from the intercept of \( I^2 \) on the \( V \) axis.

Figure 4. XRD patterns (Cu Kα) of (a) nickel substrate; (b) the Zn-Te electrodeposits on nickel substrate obtained from 40-60 mol % ZnCl₂-EMIC melt containing 50 wt % PC, 50 mM oxine, and 50 mM Te(IV) before annealing; (c) the Zn-Te electrodeposits that were annealed at 350°C for 2 h, and (d) the ZnTe standard powders. (●) Reflections for ZnTe, (△) reflections for Te, and (S) reflections for clay substrate.

Figure 5. Scanning electron micrograph of Zn-Te electrodeposits (Zn atomic fraction 0.5) annealed at 350°C for 2 h. The electrodeposits were prepared from a 40-60 mol % ZnCl₂-EMIC melt containing 50 wt % PC, 50 mM oxine, and 50 mM Te(IV) at 40°C.

Figure 6. Photocurrent vs. electrode potential recorded on Zn-Te electrodeposits obtained from the 40-60 mol % ZnCl₂-EMIC melt containing 50 wt % PC, 50 mM oxine, and 50 mM Te(IV) at 40°C.
40-60 mol % ZnCl₂-EMIC melt containing 50 wt % PC, 50 mM oxine, and 50 mM Te(IV) at 40°C. The Zn-Te electrodeposits were annealed at 350°C for 2 h.

Fig. 6 indicates that the $V_{FB}$ of the Zn-Te electrodeposit is about −0.69 V. In addition, Fig. 6 shows that the photocurrent increases as the applied potential becomes more negative, suggesting that the Zn-Te deposit is of p-type semiconductor.

Another popular method for the determination of $V_{FB}$ is based on the measurement of the potential dependence of the space-charge region capacity $C_{sc}$, which can be obtained from impedance measurements, according to the Mott-Schottky equation:

$$C_{sc}^{-2} = \text{constant}(V - V_{FB})$$  \[6\]

Similar to the photocurrent experiments, the impedance experiments were performed in a dark room using a cell containing 0.1 N S/S₂ solution with the electrodeposited nickel plate as the working electrode, and the impedance diagrams were obtained at various frequencies and potentials. Based on the values of $C_{sc}$ determined from impedance measurements in a frequency range of 0.5-5000 Hz, a Mott-Schottky plot as shown in Fig. 7 was constructed for the Zn-Te electrodeposited sample. The sign of the slope of this plot indicates that the Zn-Te electrodeposited is p-type and the $V_{FB}$ determined from this plot is −0.67 V. The results obtained from the Mott-Schottky plot are in good agreement with those obtained from the photocurrent method.

The optical absorption spectrum of the electrodeposited Zn-Te was recorded in order to determine the optical bandgap, $E_g$, of the Zn-Te electrodeposits by using the following equation:

$$(Ahv)^n = \text{constant}(hv - E_g)$$  \[7\]

where $A$ is the absorbance, $h$ is Plank’s constant, and $n$ is the frequency, and $n = 1/2$ for indirect and $n = 2$ for direct optical transitions. For each experiment, the ZnTe electrodeposits were carefully scratched off the nickel substrate and mixed thoroughly with KBr powders. The mixture was pressed in a die to yield a transparent disk. The disk is then held in the sample compartment of the UV-vis instrument for spectroscopic measurement in the wavelength between 280 and 800 nm. The spectroscopic data were then transformed into a plot of $(Ahv)^2$ vs. $hv$. As shown in Fig. 8, from the values of the optical absorbance measured for the electrodeposited Zn-Te sample, a good fitting was obtained for the plot of $(Ahv)^2$ vs. $hv$, indicating a direct transition. The value for $E_g$ derived from this plot was 2.3 eV, which agrees well with those reported in the literature (2.26 and 2.21 eV) for ZnTe.

**Conclusions**

Voltammetric investigations on the electrodeposition of Zn-Te from the 40-60 mol % ZnCl₂-EMIC molten salt containing 50 wt % PC were carried out at nickel substrate at 40°C. UPD of zinc on tellurium plays an important role in the electrodeposition of Zn-Te. The composition of the Zn-Te electrodeposits varies with the applied potential and Te(IV) concentration in the plating solution. The Zn-Te electrodeposits require annealing in order to exhibit the characteristic XRD patterns for the cubic ZnTe. Results from photocurrent experiments and Mott-Schottky experiments indicate that the Zn-Te electrodeposits are of p-type semiconductors. The optical bandgap of the Zn-Te electrodeposits is determined to be 2.3 eV.

**Acknowledgment**

This research was supported by the National Science Council of the Republic of China, Taiwan, under grant no. NSC89-2113-M0006-035. Helpful discussion with Professor M.-C. Yang of the Department of Chemical Engineering, National Cheng-Kung University, is acknowledged.

National Cheng-Kung University assisted in meeting the publication costs of this article.

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