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Thin-Layer Electrochemical Studies in the
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by Electrochemical ALE

Robert D. Herrick II and John L. Stickney

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Department of Chemistry
University of Georgia
Athens, GA 30602-2556

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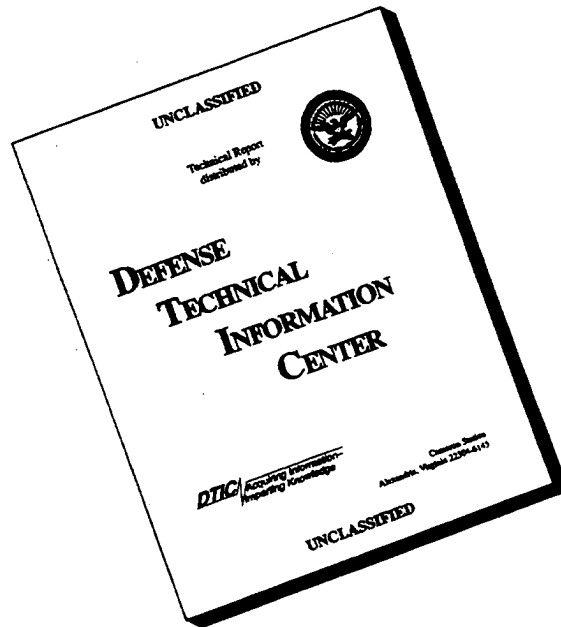
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THIN-LAYER ELECTROCHEMICAL STUDIES IN THE DEVELOPMENT OF A CYCLE OF THE FORMATION OF CuInSe_2 BY ELECTROCHEMICAL ALE

Robert D. Herrick II and John L. Stickney*
Department of Chemistry, University of Georgia
Athens, GA 30602

ABSTRACT:

A thin-layer electrochemical cell (TLEC) was used in the development of a method for the electrodeposition of CuInSe_2 . Underpotential deposition (UPD) of atomic layers of Cu, In, and Se, as well as layers of Cu_2Se , InSe and InSe_2 was performed. However, extension to layers of CuInSe_2 proved significantly more difficult due to differences in stability of Cu and In. A complexing agent was used to adjust the activity of the Cu, forcing its formal potential to more negative values. The UPD behavior of Cu on an atomic layer of Se, however, appeared to be significantly impeded by the presence of the complexing agent. The information obtained in this study is intended to facilitate the development of an Electrochemical ALE cycle for the deposition of CuInSe_2 . Future work will involve studies using an automated flow cell deposition system.

INTRODUCTION:

The thin-layer electrochemical cell (TLEC) used in these studies has several advantages over a corresponding thick-layer cell. The extremely high surface area to volume ratio, $\sim 0.33 \text{ cm}^2/\mu\text{L}$, greatly decreases the extent of contamination in the form of both electroactive and surface active species. Decreased levels of contamination result directly in more reproducible electrochemical behavior and lower background currents. Further, lower amounts of electroactive contaminants in the TLEC allow the study of processes that might otherwise be obscured by the larger faradaic currents that would be observed in a corresponding thick-layer cell. These characteristics make coulometry with the TLEC more accurate (1-3), and have been exploited in a number of areas, from spectroelectrochemical studies (4) to electrochemical detection in Liquid Chromatography (5). Several review articles highlighting the properties and uses of thin-layer electrochemical cells have been published (6,7).

TLECs have been used extensively to study the fabrication of compound semiconductors using Electrochemical ALE (ECALE) (8,9). ALE is a method in which surface-limited reactions are used in a cycle to form deposits one atomic layer at a time (10,11). In ECALE, the surface limited reactions are performed electrochemically, utilizing underpotential deposition (UPD). TLECs have been used extensively in the initial studies of the formation of II-VI compound semiconductors, such as CdTe (8,12) and a number of other binary semiconductors (13,14). The present work describes the first attempt to fabricate a ternary compound, CuInSe₂, using an ECALE cycle.

