



Electrodeposition behaviour of cadmium telluride from 1-ethyl-3-methylimidazolium chloride tetrafluoroborate ionic liquid

S.-I. HSIU and I.-W. SUN*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, ROC

(*author for correspondence, e-mail: iwsun@mail.ncku.edu.tw)

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Abstract

Voltammetry at a glassy carbon electrode was used to study the electrochemical deposition of Cd–Te from the Lewis basic 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate air-stable room temperature ionic liquid between 80 °C and 140 °C. Deposition of tellurium alone occurs through a four-electron reduction of Te(IV) to Te which could be further reduced to Te(-II) at a more negative potential. The Cd–Te electrodeposits could be obtained by the underpotential deposition (UPD) of Cd on the deposited Te. The UPD of Cd on Te was, however, limited by a slow charge transfer rate. Samples of Cd–Te electrodeposits were prepared on tungsten and titanium substrates and characterized by energy dispersive spectroscopy (EDS), scanning electron microscope (SEM), and X-ray powder diffraction (XRD). The results showed that an excess amount of Cd(II) was required in order to prepare CdTe codeposits with a Cd/Te atomic ratio approached 1/1. The deposit composition was independent of the deposition potential within the Cd UPD range. Raising the deposition temperature increased the UPD rate of Cd and promoted the formation polycrystalline CdTe.

1. Introduction

Cadmium telluride (CdTe) is a well-known II–VI semiconductor that is suitable for solar cells [1]. Historically, acidic aqueous sulfate solutions [2–7] with a pH of 0 to 2 are usually employed for electrodeposition of CdTe, even though the deposition rate is low due to the very limited solubility of Te(IV) species in the acid bath. On the other hand, the solubility of Te(IV) as TeO_3^{2-} ion is fairly high in alkaline solution with pH of 10 and successful electrodeposition of CdTe has been demonstrated recently in ammonia-alkaline solutions containing Cd(II) and Te(IV) species [8]. However, the use of strong acid and alkaline solutions for electrodeposition could be potentially dangerous because these solutions are corrosive and hazardous. In view of this, nonaqueous plating baths for the electrodeposition of CdTe have been investigated. For example, the deposition of CdTe from propylene carbonate media was attempted, but the resulting CdTe was amorphous [9]. On the other hand, stoichiometric crystalline CdTe film was obtained by electrodeposition from ethyl glycol solution at 160 °C [10]. Electrodeposition of CdTe has also been investigated in inorganic molten salts such as LiCl–KCl [11]. Although good crystalline CdTe was obtained from these high temperature molten salts, corrosion problems and vapourization of the Te species at such high temperature were noticed.

Ambient temperature ionic liquids have received attention as replacements for classic molecular solvents in fundamental research and applications including electrochemistry, catalysis, separations, and organic synthesis [12–16]. Unlike the conventional molecular solvents, ionic liquids exhibit good electrical conductivity and wide electrochemical windows. Moreover, ionic liquids are usually nonvolatile, nonflammable, and highly thermal stable. Examples of the use of ionic liquids for electrodeposition of metals and alloys can be found in recent reviews [17, 18]. Examples of the electrodeposition of semiconductors from ionic liquids are relatively fewer [19–22]. One of the advantages of using ionic liquids instead of aqueous baths is that the thermal stability of the ionic liquids makes it easier to electrodeposit crystalline semiconductors through direct electrodeposition at higher temperatures without subsequent annealing. Historically, most electrochemical studies that were carried out in ambient temperature ionic liquids employed the water and air-sensitive chloroaluminate systems. The use of air-stable ionic liquids such as the 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate (EMI–Cl–BF₄) for electrochemistry is, however, becoming well established [23–28]. This work studies the electrodeposition behaviour of CdTe from a chloride-rich EMI–Cl–BF₄ ionic liquid. The effects of deposition potential, plating bath concentrations, and deposition temperature on the

composition and morphologies of the electrodeposits were examined.

