Electrochemical Quartz Crystal Microbalance (EQCM) Studies of Cd and Te Atomic Layer Formation and their Alternation to form CdTe (EC-ALE), using a Thin Layer Flow Cell.

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An electrochemical quartz crystal microbalance (EQCM) has been incorporated into a thin layer electrochemical cell to study the deposition of Cd and Te atomic layer formation and the alternated deposition of Cd and Te atomic layers to form CdTe using the EC-ALE methodology. 9 MHz AT-cut quartz crystals, with 5 mm diameter sputtered Au electrodes on each side (Seiko), were used as substrates in a thin layer electrochemical flow cell. The cell consisted of Plexiglas blocks and silicon gaskets, allowing the Au on one side to be used as the working electrode while the other electrode was open to the air. The cell volume was ~50 μL. A thin Au wire and Ag/AgCl were used as auxiliary and reference electrodes, respectively. The flow cell was housed inside a wire Faraday cage to minimize noise in frequency measurements. The Faraday cage was housed in a Plexiglas box to help exclude oxygen. Solutions were contained in Pyrex glass bottles, held inside a second Plexiglas box, again to limit oxygen exposure. Solutions were delivered through a Teflon distribution valve. The solution flow rate was controlled by pressurizing the solution bottles and use of a micro-metering valve.

The EQCM (EG&G) was calibrated by using silver electrodeposition combined with cyclic voltammetry under static condition. The calibration constant was 4.787 ng Hz^{-1} cm^{-2}.

Fig. 1 shows current and frequency change vs. applied potential for Cd electrodeposition. The potential was scanned negatively to record the reductive current and frequency change corresponding to Cd UPD. The reductive Cd coverage (0.278 ML) was much smaller than the 1.159 ML calculated from frequency change. The extra mass was assigned to sulfate adsorption on the deposited Cd.

Fig. 3 shows current and frequency change vs. applied potential for Te electrodeposition. At E = +0.2 V, a tellurite species was believed to be adsorbed on the Au substrate. This was confirmed using XPS in a UHV-EC study. The observed reductive current between E = +0.1 to –0.55 V corresponded to UPD Te deposition. However, the frequency change indicated a large mass loss between E = +0.1 to –0.28 V. This was due to desorption of tellurite species from the substrate, along with a small amount of Te UPD. At more negative potential, bulk Te deposition occurred. When the potential scan was reversed to the positive direction, the oxidative current and frequency change corresponded to Te stripping and re-adsorption of the tellurite species. Te coverages calculated from reductive and oxidative currents were ~0.7 ML. STM and UHV-EC studies are currently underway to gain better understanding of the Te electrodeposition process.

Fig. 4 shows current and frequency change vs. deposition time in initial studies of the alternated deposition of Cd and Te. Solutions were continuously delivered to the deposition cell while the solutions were changed every 200 s in the following order: Blank Cd, Cd, Blank Cd, Blank Te, Te, and Blank Te. Cd coverages calculated from reductive current and frequency change

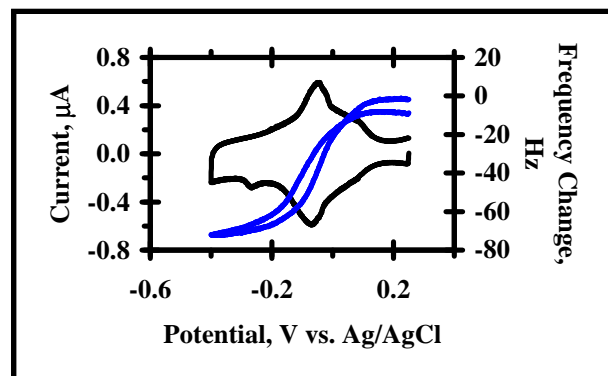were ~0.8 ML. The extra charge was probably due to hydrogen evolution and dissolved oxygen reduction.

Figure 1. Frequency change (blue) and current (black) of a Au electrode in 5 mM CdSO$_4$ + 0.5 M Na$_2$SO$_4$ + 50 mM NaOAc, pH = 5.7. Scan rate is 5 mV/s.
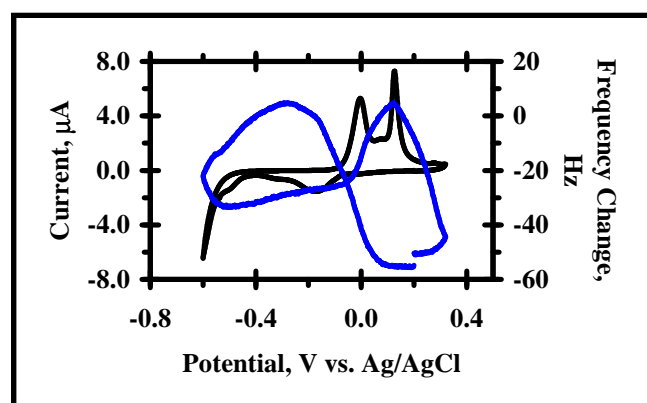

Figure 2. Frequency change (blue) and current (black) of a Au electrode in 0.25 mM TeO$_2$ + 0.5 M Na$_2$SO$_4$ + 10 mM Na$_2$B$_4$O$_7$, pH = 9.2. Scan rate is 5 mV/s.

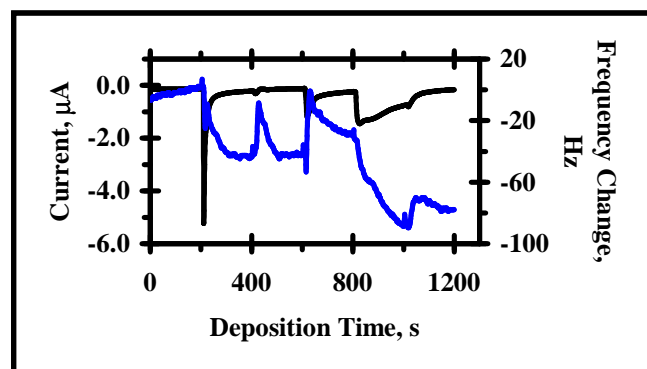

Figure 3. Frequency (blue) and current (black) vs. deposition time at constant E = -0.5 V for CdTe (EC-ALE) on Au EQCM electrode. Solution flow rate is 2 mL/min.