Evidence of Induced Underpotential Deposition of Crystalline Copper Antimonide via Instantaneous Nucleation

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Cu$_2$Sb was electrodeposited onto transmission electron microscopy (TEM) grids to investigate changes in morphology, composition, and crystal structure during the early stages of nucleation and growth. Multiple transitions were observed within the first second of the deposition, leading to the formation of crystalline Cu$_2$Sb. These transitions were analyzed using TEM, scanning electron microscopy, selected area electron diffraction, and energy-dispersive X-ray spectroscopy. The nucleation sites are initially polycrystalline antimony with amorphous copper, which then transition through a polycrystalline copper intermediate containing some antimony before forming crystalline Cu$_2$Sb. These analyses provide direct evidence that Cu$_2$Sb does not deposit directly from solution but deposits by induced underpotential deposition. This is indicative of the electrodeposition of a typical alloy initially, but what is unusual is that the deposit at longer time scales is a highly crystalline intermetallic. This investigation is unique because TEM grids allow the interface between the deposited material and the substrate to be investigated. This is possible because the composite carbon film on the TEM grid behaves as a transparent substrate. This approach can be extended to other systems, allowing the development of a comprehensive understanding of the electrodeposition of intermetallic compounds.

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Electrodeposition is a popular material synthesis technique for a variety of applications, including electronics, surface finishing, and microfabrication.1,2 This synthetic method can provide control over the composition and crystallinity of the final material and can be used to deposit onto surfaces of various sizes and shapes. Recently, a procedure for the single-potential deposition of Cu$_2$Sb from aqueous solutions was used to obtain crystalline thin films.3 This compound is of interest as an anode material for Li-ion rechargeable batteries; the composition and crystal structure are critical for the desired physical properties. Also, the ability to deposit directly onto a current collector with excellent electrical contact provides a direct route toward the incorporation of the anode material into a battery without the need for additional binders. A deeper understanding of the electrodeposition of this compound would be useful for extending this technique to other crystalline intermetallics with applications in a variety of electronic devices.

Control over the morphology and crystallinity of electrodeposited materials is a function of nucleation and subsequent growth. In addition, the competition between nucleation and growth also determines the grain size of the deposited material, which can lead to significant differences in the physical properties.4 For these reasons, the nucleation and growth of metal deposits have been studied extensively using a variety of microscopy techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). An added complexity arises for the deposition of intermetallics, semiconductors, and alloys as opposed to the electrodeposition of single elements because the composition, crystallinity, and morphology depend not only on the nucleation and growth, but also on the reduction potentials of the different constituents being codeposited. It is imperative to be able to investigate the crystal structure, composition, and morphology during the nucleation and growth of multielement materials with high spatial resolution in order to develop a deeper understanding of the deposition mechanism.

One example that has provided a wealth of information is the investigation into the time-dependent nucleation and growth of electrodeposited copper. AFM, SEM, and TEM studies on the electrodeposition of copper have contributed to the development of various models for the nucleation and growth processes that occur during electrodeposition.5,6 Specifically, it is common to use the previously mentioned microscopy techniques to determine whether the deposition can be modeled by either instantaneous or progressive nucleation. The information gathered from these types of studies has led to a higher degree of control over the deposition process, thereby facilitating the synthesis of deposits with desired physical and mechanical properties. For example, in situ AFM was used to examine the effect of Cu$^{2+}$ concentration, potential, pH, and additives on the resulting deposition. It was observed that the pH dictated whether the nucleation was instantaneous or progressive.10 In another case, Radisic et al. used real time in situ TEM to demonstrate that the electrodeposition of copper fits first-order nucleation kinetics.11 It was also determined that under the deposition conditions examined, the nucleation could not be described by either the instantaneous or the progressive model inclusively.11 These are just two instances where microscopy techniques have been used to improve the understanding of nucleation and growth of electrodeposited metals. Although, the electrodeposition of copper has received much of the attention, the information gained from these experiments provide a starting point for the electrodeposition of other metals. It is not as common, however, to use microscopy techniques such as these to investigate the electrodeposition of multielement materials because the focus has traditionally been on the relative deposition efficiencies of the individual elements.

