Comparison of Microstructures of CdTe Layers Electrodeposited from Basic Ammoniacal and Acidic Sulfate Electrolytes

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Thin-layered CdTe semiconductors have been extensively investigated for n-CdS/p-CdTe heterojunction solar cell applications, since its direct band gap of 1.45 eV at room temperature is suitable for energy conversion from sunlight to electricity. Another advantage of CdTe is that the layer can easily prepared by electrodeposition from aqueous solutions under mild conditions. In addition to acidic sulfate baths, which have traditionally been employed for CdTe electrodeposition, we developed novel basic ammoniacal baths with a relatively high solubility of Te(IV) ions.¹ Although both acidic and basic baths gave stoichiometric and uniform CdTe layers, it was found that the as-deposited CdTe layers from the basic baths are p-type,² while those from acidic ones are n-type unless the deposition potentials are relatively positive. This suggests that the CdTe layers from basic baths have a potential to be built into n-CdS/p-CdTe solar cell without post-deposition annealing. The carrier density and resistivity of as-deposited CdTe layers were, however, on a low level. Since the CdTe layers are polycrystalline, structural defects, which act as a barrier and a recombination center for carriers, are always detrimental. In the present work, the microstructures of CdTe layers from the basic baths have been investigated by transmission electron microscopy (TEM). The structures were observed and compared with those from a typical acidic bath.²

A typical basic bath¹ (40-60 mM CdSO₄, 10 mM TeO₂, 4.0 M NH₃, and 0.5 M (NH₄)₂SO₄, pH 10.7, 70 °C; $M = mol dm^{-3}$) and an acidic bath⁴ (1.0 M CdSO₄, 300 μM TeO2, pH 2.5 by H2SO4, 85 °C) were employed for using electrodeposition conventional CdTe а three-electrode cell: WE, Au-plated Cu-sheet; CE, Pt-sheet; RE, Ag/AgCl in 3.33 M KCl (all potentials were re-calculated for SHE). After dimple grinding followed by ion thinning, microstructures of the deposits were observed with JEM-2000FX and JEM-4000EX TEM operated at an accelerating voltage of 200 and 300 kV, respectively.

As-deposited CdTe layers from the basic bath were composed of randomly oriented crystallites with a grain size of ca. 10 nm (Fig. 1, 2), while those from the acidic electrolyte consisted of defective columnar grains with a $\langle 111 \rangle$ preferred growth orientation (Fig. 3). By annealing, CdTe grains from the basic baths grew, but at the same time, voids were introduced at the grain boundaries. Although a potential-pH diagram for the Cd-Te-NH₃-H₂O system⁵ implies that the CdTe layers from the basic baths contain a trace amount of elemental Te, elemental mapping of the CdTe layer using nano-probe energy-dispersive spectroscopy (EDS) revealed that both Cd and Te were distributed uniformly in the entire layer (Fig. 4). The chemical composition at grain boundaries was the same as that of bulk CdTe grains, indicating that the electrodeposited layer was single-phased CdTe, which formed a solid solution with excess Te, if any.

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Figure 1. TEM images and corresponding SAED patterns of as-prepared CdTe layer electrodeposited from basic bath at -0.70 V; (a) plan-view, (b) cross-sectional view.



Figure 2. High resolution TEM image of the same layer shown in Fig. 1. White arrows indicate planar defects on {111} plane.



Figure 3. High resolution TEM image of as-prepared CdTe layer electrodeposited from acidic bath at -0.37 V.



20 nm 20 nm 20 nm **Figure 4**. (a) High resolution scanning TEM image and (b, c) elemental distribution map of the same layer shown in Fig. 1; (b) Cd and (c) Te.