Characterization of Thin Telluride Films Grown By Electrochemical Atomic Layer Epitaxy Using EQCM and XRD

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We are exploring the use of electrodeposition techniques such as electrochemical atomic layer epitaxy (EC-ALE) and its variants to produce low-dimensional phases on electrode surfaces.

In this paper, we report on the characterization of thin films of PbTe, CdTe, Bi_2Te_3 , Sb_2Te_3 as well as PbTe/CdTe and Bi_2Te_3/Sb_2Te_3 superlattices grown onto Au substrates using EQCM and XRD.

In EC-ALE, a surface-limited electrochemical reaction—typically underpotential deposition (UPD)—is used to synthesize a binary compound by carrying out successive depositions of each element from its respective solution precursor. In the case of the tellurides, however, because of slow deposition kinetics, successive reductive 'UPD' reactions can be used to deposit binary tellurides from a single solution. The two half reactions generally have the form (here M=metal):

$$\begin{split} M^{n^{+}} + ne^{-} &=== M & (fast) \\ HTeO_2^{+} + 4e^{-} + 3H^{+} &=== Te + 2H_2O & (slow) \end{split}$$

As an example, the voltammetric and mass change data for the co-UPD of Pb and Te from an acidic aqueous solution containing both Pb^{2+} and TeO_2 is shown in the figure below. In this graph, mass change data are shown in black (dark) and voltammetric data are shown in red (light).



In the CV data, the initial (reductive) deposition scan for co-deposition is almost identical to what was observed in the case of Pb UPD (i.e., no TeO₂ present). That is, it appears that Pb deposits first in spite of the fact that the UPD wave for Te in the absence of Pb is actually positive of the Pb UPD wave (in the absence of Te). This behavior is due to the slow Te deposition kinetics-we observe a nearly 0.7 V deposition overpotential for the Te 'UPD' wave. Interestingly, once the potential becomes positive of the Pb UPD potential, the deposition ceases entirely (mass change goes to 0). At this potential, the Te monolayer has completely covered the Pb UPD layer and since there isn't sufficient driving force to cause bulk Te deposition, growth stops. Thus, the first two atomic layers appear to effectively deposit in a layer-by-layer fashion due to the slow deposition of Te. At this point, the total mass change corresponds to about 0.08 µg, which

corresponds to the sum of the mass changes observed for individual Pb and Te monolayers deposited separately. Once the potential is swept even more positive, there is a stripping process, slow at first and then faster near the Te stripping peak at about 0.4 V. We believe this corresponds to the slow stripping of Pb followed by the stripping of the Te monolayer.

XRD data for these systems will also be discussed. The data shown below illustrate the coincidence epitaxy that occurs in these systems. The bright spots correspond to diffraction from the Au substrate, while the powder rings correspond in this case to a film of PbTe.

