Galvanic Contact Deposition of CdTe Layers using Ammoniacal Basic Aqueous Solution

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Cathodic electrodeposition is one of the key techniques for the preparation of thin-layered compound semiconductors (*e.g.* CdTe and CuInSe$_2$) for solar cell applications and the cell made up of an n-CdS/p-CdTe heterojunction has been applied to production on an industrial scale. Since the pioneering work of Kröger's group in the late 1970s, aqueous acidic sulfate solutions have historically and almost exclusively been employed for the bath for CdTe electrodeposition. We have proposed that aqueous basic, or alkaline, solutions containing ammonia or amine ligands are also suitable for the electrodeposition of uniform CdTe layers, since the basic solutions have a relatively high solubility of Te(IV) species as TeO_3^{2-} ions.[1, 2] In the present work, CdTe deposition from ammoniacal basic aqueous solutions was conducted not by electrodeposition using an external power supply but by galvanic contact deposition, and the deposition behavior and characteristics of the resulting deposits were examined. The contact deposition is a method wherein an appropriate less noble metal electrode, e.g. Cd, immersed in CdTe deposition bath is short-circuited with a substrate for CdTe deposition, and that CdTe is generated on the substrate by spontaneously occurring cathodic reaction. The contact deposition method, which does not use an external power supply, seems to be advantageous when applied on an industrial level.

Basic aqueous baths were prepared by dissolving 40–60 mM CdSO$_4$·8/3H$_2$O and 10 mM TeO$_2$ in an ammoniacal buffer solution containing 4.0 M NH$_3$(aq) and 0.5 M (NH$_4$)$_2$SO$_4$. Cd sheet and Au-plated Cu substrate were immersed in this bath as an anode and cathode, respectively, and then short-circuited externally. Cathode potentials and current densities were measured by a reference electrode and a zero-shunt ammeter, respectively. The bath was thermostatted at 70 °C and stirred at approximately 500 rpm during deposition. Deposition was performed under white light irradiation or in the dark. A 500 W xenon arc lamp installed in a lamp housing was used for the irradiation. The approximate integrated irradiance of the white light just before the electrolytic vessel was 300 mW cm^{-2}. When deposited in the dark, the electrolytic cell was placed in a light-resistant box. The concentration of Cd(II) ions was set at 40 mM under illumination and 60 mM in the dark as being optimized for electrodeposition.[2]

Figure 1 illustrates the variation of cathode potentials and current densities during the deposition. The cathode potentials were spontaneously kept at around –0.7 V throughout the deposition both under illumination and in dark, indicating that the same situation as potentiostatic electrodeposition was realized without an external potentiostat with a reference electrode. On the other hand, current densities decreased as time elapsed, just as the electrodeposition of CdTe from the same electrolytes. The resulting deposits by the contact deposition were identified as polycrystalline CdTe with almost stoichiometric composition (49.8 at.% Cd under illumination; 49.5 at.% Cd in dark) by XRD and EPMA. Hence the main cathode reaction was the deposition of CdTe (Cd(NH$_3$)$_4^{2+}$ + TeO$_3^{2-}$ + 6H$^+$ + 6e → CdTe + 3H$_2$O + 4NH$_3$), while the anode reaction was the dissolution of Cd (Cd + 4NH$_3$ → Cd(NH$_3$)$_4^{2+}$ + 2e).

The resulting CdTe layers were transferred from the Au-plated Cu substrate onto nonconductive epoxy resin for electrical characterization.[3] The electrical properties of thin CdTe layers below 3 μm in thickness were impossible to determine due to the high resistivity of CdTe. Therefore, the electrical properties were measured for thick layers more than 10 μm. In this case, the layers were prepared under illumination, since it was difficult to prepare such thick layers in dark due to a slow deposition rate. Conduction type and resistivity of CdTe by the contact deposition was p-type and 6.1×10^7 Ω cm, respectively. Carrier density and carrier mobility calculated from the resistivity and Hall voltage were 4.4×10^{11} cm^{-3} and 0.24 cm^2 V^{-1} s^{-1}, respectively. These values were almost the same as those for CdTe layers by electrodeposition from the basic electrolytes[3] (resistivity: 10^8 Ω cm; carrier density: 10^{11} cm^{-3}; carrier mobility: 1 cm^2 V^{-1} s^{-1}).

1. K. Murase *et al.*, *J. Electrochem. Soc.*, **146**, 531 (1999); **146**, 1798 (1999); **146**, 4477 (1999).
2. K. Murase *et al.*, *J. Electrochem. Soc.*, **150**, C44 (2003).
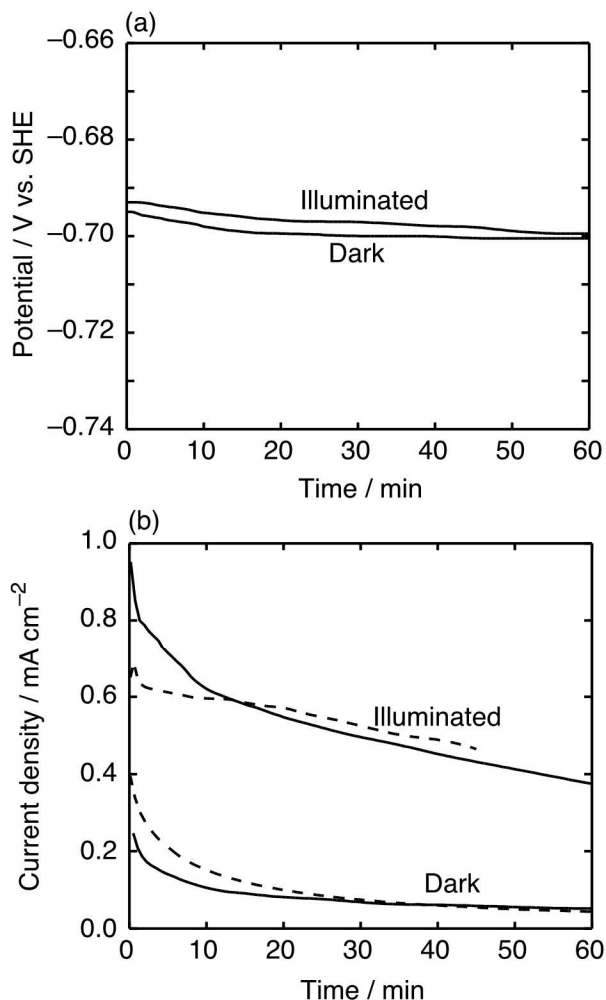3. M. Miyake *et al.*, *J. Electrochem. Soc.*, **150**, C413 (2003).

Figure 1. Variations of (a) cathode potentials and (b) current densities during galvanic contact deposition from ammoniacal basic solution. Dashed lines in (b) are the data of electrodeposition under illuminated and dark conditions.