2. Experimental details

2.1. Apparatus

All electrochemical experiments were conducted in a N_2 -filled glove-box system (Vacuum Atmosphere Co.) in which the moisture and oxygen contents were kept below 1 ppm. The electrochemical experiments were accomplished by an EG & G Princeton Applied Research Corporation (PAR) model 273A potentiostat controlled by EG & G PAR model 270 software. A three-electrode cell was used for electrochemical experiments. For static voltammetry, the working electrode was a glassy carbon (GC) ($A = 0.07 \text{ cm}^2$) disc electrode. The counter electrode was an aluminum (Aldrich, 99.99%) spiral immersed in the pure ionic liquid contained in a glass tube having a fine porosity tip. The reference electrode was an aluminium wire immersed in a 60–40 mol % $AlCl_3$ -EMIC ionic liquid contained in the same type of glass tube as the counter electrode. A Pine model AFMSR electrode rotator was employed for rotating disc electrode voltammetry. Electrodeposition experiments were conducted on tungsten and titanium plates (Aldrich 99.99%). A Hitachi S-4200 field effect scanning electron microscope (SEM) with an energy dispersive spectroscope (EDS) working at 15 kV was used to examine the surface morphology of the electrodeposits. The crystalline phases of the deposits were studied with a Shimadzu XD-D1 X-ray diffractometer (XRD).

2.2. Chemicals

1-ethyl-3-methylimidazolium chloride was prepared and purified according to the literature [29]. Sodium tetrafluoroborate (Aldrich, 98%), anhydrous $CdCl_2$ (Aldrich, 99.9%), anhydrous $TeCl_4$ (Stream, 99.9%) were used as received. The EMI-Cl-BF₄ ionic liquid was prepared by direct reaction of appropriate amounts of EMIC and NaBF₄ in acetone. The ionic liquid used in this study contains 0.80 M chloride, which was introduced by dissolution of EMIC.

3. Results and discussion

3.1. Voltammetric behaviour of Te(IV) and Cd(II)

Both $TeCl_4$ and $CdCl_2$ dissolve readily in basic EMI-Cl-BF₄ ionic liquids. Previous literature indicated that Te(IV) and Cd(II) exist as $[TeCl_6]^{2-}$ and $[CdCl_4]^{2-}$ complex anions, respectively, in chloride-rich ionic liquids [24, 30]. A typical cyclic voltammogram recorded at a glassy carbon electrode for 5 mM Te(IV) in the basic EMI-Cl-BF₄ ionic liquid at 140 °C is shown in Fig-

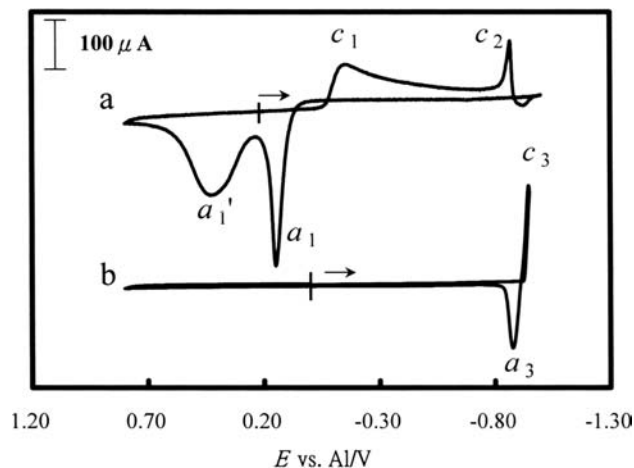


Fig. 1. Cyclic voltammograms of (a) 5 mM Te(IV) and (b) 20 mM Cd(II) at a GC electrode in basic EMI-Cl-BF₄ ionic liquid at 140 °C. Potential scan rate 100 mV s⁻¹.

ure 1(a). Two cathodic waves (c_1 and c_2) and two anodic waves (a_1 , a_1') can be seen. Data collected from cyclic voltammetry, controlled potential electrolysis, and XRD experiments reveal that the electrochemical behaviour of Te(IV) in this ionic liquid is essentially the same as those observed for Te(IV) in basic $AlCl_3$ -EMIC ionic liquids [30]. Thus, it can be concluded that wave c_1 is due to the electroreduction of Te(IV) to Te whereas waves a_1 and a_1' are due to the anodic stripping of the Te deposits that are directly in contact with the electrode and the bulk Te deposits, respectively. The electrodeposited Te can be further reduced to Te(-II) at wave c_2 . Because the Te(-II) generated at wave c_2 reacts with the Te(IV) in the vicinity of the electrode surface to form Te, an anodic wave due to the re-oxidation of Te(-II) to Te is not seen during the reverse scan.