For the electrodeposition of multielement materials, the concentration of the precursors and the deposition potential are the two most important conditions affecting the material properties.2,14 Improved control over the electrodeposition of intermetallics, semiconductors, and alloys is still needed because of their increased use in electronic applications. These applications require a high degree of control over the electrodeposition to be used for device fabrication. For this control to be realized, the processes that occur during nucleation need to be determined. There are many cases in the literature where the electrodeposition of multielement materials occurs by either anomalous codeposition (ACD) or induced underpotential deposition (IUPD).2,14-16 Both ACD and IUPD involve, first, the deposition of one element followed by, and/or accompanied by, the deposition of the second element.15 Specifically, ACD occurs when the less noble metal is deposited preferentially to the other metal. This can result in the deposited material having a stoichiometry not consistent with the current density of each element depositing individually. In contrast, IUPD describes the case where the deposition of one element allows for the deposition of a second element that otherwise would not deposit for the given deposition conditions.15 This is also thought to be the route by which multielement semiconductors are electrodeposited.16 One example where a microscopy
technique has been used to analyze the nucleation of a mixed element deposition is reported by Han et al.\textsuperscript{17} Although it was determined that the codeposition of Sn–Cu followed the progressive nucleation model, a connection between the nucleation model and ACD or IUPD was not presented.\textsuperscript{17}

Recently, we developed a method to electrodeposits crystalline Cu$_2$Sb from aqueous solutions at a single potential.\textsuperscript{2} To accomplish this, citric acid was used as a complexing agent to force Sb$^{3+}$ into nonacidic aqueous solutions. After the pH was adjusted to 6, Cu$_2$Sb could be deposited at a single potential, 1.05 V vs saturated sodium calomel electrode (SSCE), while at more acidic or basic conditions this was not the case.\textsuperscript{3} (See Mosby and Prieto for a more complete description.\textsuperscript{3}) The dependence of the deposition on pH is thought to be due to the speciation in solution playing an important role in the deposition. It was not, however, determined whether the material deposited directly as Cu$_2$Sb or if the deposition followed a route similar to ACD or IUPD.\textsuperscript{3} This information is vital if single-potential deposition procedures similar to the one used for Cu$_2$Sb can be applied to the deposition of other intermetallics, semiconductors, or alloys. To this end, Cu$_2$Sb has been deposited directly onto TEM grids, allowing the nucleation process to be studied along with changes in the composition, crystallinity, and morphology. To the authors’ knowledge, the results presented here are the first direct evidence illustrating how a deposition similar to ACD or IUPD proceeds during the first stages of nucleation and growth for a crystalline intermetallic. Within the first second of the deposition, the nucleation sites transition through multiple compositions and crystal structures before forming Cu$_2$Sb, providing evidence that the solution chemistry is not solely responsible for the single-potential deposition of Cu$_2$Sb. These findings demonstrate the applicability of TEM coupled with selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) as an analytical tool to probe the nucleation and growth of multielement electrodeposited materials. Traditional electron microscopy studies are limited because the anode or cathode material for lithium-ion batteries is combined with a binder consisting of carbon and a polymer, which are difficult to remove after the lithiation or delithiation process.\textsuperscript{3,16,22}

Further studies of the electrodeposited Cu$_2$Sb on TEM grids provide an unhindered investigation of the crystal structure, composition, and morphology changes that occur during the lithiation and delithiation of the material as an anode for lithium-ion batteries.

