

Photo-assisted Electrodeposition of CdTe Film from Basic Aqueous Electrolytes

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Electrodeposition of CdTe film for photovoltaic applications has been well investigated by many research groups.¹ Although acidic aqueous sulfate solutions have historically been employed for the electrolytes in electrodeposition, we have proposed that ammoniacal basic aqueous solutions are also suitable,² since the basic solutions have a relatively high solubility of Te(IV) species as TeO_3^{2-} ions. Recently, we reported briefly³ that cathodic current for CdTe deposition was enhanced under photo-irradiation of the cathode surface. This photo-effect was observed for acidic media, but considered that the effect was more pronounced for ammoniacal media. In the present paper, we report more detailed results on the photo-assisted electrodeposition.

Aqueous basic electrolytes containing 10–100 mM CdSO_4 , 10 mM TeO_2 , 4.0 M $\text{NH}_3(\text{aq})$, and 0.5 M $(\text{NH}_4)_2\text{SO}_4$ (pH 10.7; $M = \text{mol dm}^{-3}$) were used for the electrodeposition of CdTe. Cathodic electrodeposition was performed at 70 °C under potentiostatic conditions using a conventional three electrode setup: WE, Au-plated Cu sheet; CE, Pt sheet; RE, Ag/AgCl electrode immersed in 3.3 M KCl. The electrolyte was agitated at 500 rpm with a magnetic stirring unit. The irradiation source was a 500 W xenon arc lamp and the integrated irradiance of the white light just in front of the electrolytic vessel was about 2 W cm^{-2} .

The cathodic part of the cyclic voltammogram (1st scan) for the ammoniacal bath (60 mM Cd(II) – 10 mM Te(IV)) obtained under pulsed irradiation are shown in Figure 1. Photo-response occurred at potentials negative of -0.3 V vs. SHE . On the anodic scan after switching at -0.75 V , the response was observed up to 0.0 V. Redox potential of CdTe deposition: $\text{Cd}(\text{NH}_3)_4^{2+} + \text{Te} + 2e = \text{CdTe} + 4\text{NH}_3$ is -0.216 V for this solution, which suggested that the photo-response was due to the CdTe deposited on the cathode surface. A wavelength dependence of photo-response during potentiostatic electrolysis also suggested that the photo-assistance is due to a photocatalytic effect of CdTe.

Both illuminated and dark conditions gave near-stoichiometric CdTe in the range from -0.74 to -0.30 V . Figure 2 summarizes SEM photos of CdTe deposits, together with compositions of the deposits and times required for the electrolysis of 1.5 C. Cd content for the illuminated condition was slightly higher than that for the corresponding dark condition and the deposits at around -0.70 V were nearly stoichiometric but slightly Cd-rich. XRD measurement revealed that the Cd-rich deposits contained small amounts of elemental Cd, which was deposited via a photo-induced underpotential deposition. Granular morphology recognized for the Cd-rich deposits was speculated to be due to the inclusion of elemental Cd.

Figure 3 shows the photo-responses of current density under periodic illumination during the electrodeposition at -0.70 V . The current under illumination was more than 20 times larger than that under dark conditions and the current efficiency for CdTe deposition was almost 100% for all conditions examined. Thus, the time required to deposit CdTe film with a sufficient thickness, 1–2 μm , was markedly shortened (see Fig. 2).

1. For example, J. L. Stickney, *Electroanalytical Chemistry*, A. J. Bard *et al.* (eds.), Marcel Dekker, NY, p. 75 (1999) and references cited therein.
2. K. Murase *et al.*, *J. Electrochem. Soc.*, **146**, 4477 (1999) and references cited therein.
3. K. Murase *et al.*, *Electrochemistry* (formerly *Denki Kagaku*), **67**, 331 (1999).

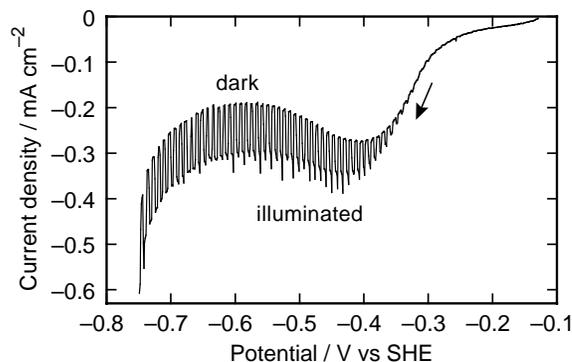
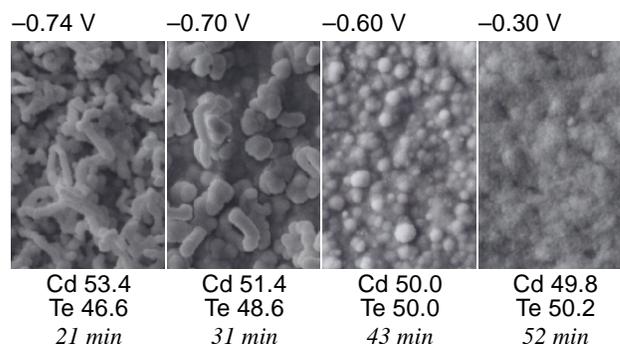


Figure 1. Cathodic polarization curve for ammoniacal solution (60 mM Cd(II), 10 mM Te(IV)) employed for CdTe deposition. Sweep rate, 10 mV s^{-1} .

(a) illuminated



(b) dark

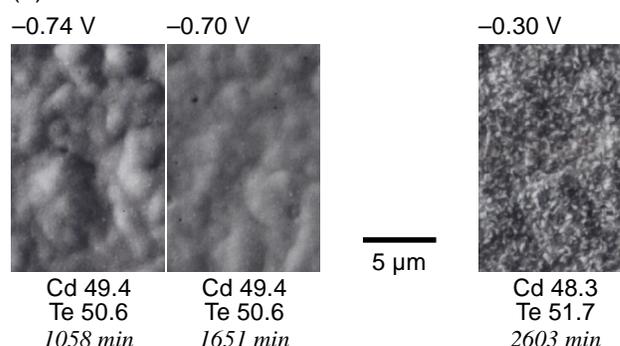


Figure 2. SEMs of CdTe deposited as various potentials from ammoniacal solution (60 mM Cd(II), 10 mM Te(IV)) under (a) illuminated or (b) dark condition. Compositions (at.%) and deposition times (see the text) are also indicated.

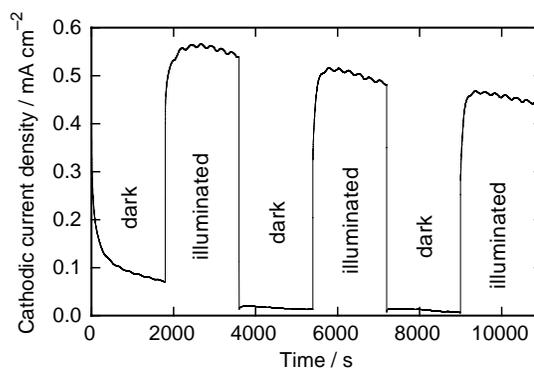


Figure 3. Photo-response of current density during potentiostatic cathodic electrodeposition of CdTe at -0.70 V from ammoniacal bath (60 mM Cd(II) – 10 mM Te(IV)).