The electrochemistry of Cd(II) in the basic EMI-Cl-BF₄ ionic liquid has been studied previously [24] and a typical cyclic voltammogram of 20 mM Cd(II) at a glassy carbon electrode in the basic EMI-Cl-BF₄ ionic liquid at 140 °C is presented in Figure 1(b) for illustration. The cyclic voltammograms in Figure 1 reveal that the redox reaction of the Cd(II)/Cd couple (waves c_3 and a_3) occurs at a potential more negative than those of the Te(IV)/Te and Te/Te(-II) couples.

Figure 2(a) shows the cyclic voltammogram of a solution containing 5 mM Te(IV) and 100 mM Cd(II) in the basic EMI-Cl-BF₄ ionic liquid at 140 °C. The potential was initially scanned negatively and reversed prior to the bulk deposition of cadmium. The Cd(II)/Cd redox reaction (waves c_3 and a_3) has shifted to more negative potential so that it is not seen in this Figure. Furthermore, Figure 2 indicates that the presence of Cd(II) results in new redox waves (waves c_4 and a_4) in addition to the waves that are due to the Te(IV)/Te and Te/Te(-II) couples. The EDS data of the electrodeposits obtained by constant potential electrolysis at the peak of wave c_4 revealed that the deposits contained both Te and Cd, indicating that Cd was codeposited with Te.

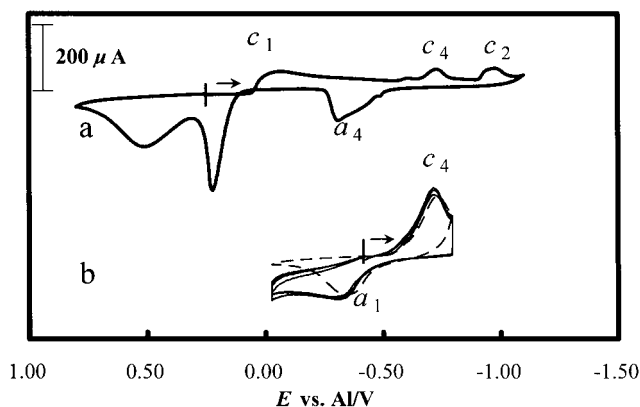
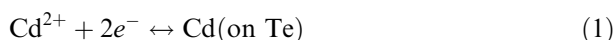


Fig. 2. Cyclic voltammograms of (a) 5 mM Te(IV) and 100 mM Cd(II) recorded at a GC electrode and (b) 200 mM Cd(II) at a Te lump electrode (surface area not known) at 140 °C. In (b), the potential was hold after wave c_4 for 0, 30, 60, 120 and 240 s before reverse. Potential scan rate 100 mV s⁻¹.

Because wave c_4 occurs at a potential more positive than the potential for bulk deposition of Cd, it may arise from the underpotential deposition (UPD) of Cd on Te, and the associated wave a_4 is due to the anodic stripping of the underpotential deposited Cd as depicted by the following equation:



To verify that the UPD of Cd on Te does occur at wave c_4 , cyclic voltammograms of an ionic liquid contained only Cd(II) were recorded at a large solid tellurium lump electrode (surface area not known). As shown in Figure 2(b), waves c_4 and a_4 are clearly seen in this voltammogram. It is found that prolonging the deposition time at wave c_4 does not increase the anodic current (or the accumulated charge) of wave a_4 , indicating that once the cadmium layer becomes thicker than one layer, deposition no longer occurs, which is typical for a UPD behaviour.