Experimental

Electrochemistry.— All electrodeposits baths consisted of aqueous 0.4 M citric acid solutions (99.5%, Aldrich) containing 0.025 M antimony(III) oxide (nanopowder, 99.9 + %, Aldrich) and 0.1 M copper(II) nitrate hemipentahydrate (99.9 + %, Aldrich). A detailed preparation procedure was reported previously.\textsuperscript{3} Briefly, citric acid was added to Millipore water (18 Ω) followed by the addition of Sb$_2$O$_5$. After the dissolution of Sb$_2$O$_5$, Cu(NO$_3$)$_2$ was added. The solution pH was then adjusted to 6 using 5 M potassium hydroxide (ACS certified), and the depositions were carried out at 50°C to increase the crystallinity of the final product so that SAED analysis could be used more effectively. Cu$_2$Sb was deposited potentiostatically using a Gamry Reference 3000 controlled by Gamry Framework version 5.56 software. The depositions were performed using a three-electrode cell consisting of a Pt mesh flag as the counter electrode and a SSCE as the reference electrode. Cyclic voltammograms (CVs) were performed on a platinum disk electrode purchased from BASi (2.01 mm$^2$) and gold TEM grids with a geometric area of 7.3 mm$^2$. For the chronoamperometry plot, a copper flag (0.25 mm thick, 3.98%, Aldrich) and a TEM grid with copper mesh were used as the working electrode (WE). The analyses performed on the nucleation and growth of Cu$_2$Sb were conducted by directly depositing the material onto TEM grids while using the grids as the WE. Carbon composite TEM grids with copper 200 mesh were purchased from Structure Probe, Inc. (SPI) and were used to analyze the nucleation, growth, and changes in crystal structure, while indexed TEM grids with gold 200 mesh (SPI) were used to collect EDS spectra as gold is not an element contained in the deposition product. An optical microscope image of a TEM grid with gold mesh is shown in the inset of Fig. 1. The 95 μm square holes and 20 μm bars, which make up a 200 mesh TEM grid, can clearly be seen. The carbon composite (conducting polymer film blended with carbon fibers)\textsuperscript{23} can also be seen within the 95 μm square holes of the grid.

Characterization.— The optical microscope image of the TEM grid was taken on an Olympus BX52 equipped with a polarizer (model no. U-AN300-3) using an Olympus UMPPlanFI lens with a magnification of 10×. A QColor5 Olympus camera was used to obtain digital images using software QCapture Pro+, version 5.1.1.14. High resolution transmission electron microscopy (HR-TEM) and SEM images, SAED patterns, and EDS spectra were collected after washing the TEM grids with excess water and methanol. TEM–EDS and SAED data were collected using a Philips CM200 STEM equipped with a Princeton Gamma Tech Prizm 2000 energy-dispersive spectrometer operating at an accelerating voltage of 200 kV. SEM–EDS analyses were performed using a JEOL JSM-6500F equipped with a Thermo Electron energy-dispersive spectroscopy detector with an applied voltage of 10 kV. The particle sizes were determined by counting at least 300 particles from a particular deposition time from multiple regions of a SEM or TEM image.

Results and Discussion

Cyclic voltammetry.— Cyclic voltammetry was used in a previous study to develop a single-potential deposition procedure for Cu$_2$Sb from aqueous citrate solutions containing Cu$^{2+}$ and Sb$^{3+}$. CVs of citrate solutions containing the individual ions as well as solutions containing both ions were analyzed in the pH range of 1–8. We found that the electrochemistry changed significantly with pH, and at pH 6, crystalline films of Cu$_2$Sb could be deposited at −1.05 V vs SSCE. Another observation was that the reduction and corresponding oxidation peak for the deposition of copper metal were not present in the CVs of Cu$^{2+}$ complexed with citrate unless the solution also contained Sb$^{3+}$ at pH 6. Also, the reduction peak for the deposition of antimony metal was shifted in the positive direction when Cu$^{2+}$ was present. For further details, readers are referred to Mosby and Prieto.\textsuperscript{3} For the present study, the CVs of the deposition solution were taken using TEM grids as WE and are shown in Fig. 1. Comparing the platinum WE to the TEM WEs, the...
reduction peaks on the TEM WE were shifted slightly in the negative direction, while the corresponding oxidation peaks were shifted in the positive direction. This shift in potential and a slight difference in peak shape indicate that the conductivity of the TEM WEs is lower than the conductivity of the platinum disk electrode. This is not surprising considering that the crystallinity of the platinum WE is much higher than the metals and carbon composite of the TEM WEs.

