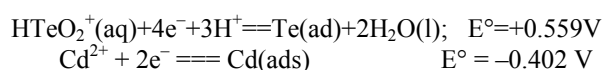


Electrodeposition of Low-Dimensional Phases on Au
Studied by EQCM and XRD
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Thin films of metal telluride phases such as PbTe and CdTe are promising candidates for a wide range of device applications, including thermoelectric coolers for thermal management of high density ICs and lab-on-a-chip devices. All of the common binary telluride phases can be deposited electrochemically from aqueous solution.

CdTe is a direct gap semiconductor with a band gap of 1.7 eV at room temperature. The electrodeposition of CdTe is normally carried out at cathodic potentials in aqueous H₂SO₄ solutions (pH < 2.5) using Cd²⁺ and TeO₂ as precursors. Acidic solutions are used to prevent the formation of cadmium hydroxide phases and to increase the solubility of TeO₂. In most cases, the so-called induced co-deposition method of Kröger has been followed. In this approach, the two elemental precursors are simultaneously reduced at the working electrode from the same solution according to the following half-reactions.



In induced co-deposition, the reduction of the more noble chalcogen ($E^\circ_{\text{Te}} > E^\circ_{\text{Cd}}$) induces the reduction of the less noble metal to occur at a more positive potential than where it would reduce alone due to the negative free energy of compound formation. The mechanism of induced co-deposition is therefore analogous to the underpotential deposition (UPD) of a metal onto the surface of a dissimilar metal. UPD is used in growth techniques such as electrochemical atomic layer epitaxy (EC-ALE). Typically, the concentration of the metal precursor is kept higher than that of chalcogen to insure that the rate of codeposition is greater than the rate of bulk electrodeposition of chalcogen. Generally, CdTe films grown by co-deposition are polycrystalline with the cubic crystal structure, although epitaxial deposits can be formed on lattice matched substrates such as single crystal InP.

In this study, we investigated the mechanistic details of the co-deposition of CdTe onto Au surfaces using electrochemical quartz microgravimetry (EQCM) and electrochemical techniques

The potential dependent mass changes observed from a solution containing both Cd and Te are shown in Figure 1. The deposition (cathodic) sweep is characterized by three distinct regions. The first, which spans potentials from 0.500 V to 0.200 V involves an approximately 20 ng mass decrease. As we have previously shown, this mass decrease is associated with the reduction of adsorbed Te(IV) (as either HTeO₂⁺ or HTeO₃⁻).

The second region occurs between about 0.2 V and -0.2 V and is characterized by a slow increase in mass of about 20 ng. This mass increase is due to a Te UPD process and bulk Te deposition, which occur in parallel at this potential. The third region onsets at potentials just negative of -0.2 V, and is characterized by a rapid increase in the rate of deposition. This corresponds to the onset of CdTe co-deposition. Note that the co-deposition potential of ca. -0.2 V is shifted by about 400 mV positive of the Nernst potential for Cd deposition (-0.402 V vs. NHE, -0.599 V vs. Ag|AgCl). Given a ΔG°_f of -99.66 kJ/mol for CdTe, a shift of $-(\Delta G)/2F = +0.516\text{V}$ is expected, in reasonable agreement with experiment. When the potential scan is reversed and swept anodically from -0.4 to +0.8 V, deposition continues to occur at the same rate until the potential becomes more positive than the co-deposition potential of ca. -0.2 V, at which point growth ceases (the maximum in the Δmass vs. E curve). At more positive potentials, we observe the sequential stripping of Cd and Te from the surface. Since the free energy for this process is positive, the elements strip sequentially. The less noble Cd is removed first, followed by the more noble Te. When CdTe is co-deposited on Au(111) XRD experiments show a strong preferred orientation along the [111] direction (cubic CdTe) in spite of the poor lattice match in this system.

In addition to CdTe, we have carried out similar experiments on the growth of PbTe and CdTe/PbTe superlattice structures, and these systems will also be discussed.

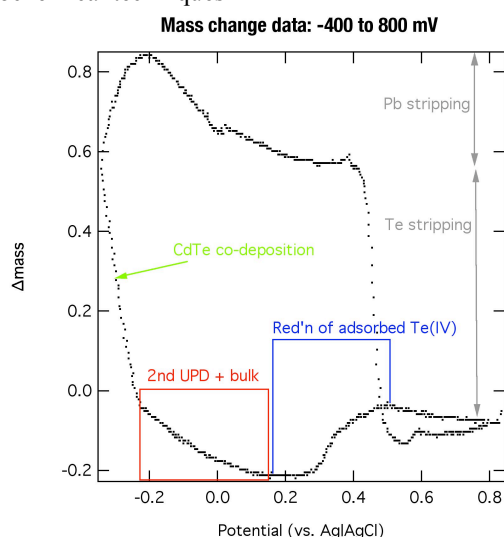


Figure 1. In situ mass change data during the co-deposition of CdTe on Au.