Rotating disc electrode cyclic voltammetry (RDECV) was also employed to study the UPD of Cd at Te. Because the RDE used in this study is stable only at temperatures below 80 °C, the experiments were conducted at 70 °C. For comparison a RDE cyclic voltammogram (Figure 3(a)) of a 200 mM Cd(II) solution in the absence of Te(IV) was recorded at a bare GCRDE to show the bulk deposition/stripping of Cd (peaks c_3 and a_3) at this temperature. The UPD behaviour was studied at the GCRDE that had been preelectrodeposited with a thin film of tellurium. A typical RDE cyclic voltammogram recorded at such a Te-coated electrode in a pure basic EMI-Cl-BF₄ ionic liquid is presented in Figure 3(b). This Figure shows only a sharp cathodic peak (c_2) due to the reduction of the Te deposits to Te(-II) species. Because Te(-II) is soluble in the ionic liquid, it is swept away from the electrode surface as soon as it is generated from the reduction of Te. As a result, the oxidation wave of Te(-II) is not observed during the reverse scan in this Figure. When the pure ionic liquid is

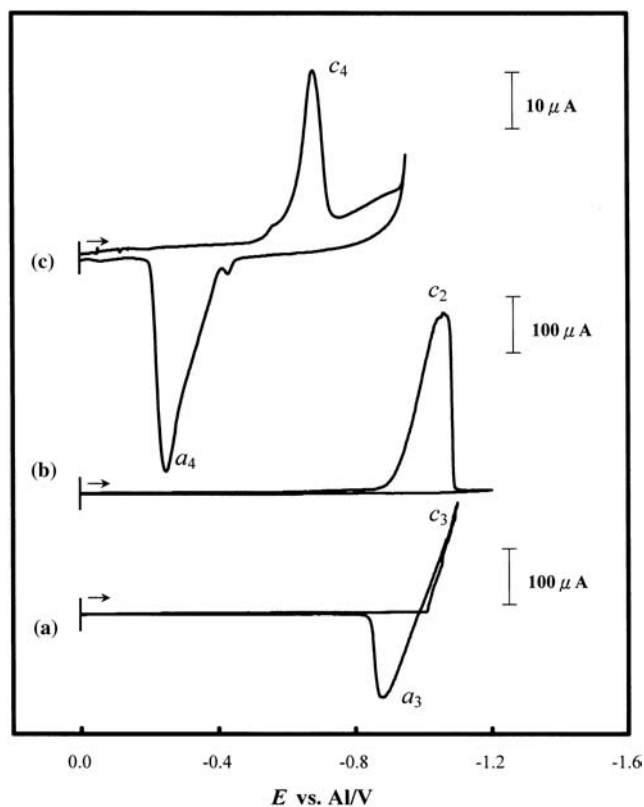


Fig. 3. Rotating disc electrode cyclic voltammograms of (a) 200 mM Cd(II) in ionic liquid at a GCRDE, (b) pure ionic liquid at a Te-coated GCRDE, and (c) 200 mM Cd(II) in ionic liquid at a Te-coated GCRDE. Temperature 140 °C; potential scan rate 5 mV s⁻¹.

replaced with a 200 mM Cd(II) solution, the RDE cyclic voltammogram as shown in Figure 3(c) was obtained at the Te-coated electrode. This voltammogram indicates that peak c_4 appears prior to the Te/Te(-II) couple (wave c_2) and the bulk overpotential-driven electrodeposition of Cd (wave c_3). Under the convective-diffusion condition of RDECV, the symmetrical peak shape of c_4 , rather than a sigmoid wave, is consistent with the UPD of a film on the electrode surface; that is, the deposition stops when a limited layer of the deposit is produced. The appearance of the anodic stripping peak a_4 during the reverse scan also confirms the formation of an insoluble film on the electrode surface at wave c_4 . Taken together, the above results strongly suggest that wave c_4 is due to the UPD of Cd on Te. Because the free energy change for the formation of CdTe from Cd and Te is -92.5 kJ mol⁻¹, the UPD of Cd on Te is expected. UPD can also be related to the fact that the work function of the electrodeposited metal ($\phi_{\text{Cd}} = 4.22$ eV) is smaller than the work function of the electrode material ($\phi_{\text{Te}} = 4.95$ eV). UPD of Cd on Te has also been observed in aqueous solutions [7, 8].