CVs were also taken on TEM grids with copper mesh but are not shown due the oxidation of copper, which starts to occur at a potential similar to the oxidation of Cu$_2$Sb. The reduction peaks on the TEM electrodes with copper mesh are similar to those shown in Fig. 1b and c. SPI reports that the TEM grids are 55% open space, which is the main reason for the lower current density seen in the CVs taken with the TEM WE. While the CV in Fig. 1b was performed on a TEM grid in which the carbon composite was removed and thus had the lowest current density, it was not 55% lower than the TEM grid with the carbon composite (Fig. 1c). This indicates that the carbon composite conductivity is much lower than the material (i.e., gold) of the TEM grid. This is also evident from depictions carried out on TEM WEs as the mesh material has a higher packing density of Cu$_2$Sb than the carbon composite at short times. This is beneficial for this study because the nucleation step for the deposition is slowed sufficiently such that potentials can be chronologically applied on a reasonable time scale. The implication is that the times reported here are not quantitative representations of the Cu$_2$Sb depositions carried out on a “normal” electrode but, instead, are used to chronologically describe the events that occur during the early stages of the single-potential deposition of Cu$_2$Sb.

**Chronoamperometry.**—The electrodeposition of Cu$_2$Sb from aqueous citrate solutions containing Cu$^{2+}$ and Sb$^{3+}$ in a ratio of 2:1 at a potential of −1.05 V vs SSCE leads to a high nucleation density at time periods less than 1 s. A comparison of the dimensionless current transients between Cu$_2$Sb electrodeposition and the theoretical models developed by Scharifker and Hills for instantaneous nucleation (Eq. 1) and progressive nucleation (Eq. 2) is plotted in Fig. 2:

\[
\frac{i}{i_{eq}} = 1.954\left(1 - \exp\left[-\frac{1.2564}{t/t_m}\right]\right)^2 \tag{1}
\]

\[
\frac{i}{i_{eq}} = 1.2254\left(1 - \exp\left[-\frac{2.3367}{t/t_m}\right]\right)^2 \tag{2}
\]

Here, $i_{eq}$ corresponds to the current at the time for which the derivative of the current with respect to time is zero ($t_m$). Figure 2a clearly illustrates that at short $t/t_m$ the deposition of Cu$_2$Sb onto copper foil (□) and TEM grids with copper mesh (△) follow the instantaneous nucleation model. It should be noted that a slight deviation between the two plotted current transients is observed. This is a consequence of depositing onto a TEM grid; as stated, Cu$_2$Sb deposits onto two different surfaces of varying conductivity, the copper or gold mesh of the TEM grid and the carbon composite film between the mesh. Regardless of the deposition substrate, the experimental data deviate from both the instantaneous and progressive nucleation models after $t/t_m > 1$. A known cause of the observed deviation from the theoretical models is hydrogen evolution, which is substrate dependent because the rate of H$_2$(g) evolution is a function of the electrode material. Hydrogen evolution must be considered in this system as well and will occur at very different rates on the carbon composite compared to the mesh of the grid.

**SEM.**—Additional evidence that the nucleation of Cu$_2$Sb is instantaneous can be found by evaluating representative low magnification SEM images. Figure 3a contains a SEM image of Cu$_2$Sb after a 5 s deposition onto the carbon composite of a TEM grid and shows a nucleation density of 4.8 sites/μm$^2$. Comparing this image to Fig. 3b, which is an image of a 30 s deposition with a nucleation density of 5.0 sites/μm$^2$, the number of sites apparently does not significantly increase between the two times, but instead separate nucleation sites have started to merge. This process is the probable cause of the large size distribution observed at longer deposition times. As the deposition time proceeds, the diameter of the nucleation sites increases where measurements taken at 0.5, 5, and 30 s show diameters of 79 ± 15 nm (image not shown), 223 ± 40 nm (Fig. 3a), and 395 ± 133 nm (Fig. 3b), respectively. Overlapping of the nucleation sites starts to occur after depositing for 30 s (Fig. 3b), and a 45 s deposition results in merged nucleation sites creating micrometer-sized islands of deposited material with a cubic morphology (Fig. 4a). This morphology is consistent with the morphology observed for Cu$_2$Sb deposited on the mesh part of the TEM grids and films deposited on metal foil substrates from the previous study.