CuInSe₂ has great promise for application to solar cell device fabrication due to its direct electronic transition and ideal bandgap, 1.07 eV (15). However, the actual synthesis of a highly crystalline thin film of the semiconductor appears to be relatively difficult. Past electrochemical approaches to its fabrication have utilized coelectrodeposition of the three elements (16-18), electrodeposition of an alloy of the metals followed by selenization using gaseous Se sources at high temperatures (19,20), and electrodeposition of the metal selenides followed by high-temperature interdiffusion of the layers (21,22). In addition, a number of non-electrochemical methods have been applied to the formation of CuInSe₂, including standard high-temperature MBE (23). Each approach has necessitated either a high-temperature reaction, a post-deposition annealing process, or both. Electrochemical ALE offers the possible benefit of direct epitaxial electrodeposition of the semiconductor, eliminating the need for a post-deposition annealing step. Further, the use of a TLEC to study the deposition of a ternary compound semiconductor presents new opportunities to observe the reactivity between alternately deposited atomic layers.

EXPERIMENTAL:

The thin-layer electrochemical cell utilized in this work is depicted in Figure 1. The actual cell consisted of a precision vacuum shrunk Pyrex glass cavity of dimensions just large enough to contain a polycrystalline cylindrical gold billet. The cell was designed so that the distance between the gold surface and the Pyrex cell wall was 0.001". The cell was filled by capillary action through the pinholes, and emptied by applying a N₂ overpressure to blow the solution out. Coulometric measurements were based on the calculated surface area of the electrode from physical dimensions and assuming a roughness factor of 1.2. A monolayer (ML) was based upon the calculated area, assuming a density of surface atoms equivalent to the Au (100) crystal surface (1.17 x 10⁻¹⁵ atoms/cm²). The volume of the TLE was determined experimentally using a standard solution of Fe²⁺ (7).

The solutions were prepared from Nanopure water and reagents that were used without further purification. The solutions prepared were 5 mM CuSO₄·5 H₂O (Fisher Scientific, 99.6%), 4 mM CuSO₄·5 H₂O + 20 mM (Ethylenedinitrilo)tetraacetic acid

(EDTA) (Fisher Scientific, 99.6%), 2 mM $\text{InCl}_3 \cdot 4 \text{H}_2\text{O}$ (Alfa Inorganics, 99%), and 5 mM SeO_2 (Aldrich Chemicals, 99.999%). All solutions contained 0.5 M Na_2SO_4 as a supporting electrolyte and were adjusted to pH 2 with H_2SO_4 with the exception of the $\text{CuSO}_4/\text{EDTA}$ solution, which was adjusted to pH 7 with NaOH . Prior to use in the TLE, the solutions were deaerated by bubbling with N_2 for at least 5 minutes. All potentials were referenced to a Ag/AgCl (1 M NaCl) reference electrode.

RESULTS AND DISCUSSION:

The voltammetry of the Au electrode in 1.0 M H_2SO_4 is shown in Figure 2a. The voltammetry of the individual elements is shown in Figure 2b-d. All three elements display a definite UPD region at potentials prior to the bulk deposition for the element. The peaks are wider than might be expected in a thick-layer cell for two reasons: first, due to the small amount of reactant present in the cell, faradaic processes quickly deplete the reactant, producing significant changes in its activity over the course of deposition. Further, the TLE suffers from a significant iR drop, which contributes to the peak width and splitting often exhibited in the voltammetry.

The UPD deposition of Cu on Au is a well studied system (24,25). Cu UPD in our TLE is similar to that reported by other workers on polycrystalline Au electrodes, from +0.300 V to -0.020 V. The deposition of In on Au (Figure 2c) also displays a UPD region, which extends from -0.100 V to -0.400 V, but the UPD feature is less defined than that for Cu. Formation of an atomic layer of the metals was performed by stepping to a potential within the UPD region and holding for 2 minutes. Window opening experiments indicated that optimal atomic layers of the metals were obtained at +0.200 V for Cu and -0.350 V for In. All coverages were determined coulometrically using a linear scan to strip the deposits.