Previous literature on the electrodeposition of CdTe from aqueous solutions [7, 8] showed that Cd(II) species may adsorb on the electrode surface and suppress the bulk deposition of Te. This kind of behaviour was also observed in this study. Table 1 collects the peak currents of Te(IV)/Te redox couple measured from the cyclic

Table 1. Peak currents of Te(IV)/Te and Te/Te(-II) redox couples and UPD of Cd(II)/Cd measured from the cyclic voltammograms recorded at in EMI-Cl-BF₄ ionic liquid containing 5 mM Te(IV) and various amounts of Cd(II) at 140 °C

Cd(II) concentration /mM	i_p of Te(IV)/Te/ μ A	i_p of Te/Te(-II)/ μ A	i_p of Cd(II)/Cd UPD/ μ A
0	146	216	–
60	113	227	111
80	110	160	116
100	107	122	117
120	94	–	114

Potential scan rate was 100 mV s⁻¹.

voltammograms recorded in the EMIC-Cl-BF₄ ionic liquid containing 5 mM Te(IV) and various amounts of Cd(II). The peak currents of the Te(IV)/Te couple diminish with increasing Cd(II) concentration because the adsorption of Cd(II) on the electrode suppresses the deposition of Te. The data in Table 1 also show that the reduction current of Te to Te(-II) decreases with increasing Cd(II) concentration, indicating that the occurrence of UPD of Cd on Te may result in the formation of CdTe and thus impedes the reduction of Te to Te(-II).

It is noticed in Figure 2 and Table 1 that the peak current of the UPD of Cd on Te (wave c_4) exhibits about the same magnitude as the peak current of the bulk deposition of Te (wave c_1), although the concentration of Cd(II) in the solution is significantly higher than that of the Te(IV). In addition, the data in Table 1 reveal that increase the Cd(II) concentration does not enhance the UPD of Cd on Te (wave c_4). Further experiments showed that increasing the Te(IV) concentration enhanced reduction of Te(IV) (wave c_1) but not the UPD of Cd (wave c_4). Taken together, these results suggest that the UPD of Cd on Te is much slower than the deposition rate of Te. Otherwise, the Cd UPD current (wave c_4) should be able to increase with increase in the Te deposition rate (wave c_1), that is, once the Te is deposited the UPD Cd should have occur immediately

Table 2. Compositions of Cd-Te electrodeposits prepared from EMI-Cl-BF₄ ionic liquid containing 0.15 mM Te(IV) and 200 mM Cd(II) at -0.70 V

Substrate	Composition expressed in Cd/Te atomic ratio		
	80 °C	120 °C	140 °C
Ti	19.0/81.0	37.9/62.1	47.4/52.6
W	13.5/86.5	34.3/65.7	48.5/51.5

