Electrochemical Quartz Crystal Microbalance Studies of CdTe Formation and Dissolution in Ammoniacal Basic Aqueous Electrolytes

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The thin-layered CdTe semiconductor has been well-investigated for photovoltaic application. In addition to some dry processes, cathodic electrodeposition of the CdTe layer has been developed and has already been industrialized to produce n-CdS/p-CdTe heterojunction solar cells, where the CdS layer is usually prepared by chemical bath deposition. While acidic sulfate electrolytes have historically been employed for CdTe electrodeposition, we proposed ammoniacal basic electrolytes, which have a relatively high solubility of Te(IV) species as TeO_3^{2-} ions.[1-3] The electrodeposition of stoichiometric CdTe from the basic electrolytes took place at potentials positive to the Nernst potential for bulk-Cd deposition and negative to that for bulk-Te, just as with acidic electrolytes. The deposition behavior was well accounted for in terms of a potential-pH diagram for the Cd-Te-NH_3-H_2O system and deposition mechanism, where (*i*) cathodic electrodeposition of surface tellurium atoms: $TeO_3^{2-} + 6H^+ + 4e \rightarrow Te_{(ads)}$ (reaction 1) is followed by (*ii*) an immediate adsorption of Cd(II) ions on the tellurium, and (*iii*) underpotential deposition of Cd(II) to form CdTe: $Cd(II) + Te_{(ads)} + 2e \rightarrow CdTe$ (reaction 2).[2] In the present work, the electrochemical CdTe deposition and dissolution behaviors were examined by an *in-situ* method using an electrochemical quartz crystal microbalance (EQCM).

Aqueous solution containing 60 mM $CdSO_4$, 10 mM TeO_2, 4.0 M NH_3, and 0.5 M $(NH_4)_2SO_4$ (pH 10.7; M = mol dm^{-3}) was used as a typical basic electrolyte for CdTe deposition.[2] All electrochemical investigations were performed at 70 ˚C using a conventional three-electrode cell: WE, 9 MHz AT-cut QCM with sputtered Au electrodes (working area 0.196 cm^2) on both sides; CE, Pt-sheet; RE, Ag/AgCl in 3.33 M (all potentials were re-calculated for SHE). The electrolyte was agitated at 500 rpm with a magnetic stirring unit.

Figure 1 shows cyclic voltammogram (CV) for the electrolyte together with the frequency f of QCM during the CV scan and a part of the potential-pH diagram for the Cd-Te-NH_3-H_2O system. The diagram indicates that CdTe is stable at potentials negative to –0.2 V at pH 10.7 and the cathodic current and frequency change (Δf) which appeared from A to B corresponds to CdTe deposition. The amount of deposited CdTe calculated from Δf was, however, smaller than that expected from the charge passed during cathodic scan by assuming a 6-electron (n = 6) deposition of CdTe (formula weight M = 240.0). This is due to the occurrence of side reaction, *i.e.* reduction of dissolved oxygen. Cathodic current after subtracting the contribution of the oxygen reduction estimated from CV for the same ammoniacal buffer without Cd(II) and Te(IV) ions, gave almost equal mass change as that obtained from Δf.

One of the important features of the potential-pH diagram is the presence of a narrow stability domain of elemental Te at pH < 11.4. Based on the diagram, we previously noted that two anodic waves (C and D) correspond to reverse processes of reactions 2 and 1, respectively. In the frequency curve, there were two crooked points (C and D) observed at the same potentials of the anodic waves, suggesting that the CdTe actually dissolves by a two-step oxidation process. These two frequency changes were well accounted for by the above stepwise oxidation, *i.e.* Cd dissolution (n = 2, M = 112.4) followed by dissolution of Te (n = 4, M = 127.6), rather than by the other oxidation mechanism, such as one-step 6-electron CdTe dissolution (n = 6, M = 240.0) which occurred at both C and D.

Potentiostatic electrodeposition of CdTe onto the QCM electrode was also carried out at –0.70 V. Partial current for CdTe deposition (I_{CdTe}) was calculated from the frequency change differentiated by time ($d(\Delta f)/dt$) assuming the formation of stoichiometric CdTe (n = 6, M = 240.0). The ratio of the partial current I_{CdTe} to overall current I gave a change in instantaneous current efficiency during the electrolysis, which increased up to 90–95% at the beginning of the electrolysis, but afterwards it gradually decreased to 60–80%.

1. K. Murase *et al.*, *J. Electrochem. Soc.*, **146**, 531 (1999).
2. K. Murase *et al.*, *J. Electrochem. Soc.*, **146**, 1798 (1999); **146**, 4477 (1999).
3. K. Murase *et al.*, *J. Electrochem. Soc.*, **150**(1) in press.

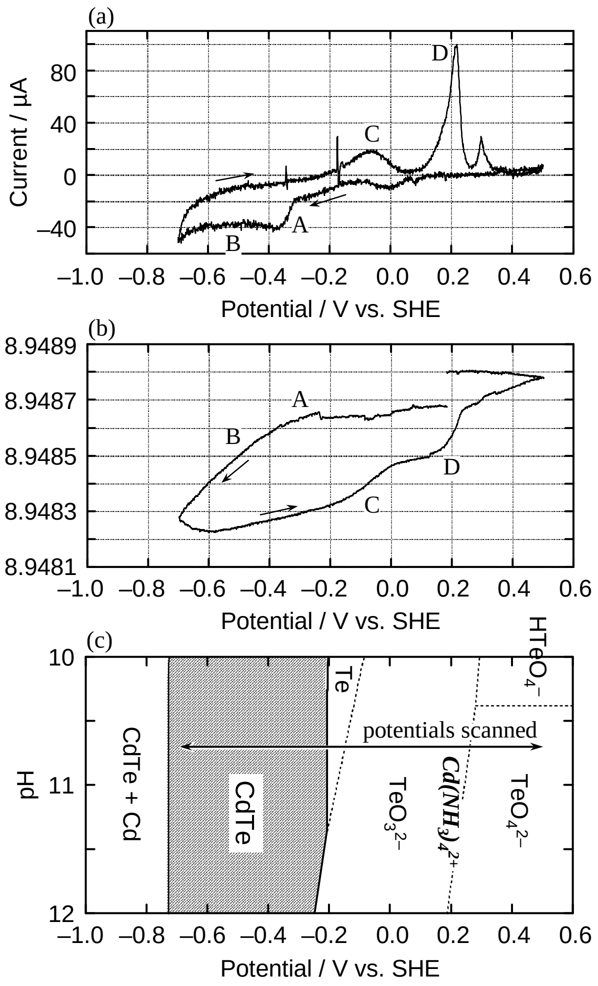

Figure 1. (a) Cyclic voltammogram (scan rate 10 mV s^{-1}) for ammoniacal solution (60 mM Cd(II), 10 mM Te(IV), 70 ˚C) employed for CdTe deposition, (b) frequency change of the QCM measured simultaneously, and (c) potential-pH diagram of the Cd-Te-NH_3-H_2O system (a_{Cd} = 0.06, a_{Te} = 0.01, $[NH_3]_{total}$ = 5.0 M, 25 ˚C).