The voltammetry for Se is significantly more complex than that of the metals. The wide splitting of the deposition and corresponding stripping peaks implies more irreversibility than for the metals (26). The formal potential of Se lies near +0.400 V, which is significantly positive of the first Se deposition feature observed at +0.300 V. The peak appears to be due to a surface-limited reaction, but because it occurs at an overpotential, it is difficult to refer to it as UPD. After this "UPD" peak, the rest of the Se aliquot is deposited in a larger peak at +0.100 V. At more negative potentials, below -0.600 V, bulk Se undergoes a reduction from Se^0 to Se^{2-} (26). This reductive stripping of bulk Se was exploited in the present work to form Se atomic layers on the metals in a two-step process. The electrode was first stepped to a potential at which bulk deposits of Se were formed. At least 1.5 ML was allowed to deposit, then the solution in the TLEC was exchanged for a supporting electrolyte containing no Se, and the potential was stepped to -1.20 V. The electrode was held at that potential for two minutes, allowing reduction of the bulk Se, leaving only an atomic layer of Se.

The alternated formation of atomic layers of elements was performed in the following way: starting with a clean Au electrode, an aliquot of the solution containing the first element was rinsed into the TLEC at the desired deposition potential. This potential was held for two minutes, and then the aliquot was expelled from the TLEC by application of a N_2 overpressure. The TLEC was then removed from the H-cell containing the first solution, maintaining a constant flow of N_2 over the electrode while the outside of the TLEC was rinsed with Nanopure water. The TLEC was then inserted at open circuit into the next H-cell, which contained a solution of the next element to be deposited. Removing the N_2 overpressure causes an aliquot of the new solution to wick into the TLEC by capillary action, completing a rinse. Three rinses of the new solution into the TLEC were performed prior to application of the desired deposition potential.

Studies of the metal coverages as a function of potential on clean Au electrodes and on Au electrodes coated with an atomic layer of Se are shown for Cu and In in Figures 3a and 3b, respectively. The graphs show clear plateau regions corresponding to UPD on the clean Au surfaces for both metals. The graph for In deposition on Se-coated Au is essentially the same as the deposition on clean Au with the exception of a slight suppression of the In deposition at positive potentials (Figure 3b). The graph of Cu deposition on a Se monolayer, on the other hand, displays a much less defined plateau region (Figure 3a). Again, the Se layer suppresses the metal deposition at positive potentials, but the Cu coverage observed just prior to bulk Cu deposition is nearly twice that observed in the absence of a Se atomic layer. It appears that the bond strength of Cu with Au is sufficient that the Cu displaces Se from Au, allowing deposition of Cu atomic layers both above and below the Se atomic layer. Similar behavior has been previously reported where Cu displaced an atomic layer of I from a Pt surface (27), although a top layer of Cu was not observed. Studies similar to those in Figure 3a, but with higher Se coverages, indicated that Cu reacts completely with several monolayers of bulk Se, whereas In will deposit only on the top layer of Se. This behavior is a clear reflection of the thermodynamic nature of the deposition process, and the increased stability of CuSe over InSe.

The inverse sequence, deposition of Se onto atomic layers of the metals, is displayed in Figure 4. The graph shows the resulting Se coverages observed as a function of the initial metal coverage. The solid line in Figure 4 shows Se deposition on various Cu coverages. Essentially, a single monolayer of Se is deposited at all but the highest coverages of Cu, where a slight increase in Se coverage occurs, probably due to roughening of the surface. The behavior of Se on In atomic layers, however, is significantly different. Like the displacement of Se from a Au surface by Cu, Se appears to displace In from the Au surface, probably indicating a greater Se-Au bond strength than In-Au bond strength. This appears to result in the deposition of Se both above and below the In layer and a gradually increasing Se coverage with increasing In coverage.