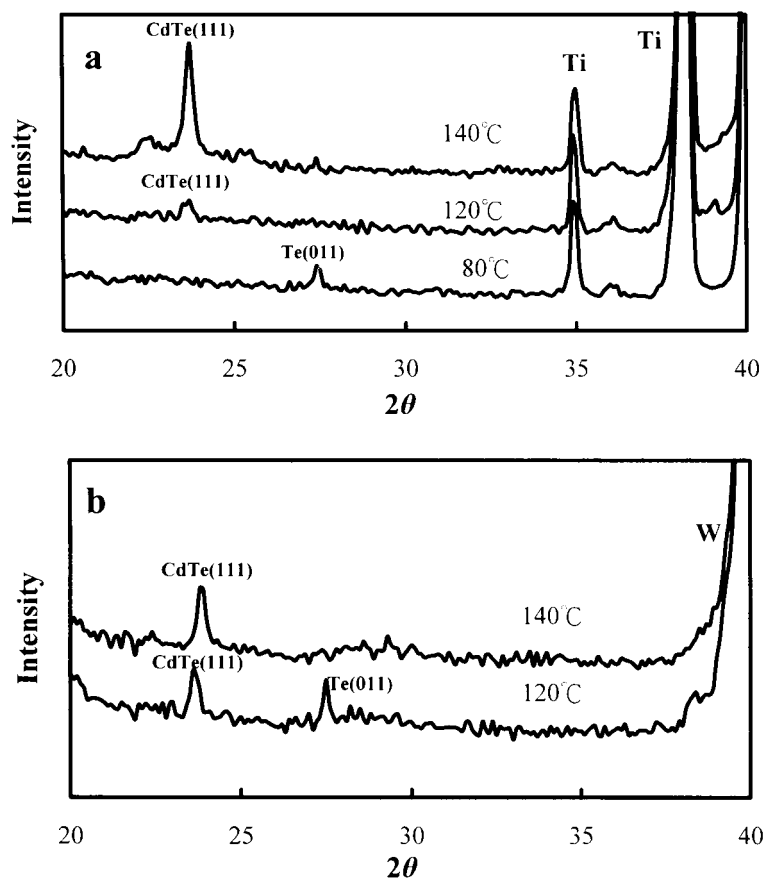


Fig. 4. XRD patterns (CuK α) of Cd-Te electrodeposits prepared at (a) titanium and (b) tungsten substrates from EMI-Cl-BF₄ ionic liquid containing 0.15 mM Te(IV) and 200 mM Cd(II) at various temperatures.

on Te if the later were faster enough. This implies that in order to obtain CdTe electrodeposits with a composition of Cd:Te close to 1:1 at the potential where UPD of Cd on Te occurs, the Cd(II) concentration must be kept much higher than that of Te(IV). On the other hand, the Cd–Te alloy may also be produced by direct reaction of Cd(II) and Te^{2-} at a more negative potential where Te is reduced to Te^{2-} (wave c_2). However, the Cd–Te deposits obtained by direct reaction of Cd(II) and Te^{2-} were very loose and did not adhere well on the electrode surface and was not further studied.

3.2. Bulk electrodeposition of CdTe

CdTe electrodeposits were prepared using constant potential electrolysis on tungsten and titanium foils ($0.5 \text{ cm} \times 0.5 \text{ cm}$) in EMI–Cl– BF_4 ionic liquids containing Te(IV) and Cd(II). Following each deposition experiment, the CdTe-coated foil was immersed in a small volume of blank ionic liquid, and transferred out of the glove box to be rinsed with deionized water to remove any residual ionic liquid. The electrodeposits were characterized by SEM, EDS and XRD analysis. The effects of deposition temperature, deposition potential, and bath composition on the electrodeposits properties were studied.

Increasing the deposition temperature may accelerate the mass transport rate of the redox species as well as the charge transfer rate of electrode reactions. As a result, the composition of the electrodeposits may be altered with temperature. Table 2 illustrates the effect of temperature on the composition of Cd–Te electrodeposits prepared on tungsten and titanium substrates from the melt containing 0.15 mM Te(IV) and 200 mM Cd(II) at 80, 120 and 140 °C at -0.70 V . Usually, increasing the deposition temperature would increase the content of the nobler element (Te in this case) in the deposit due to a faster mass transport rate at a higher temperature. However, Table 2 shows that it was the Cd content that increased significantly with increasing temperature approaching to 50 a/o. This indicates that increasing the temperature can promote the UPD of Cd on Te. The temperature effect on the crystalline nature of the CdTe electrodeposits was examined using XRD. Typical XRD patterns of the as-deposited CdTe electrodeposits obtained at different deposition temperatures are presented in Figure 4. This figure shows that the electrodeposits prepared at 80 °C produced only the characteristic diffractions of Te. However, when the deposition temperature was increased, the characteristic diffractions due to polycrystalline CdTe became obvious whereas the Te peaks reduced in magnitude. Apparently, high temperature helps the UPD of Cd on Te and the formation of CdTe compound. No XRD patterns of pure Cd were observed in the XRD patterns, suggesting that all the Cd produced during the deposition had transformed into CdTe. The surface morphologies of the electrodeposits prepared at different temperatures are shown in Figure 5. All deposits are more or less flat and

