

Electrodeposition of CdTe Thin Layer from Aqueous Media — a Comparison of Ammoniacal Basic and Acidic Sulfate Electrolytes

Kuniaki Murase*, Mikio Uematsu, Masaki Matsui, Masao Miyake, Tetsuji Hirato, and Yasuhiro Awakura
Department of Materials Science and Engineering,
Kyoto University
Sakyo-ku, Kyoto 606-8501, Japan
*e-mail murase@karma.mtl.kyoto-u.ac.jp

The thin-layered cadmium telluride (CdTe) semiconductor has been well-investigated for solar cell application, since its direct band gap of 1.44 eV is suitable for energy conversion from sunlight into electricity. In addition to some dry processes, cathodic electrodeposition of the CdTe layer has been developed and is already industrialized to form n-CdS/p-CdTe heterojunction solar cells. While acidic sulfate electrolytes have historically been employed for the CdTe electrodeposition,¹ we propose ammoniacal basic electrolytes, which have a relatively high solubility of Te(IV) species as TeO_3^{2-} ions.² Although we have endorsed the basic electrolytes in our papers, we had never tried the acidic electrolytes in practice. In this paper, we report the results of our recent comparative study regarding the morphology of the resulting CdTe as well as the photo-effect on the deposition behavior, using both ammoniacal basic and acidic sulfate electrolytes.

Table I summarizes the electrolytic conditions employed for the electrodeposition of CdTe. Cathodic electrodeposition was performed under potentiostatic conditions using a conventional three electrode setup: WE, Au-plated Cu sheet; CE, Pt sheet; RE, Ag/AgCl in 3.3 M KCl (all potentials were recalculated for SHE). The electrolyte was agitated at 500 rpm with a magnetic stirring unit. A 500 W xenon arc lamp was used, if necessary, for illuminating the cathode surface.

Figure 1 shows a set of typical X-ray diffraction patterns of CdTe. The deposit from the acidic bath gave a preferential reflection of 111 index at $2\theta = 10.9^\circ$ due to the $\langle 111 \rangle$ orientation,³ while that from the basic one gave other reflections, i.e. 220, 311, 400, 331, 422, and 531, in addition to the CdTe 111, suggesting that the CdTe crystallites from the basic bath have a random orientation. The half band width of the 111 reflection for the acidic bath is narrower than that for the basic one, indicating that the size of crystallites from the basic bath is smaller. According to Scherrer's equation, the mean crystallite size of CdTe from the basic bath lies around 10 nm. Both the basic and acidic solution gave CdTe layers with nearly stoichiometric composition at all potentials tried: from -0.74 to -0.42 V and from -0.35 to -0.21 V, respectively, and no co-deposition of elemental Te or Cd was recognized from their XRDs. Electrolysis of the acidic bath at more negative potential, e.g. -0.40 V, yielded an Cd_3Au intermetallic phase. In contrast, such an alloy formation was not found with the basic bath; the deposit at -0.75 V, for example, was only a mixture of elemental Cd and CdTe phases. This different behavior in the alloy formation may well be attributed to the different concentration, i.e. activity, of the Cd(II) species.

The cathodic part of the cyclic voltammograms (1st scan) for the basic and acidic baths obtained under pulsed irradiation are shown in Figure 2. Photo-response for the basic and acidic solutions occurred at potentials negative of -0.3 and -0.1 V, respectively, where the response for the basic media is larger than that for the acidic one. Since the CdTe deposition from the acidic bath is nearly diffusion-limiting for Te(IV), there is no room to increase the depo-

sition current even under illumination. In consequence, although the CdTe deposition from the acidic bath is faster than that from the basic one under dark conditions, the situation was reversed under illumination: the deposition from the basic bath became faster.

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. A. Kampmann, P. Cowache, J. Vedel, and D. Lincot, *J. Electroanal. Chem.*, **387**, 53 (1995).

Table I Electrolytes for CdTe deposition ($M = \text{mol dm}^{-3}$)

	Basic bath ²	Acidic bath ³
CdSO_4	40–60 mM	1.0 M
TeO_2	10 mM	300 μM
NH_3	4.0 M	–
$(\text{NH}_4)_2\text{SO}_4$	0.5 M	–
(Total ammonia)	5.0 M	
pH	10.7 (as-prepared)	2.5 (by H_2SO_4)
Temperature	70 °C (343 K)	85 °C (358 K)

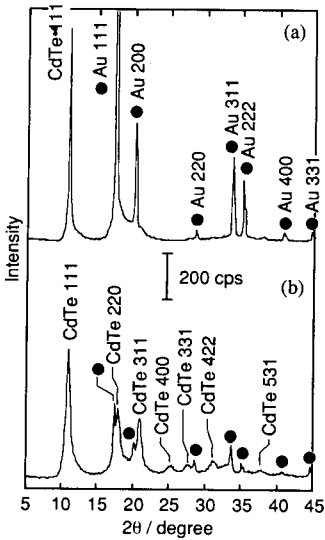


Figure 1. XRD of CdTe deposits obtained from (a) acidic and (b) basic (40 mM Cd(II)) electrolytes summarized in Table I at potentials -0.30 and -0.70 V vs. SHE, respectively. Total charges passed were (a) 1.5 C and (b) 15 C.

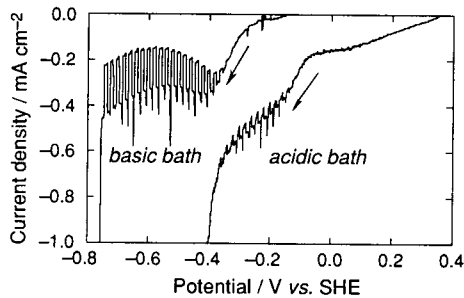


Figure 2. Cathodic polarization curves for basic (60 mM Cd(II)) and acidic electrolytes summarized in Table I.