Studies of ternary deposits were performed in a manner analogous to the studies of the binary layers. Again, the elements were alternately deposited from their respective solutions and stripping voltammetry was used to characterize the resulting deposits (Figure 5). The upper chart (Figure 5a) depicts the stripping of a deposit that was formed by first depositing a Cu atomic layer on a Au electrode, followed by a Se atomic layer on the Cu layer using the procedure described previously, and finishing with an In atomic layer on the Se layer. The stripping curve in Figure 5a shows the coverages for Cu and Se at the expected ratio, but the In coverage appears to be slightly low.

Figure 5b depicts the stripping of a deposit formed by first depositing an atomic layer of In on the Au electrode, followed by a Se atomic layer on the In layer as described previously, and finally a Cu atomic layer on the Se layer. In contrast to Figure 5a, Figure 5b shows no peak for In stripping. The absence of the In stripping peak can be explained by considering the deposition sequence. The initial In layer was formed, as depicted in Figure 6a, followed by formation of the Se layer, which displaced the In from the Au and resulted in the formation of an In layer between two layers of Se (Figure 6b). When the Cu layer was deposited on the InSe_2 layer, the In was unstable and stripped from the layer due to its instability at the potential necessary to underpotentially deposit Cu (Figure 6c). As observed in Figure 3a, the Cu should then react with the Au surface as well as with the two atomic layers of Se (Figure 6d). From the coulometry (Figure 5b), this appears to have occurred, as the coverages of both Se and Cu are larger than those observed in Figure 5a.

The stripping of In from the deposit presents a significant obstacle to the development of a working ECALE cycle. One possible solution involves adjusting the activity of Cu in solution. By complexing the Cu with a suitable complexing agent, it is possible to drop the Cu^{2+} activity sufficiently to force the formal potential negative. It is desirable to shift the UPD potential for Cu so that it more closely matches the UPD potential for In. The addition of 20 mM EDTA (pH 7) to the Cu solution shifted the Cu deposition potential negative by over 0.4 V, as is evident in Figure 7. Figure 7, however, presents results for the deposition of Cu onto a clean Au electrode. Attempts to deposit Cu from the EDTA solution on a Se atomic layer proved to be more difficult. Cu UPD on Se from an EDTA solution is presently under study.

CONCLUSION:

The qualities of a TLEC, facile exchange of solutions and accurate coulometry, have been utilized in an attempt to develop an ECALE cycle for CuInSe_2 . Monolayer formation of Cu, In and Se, as well as Cu_2Se , InSe , and InSe_2 was observed, but the formation of CuInSe_2 proved to be problematic. The UPD potentials for Cu and In are separated by approximately 0.4 V, and attempts to underpotentially deposit Cu on a deposit containing an atomic layer of In resulted in stripping of the In from the deposit.

Attempts to complex the Cu and force its formal potential more negative were promising. The formal potential was easily shifted, and UPD of Cu on Au was observed. However, deposition of atomic layers of Cu from the EDTA complex on atomic layers of Se resulted in inconclusive voltammetry, and is currently under study. Future work will include attempts to form a thin film of CuInSe₂ in an automated thick-layer flow deposition system.