A significant advantage of depositing onto TEM grids is that the nucleation sites can be imaged from both the front and the back of the grid using SEM and can be analyzed from both sides as well using EDS. The nanometer thick carbon composite film acts essentially as a transparent growth substrate, allowing the analysis of the interface between Cu$_2$Sb and the growth substrate. A representative image of the nucleation sites imaged through the carbon film for a 45 s deposition is shown in the inset of Fig. 4a. Separating the nucleation sites from the bulk material is a low density region that
manifests as a dark ring in the SEM images. This contrast difference can be readily observed in the SEM image shown in the inset of Fig. 4b. To determine if the composition of the nucleation sites and that of the bulk material is equivalent, an EDS elemental mapping analysis was performed on an area surrounding a single nucleation site. A representative SEM image is contained in the inset of Fig. 4b. Two distinct phases are overlaid in false color on the SEM image, as seen in Fig. 4b. The only elements found to be present in measurable quantities were carbon due to the carbon composite associated with the TEM grid, copper, and antimony. The first phase, represented as blue in Fig. 4b, is copper rich and is mainly associated with the low density ring separating the nucleation site from the bulk material. The phase analysis shows that both phases are present in roughly the same amount in the bulk material. SAED analysis confirms that crystalline Cu₂Sb is present at this deposition time. We suspect that instead of there being equal amounts of the copper-rich and antimony-rich phases present (which would result in the overall 2:1 Cu₂Sb stoichiometry), the EDS spatial resolution is not high enough to distinguish the bulk Cu₂Sb as a third phase with the appropriate stoichiometric ratio of copper to antimony. The hypothesis is that there is a copper-rich phase that forms at the initial nucleation site. This phase is separated from the bulk Cu₂Sb by an antimony-rich phase. TEM–SAED analyses were performed at various deposition times to provide higher spatial resolution data.

**TEM.**—After applying −1.05 V vs SSCE for 0.1 s, the carbon composite on the TEM grid contains a large number of nucleation sites. However, the density of nucleation sites is not uniform, and we observed that there is an even distribution covering the carbon composite film (Fig. 3) in some grid windows, while other grid windows show areas of high nucleation density separated by low density regions (images not shown). This is most likely because the carbon composite associated with the TEM grids are not uniform and thus have localized variations in electrical conductivity, resulting in varying current densities during the depositions. Even though the population densities across the TEM grid can vary, the overall morphology of the nucleation sites is consistent. A representative TEM image of the nucleation site morphology for depositions lasting less than 0.5 s is shown in Fig. 5a. Beginning with a 0.1 s deposition, lattice fringes with a measured separation of 2.2 Å, corresponding to (110) planes of antimony (PDF no. 01-071-3720), are present in the HRTEM image shown in Fig. 5b. Further analysis of the image reveals that lattice fringes are not visible over the entire site for a single zone axis. Also, the contrast difference observed within a
single nucleation site alludes to there being either composition or thickness differences. These two observations suggest that the nucleation sites are polycrystalline. This conclusion is supported by the SAED pattern indexed to antimony in the inset of Fig. 5b. For a deposition time of 0.25 s, the nucleation sites have grown in size and continue to be polycrystalline, as illustrated in Fig. 5c. In addition to the increased size, a transition occurs as the measured lattice spacing decreases to 1.8 Å, which is indicative of copper planes PDF no. 01-071-4608, not antimony. A representative SAED pattern of the nucleation site that has been indexed to copper.

At a deposition time of approximately 0.5 s, the nucleation sites go through a morphological and phase change as they become circular and increasingly less crystalline, as evidenced by the lack of intense diffraction spots shown in Fig. 6a. The diffuse diffraction

Figure 5. (a) Low magnification TEM image of a nucleation site after a 0.1 s deposition on a carbon composite of a TEM grid at −1.05 V vs SSCE. (b) High magnification image showing lattice spacings of 2.2 Å, which has been assigned to antimony (110). The inset is a SAED pattern of the nucleation site that has been indexed to antimony. (c) TEM image of a nucleation site after a 0.25 s deposition on a carbon composite of a TEM grid at −1.05 V vs SSCE. The measured lattice spacing of 1.8 Å is a match for copper (200). The inset contains a SAED pattern of the deposition site that has been indexed to copper.