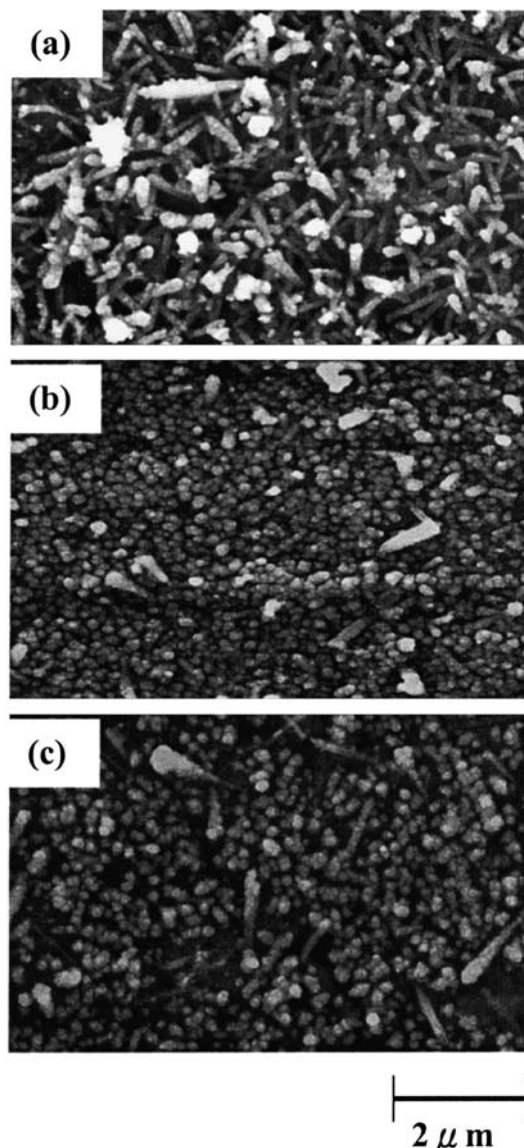


Fig. 5. SEM micrographs of Cd–Te electrodeposits prepared on titanium substrates at -0.70 V in EMI–Cl– BF_4 containing 0.15 mM Te(IV) and 200 mM Cd(II) at (a) 80 °C, (b) 120 °C and (c) 140 °C.

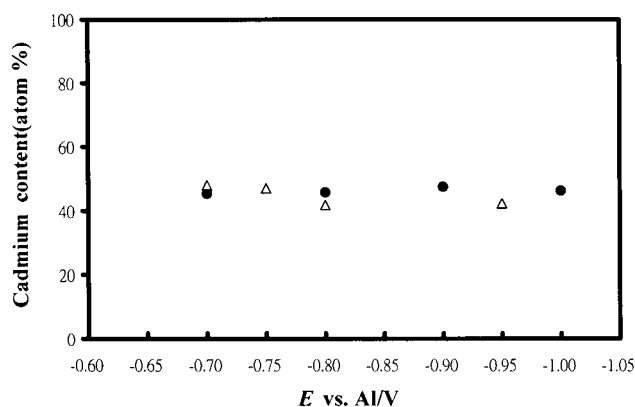


Fig. 6. Composition of Cd–Te electrodeposits prepared on (●) titanium and (Δ) tungsten substrates at 140 °C as a function of deposition potential in the basic EMI–Cl– BF_4 ionic liquid containing 0.15 mM Te(IV) and 200 mM Cd(II).

smooth. The electrodeposits obtained at 80 °C (Figure 5(a)) consisted of mainly wire-like Te crystals about 1.5–2 μm long and 200 nm wide. As shown in Figure 5(b), the deposit morphology changed when the Cd content in the deposits was increased with increasing deposition temperature to 120 °C; Te wires were replaced by CdTe grains.

The compositions of the electrodeposits obtained at 140 °C are plotted in Figure 6 as a function of deposition potential. The composition of the deposit is relatively independent of the deposition potential within

a range between -0.7 V and -1.0 V , which is the potential region for the UPD of Cd on Te. The morphologies of the electrodeposits obtained at different deposition potentials under the same conditions as Figure 6 are illustrated in Figure 7. All the electrodeposits are similar in morphology. These results indicate that precise potential control is not critical in preparing Cd–Te electrodeposits with the same composition and morphology as long as the potential falls in the -0.7 V and -1.0 V range.