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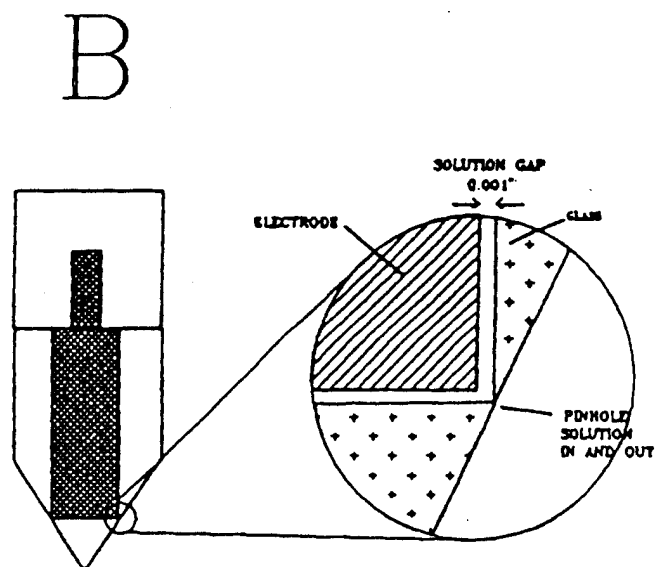
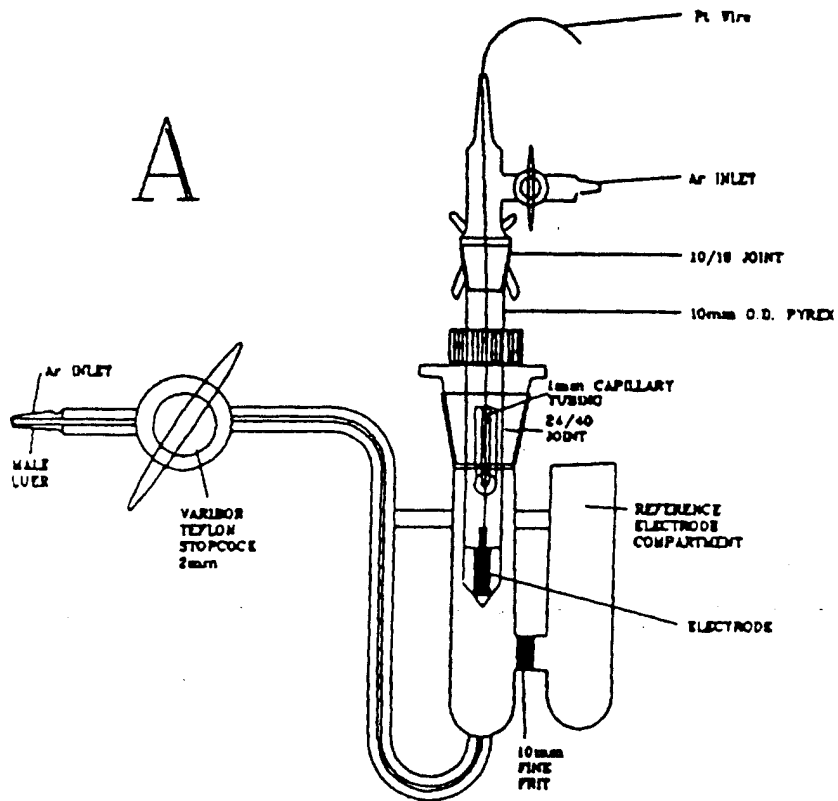


Figure 1. Schematic diagram of a thin-layer electrochemical cell (TLEC). a) The TLEC as used in an H-cell b) Close-up of the electrode in the Pyrex cylinder