Figure 6. (a) TEM image of a nucleation site after a 0.5 s deposition on a carbon composite of a TEM grid at −1.05 V vs SSCE. The inset contains a SAED pattern of the deposition site indexed to copper. (b) TEM image of a nucleation site after a 1 s deposition on a carbon composite of a TEM grid at −1.05 V vs SSCE. The inset is a SAED pattern of the site that has been indexed to Cu2Sb.
rings, however, still index to copper. This indicates that the nucleation sites are much less ordered than the sites at earlier deposition times. At deposition times longer than 0.75 s, the SAED patterns of the deposit indicate that crystalline Cu$_2$Sb (PDF no. 01-085-0492) has formed. A representative TEM image of a nucleation site after depositing for 1 s onto a TEM grid is shown in Fig. 6b with its corresponding SAED pattern. These data suggest that the circular nucleation sites with diminished long-range order observed at 0.5 s go through a transformation resulting in crystalline Cu$_2$Sb as the deposition time is increased. Because the SAED pattern of the nucleation sites at early stages of the deposition indicates that transitions in the structure of the deposited material occur, we used EDS analysis to probe the compositional changes occurring as a function of time.

To eliminate potential false signals from TEM grids with a copper mesh material, the EDS spectra were collected from samples deposited on the carbon composite of TEM grids with gold mesh. While a standard was not used to quantify the EDS data, qualitatively large compositional changes are observed during the first 1 s of the deposition. Depositions lasting between 0.1 and 0.75 s are composed of excess copper vs antimony relative to the 2:1 atomic ratio one would expect if Cu$_2$Sb were deposited directly from solution. Figure 7a contains a representative EDS spectrum taken from a 0.1 s deposition showing the presence of antimony, thereby confirming the analysis of the SAED pattern. The EDS spectrum, however, also indicates the presence of a significant amount of copper. After a 0.25 s deposition, the EDS spectrum of a nucleation site (Fig. 7b) illustrates the comparative absence of antimony when compared to copper, suggesting that the nucleation site is composed mostly of copper. The EDS of a deposition performed for 1 s, however, contains clear peaks for both copper and antimony, as shown in Fig. 7c. Utilizing the results from all of the analytical techniques presented here (cyclic voltammetry, chronoamperometry, SEM, TEM, EDS, and SAED), the processes that occur during the deposition of crystalline Cu$_2$Sb from solution are now discussed.

**Discussion.**— The results presented in this paper provide chronological details regarding the single-potential deposition of Cu$_2$Sb. For a deposition time of 0.1 s, the dimensionless current transients exponentially decrease due to the double-layer capacitance, as represented by point 1 in Fig. 2b. The TEM images collected from samples for this deposition time illustrate that the substrate is populated with nucleation sites. TEM and SAED evidence contained in Fig. 5a indicate that the sites are polycrystalline antimony. Contrary to this, the EDS spectra of the nucleation sites, for which a representative spectrum is contained in Fig. 7a, clearly show a higher atomic percent of copper when compared to antimony. This can be attributed to the presence of amorphous copper distributed within the sites because copper is not observed in the SAED patterns. In a previous report, copper-rich films (determined by X-ray photoelectron spectroscopy) were deposited at potentials more positive of $-1.05 \text{ V vs SSCE}$.

Possibly, at early times, the IR drop caused by the current from the double-layer charging changes the potential at the solution electrode interface. This would cause the potential to be positive of $-1.05 \text{ V vs SSCE}$ and thus form a copper-rich film. The unconventional sharp increase in current seen in the CVs in Fig. 1 at $-1.0 \text{ V}$ can be described by a nucleation site of antimony acting as an activation site for the overpotential deposition of copper. As soon as the antimony site is present, the copper deposition begins and the rate of the copper deposition increases dramatically.