As mentioned earlier, due to the slow kinetics of the UPD of Cd on Te, the Cd(II)sol/Te(IV) concentration ratio in the plating bath must be kept very high in order to obtain Cd–Te electrodeposits with a composition of Cd:Te close to 1:1. Because the solubility of Cd(II) in this melt is approximately 200 mM, the effect of bath composition on the electrodeposit composition was studied with solutions of 200 mM Cd(II) containing different concentrations of Te(IV). The results from these experiments showed that the Cd content in the electrodeposits increased with decreasing Te(IV) concentration, and a Te(IV) concentration lower than 0.15 mM is required for preparing Cd–Te deposits with a Cd content equal to or larger than 50 a/o.

4. Summary and conclusion

In this initial study, 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate ionic liquid was investigated as the electrolyte for electrodeposition of CdTe. Voltammetry showed that the electrodeposition of CdTe was achieved by the electrochemical reduction of Te(IV) to Te followed by UPD of Cd(II) to Cd on the electrodeposited Te. The voltammetric data also showed that the UPD of Cd on Te is a kinetically limited process, and the Cd(II) concentration in the plating bath must be much higher than the Te(IV) concentration in order to increase the Cd content in the electrodeposits. The electrodeposit composition was independent of deposition potential within the Cd UPD range but could be affected by deposition temperature; increasing temperature accelerates the UPD of Cd and increases the Cd content in the electrodeposits. Results from XRD and SEM show that it is possible to prepare polycrystalline CdTe from the EMI–Cl–BF₄ ionic liquid through direct electrodeposition without subsequent annealing.

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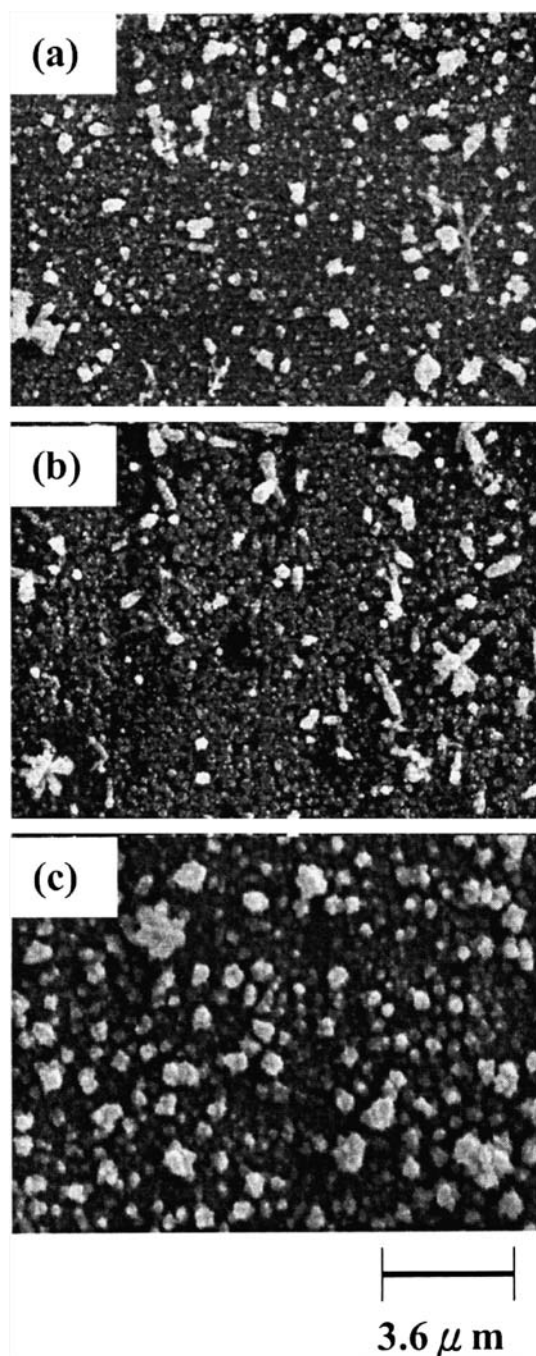


Fig. 7. SEM micrographs of Cd–Te electrodeposits prepared on titanium substrates at 140 °C in EMI–Cl–BF₄ containing 0.15 mM Te(IV) and 200 mM Cd(II) at (a) -0.70 V , (b) -0.80 V and (c) -0.95 V .

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