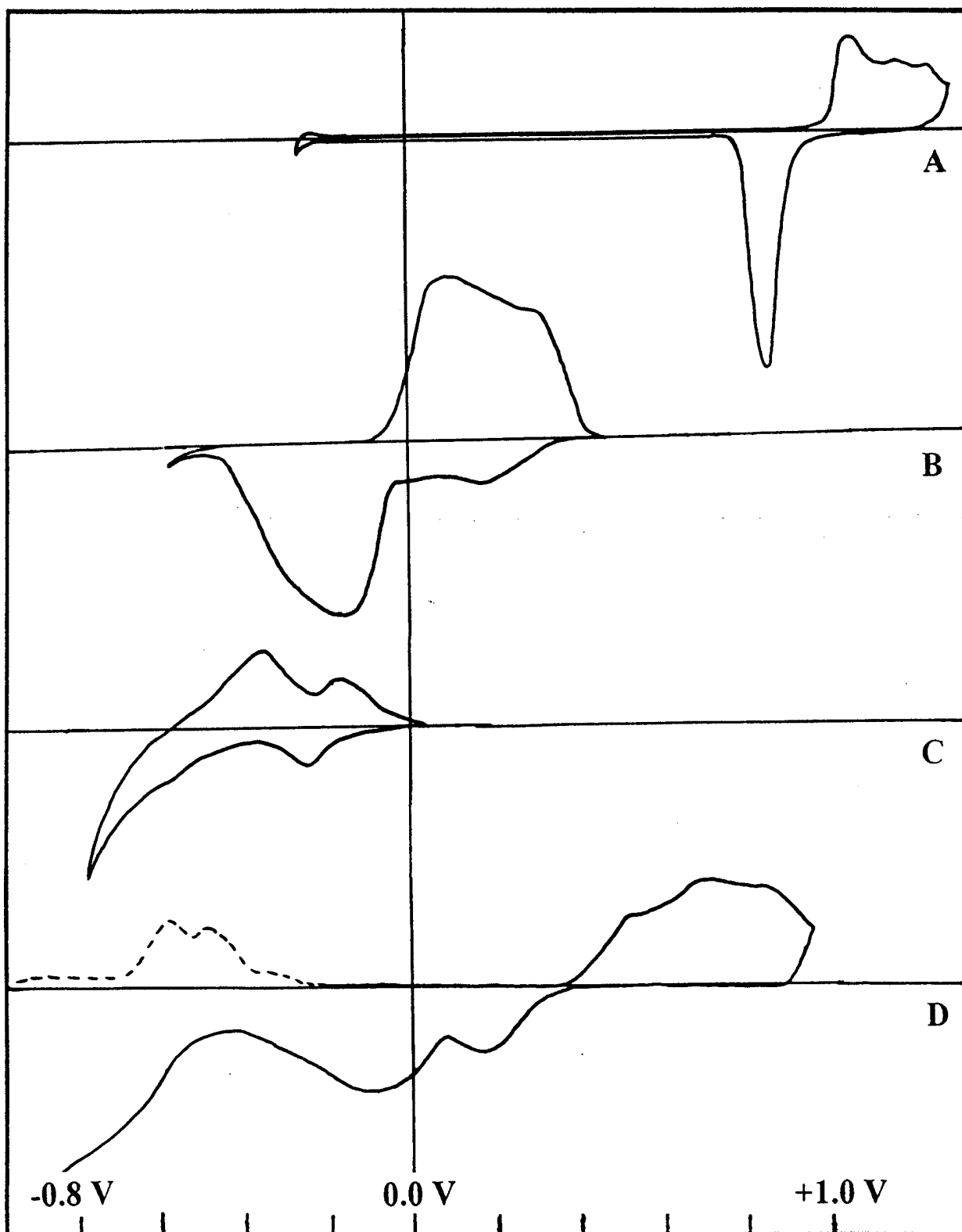


Figure 2. a) Voltammometry of a clean Au electrode in 1.0 M H₂SO₄ b) Voltammometry of 5 mM CuSO₄ c) Voltammometry of 5 mM InCl₃ d) Voltammometry of 2 mM SeO₂