Referring back to the dimensionless current vs time curve in Fig. 2b, point 2 corresponds to a deposition time of 0.25 s, which is located immediately before the curve maximum. For this deposition time, the nucleation sites are polycrystalline, but TEM and SAED evidence overwhelmingly supports the fact that the sites are the dominant crystalline species present (Fig. 5b). As in the 0.1 s deposition, the EDS data (Fig. 7b) continue to show a higher atomic percent of copper when compared to antimony if Cu$_2$Sb were the only species present. Again, because the current is still higher than at times when the deposition is diffusion limited, the excess copper could be attributed to a higher deposition rate for copper because it is at an overpotential. Clearly, however, the nucleation sites contain detectable amounts of antimony even though the element is not observed in the SAED patterns. This could be because (i) the antimony has transitioned to an amorphous phase or (ii) the antimony is still crystalline, but the large discrepancy in the atomic percent, which favors copper, overwhelms the diffraction signal from antimony, making it unobservable. The conclusion based on the data collected from samples deposited at 0.1 and 0.25 s is that polycrystalline antimony is deposited first and subsequently acts as an activation site for the deposition of copper. This is further supported by the previous study conducted by Mosby and Prieto as copper metal does not deposit without the antimony species being present in solution.

After antimony acts as an activation site for the deposition of copper, the deposition sites undergo a phase transition at a deposi-
tion time of approximately 0.5 s in which the crystallinity of the nucleation sites dramatically decreases, as illustrated in Fig. 6a. With respect to the dimensionless current transient curve in Fig. 2b, a 0.5 s deposition (point 3) occurs after the maximum when neglecting the data points due to the double layer. As the nucleation site transitions further into crystalline copper, the deposition rate for the copper decreases as antimony is required for the copper overpotential deposition. The deposition rate of antimony then exceeds that of copper, and the nucleation site becomes a solid solution of antimony and copper instead of polycrystalline copper. This results in the amorphous properties observed in the TEM images and SAED patterns. As the deposition time increases from 0.5 to 0.75 s (Fig. 2b, point 4), the nucleation sites begin to transition to the final deposition product, crystalline Cu$_2$Sb. The effect of the IR drop on the applied potential at times greater than 0.75 s is small and relatively constant. Once the transformation to Cu$_2$Sb is initiated, the crystallinity of the deposited material increases with an increase in deposition time, as evidenced by the SAED pattern indexed to Cu$_2$Sb contained in Fig. 6b. The presence of the amorphous phase and the diffusion-limited deposition results in Cu$_2$Sb instead of the individual elements. It is reassuring to know that even though the deposition occurred onto the carbon composite of the TEM grids, the deposited Cu$_2$Sb had the same preferred orientation that was observed for the subsequent copper deposition and formation of Cu$_2$Sb, it is not unexpected that the dimensionless current transients contained in Fig. 2 can be fitted to the instantaneous nucleation model. These observations and the data reported here suggest that the single-potential deposition of Cu$_2$Sb occurs through a mix of ACD and IUPD at early times. Thus, antimony is deposited at an underpotential in the presence of Cu$_2$Sb, and copper deposition is induced by the nucleation site created by the less noble element. However, we cannot yet determine if the excess copper deposited at approximately 0.5 s causes the transition to Cu$_2$Sb through solid-state diffusion or if the morphology and elemental composition of the nucleation sites at this time, along with the deposition being diffusion limited, result in the direct deposition of Cu$_2$Sb out of solution for all deposition times greater than 0.5 s.

**Conclusions**

The results from the investigation described here provide evidence that the single-potential deposition of Cu$_2$Sb can be described by a mix of the ACD and IUPD models. While the times reported in this study are not quantitatively relevant to the depositions on normal substrates, this investigation is unique because TEM grids were used as the WE, thereby providing direct compositional, morphological, and crystal structure evidence of the nucleation and growth process. This unique investigation illustrates that the nucleation sites undergo transitions that are based not only on the diffusion of the required elements, but also on the interaction of the elements within the nucleation sites. The multiple transitions that occur ultimately lead to the deposition of polycrystalline Cu$_2$Sb instead of a solid-state alloy of copper and antimony, which could be a consequence of the high solubility of copper and antimony in each other at moderate temperatures. This solubility may be responsible for allowing the solid-state transformations required for the direct deposition of Cu$_2$Sb. The knowledge gained from these experiments aids in developing a more complete understanding and, ultimately, better control of the single-potential deposition of crystalline intermetallics from aqueous solutions and is already being used to aid in a procedure to uniformly deposit Cu$_2$Sb nanowire arrays.

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