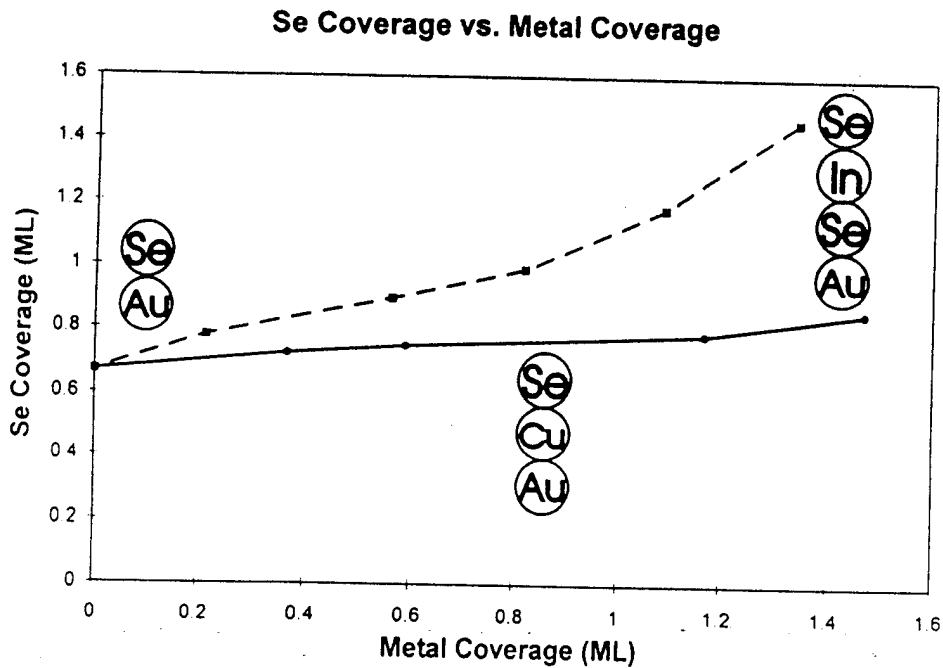


Figure 4. Se coverage vs. metal coverage. Se appears to displace In to form an atomic layer of In between two atomic layers of Se. Cu does not appear to be displaced by Se.

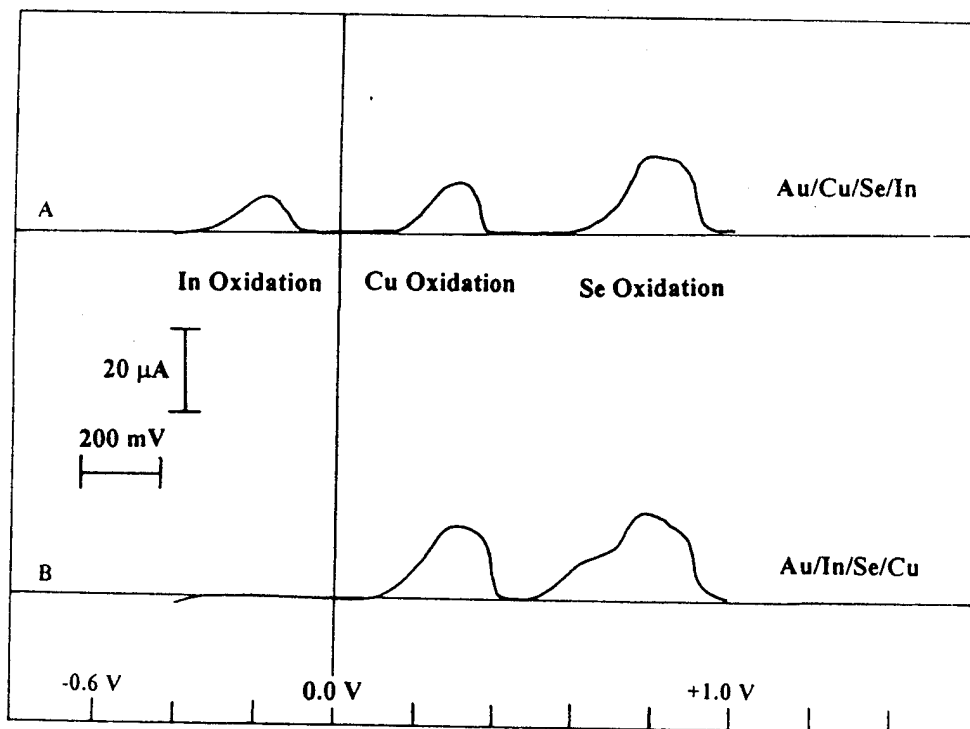


Figure 5. a) Stripping voltammetry of a Cu/Se/In deposit. The coverages of Cu and Se appear to be stoichiometric, but the coverage of In is slightly low. b) Stripping voltammetry of an In/Se/Cu deposit. Because of the instability of In, no In stripping is observed after deposition of Cu.

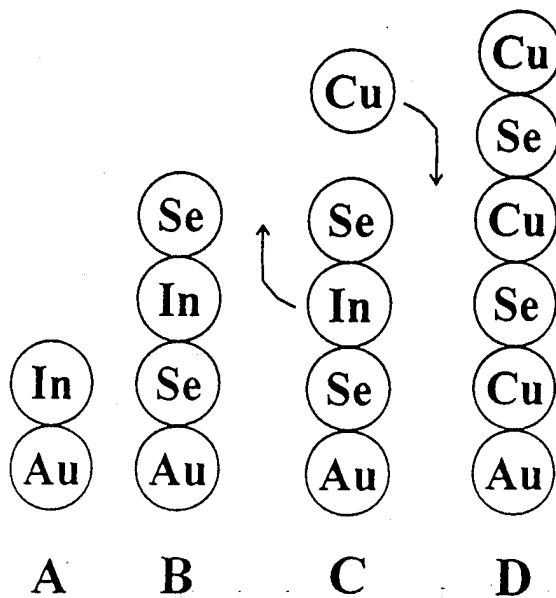


Figure 6. a) Schematic diagram of an In atomic layer b) In atomic layer after Se deposition c) During Cu deposition, In strips from the deposit d) Final deposit after deposition of Cu

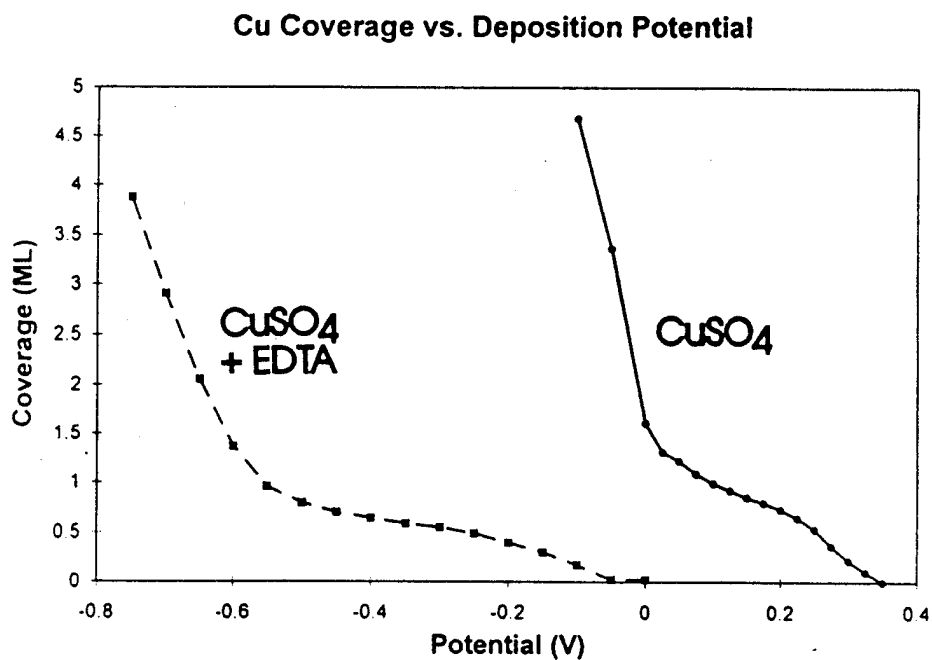


Figure 7. Cu coverage as a function of deposition potential. With the addition of EDTA, the voltammetry shifts by approximately 0.4 V.