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Epitaxial Growth of Cu on Au(111) and Ag(111) by Surface Limited Redox Replacement−An Electrochemical and STM Study

L. T. Viyannalage,[†] R. Vasilic,[‡] and N. Dimitrov*,[†,‡]

Department of Chemistry, and Materials Science and Engineering Program, State University of New York at Binghamton, P.O. Box 6000, Binghamton, New York 13902-6000

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The growth of ultrathin copper films by surface limited redox replacement is discussed and experimentally illustrated. Cyclic voltammetry, in situ scanning tunneling microscopy (STM), and X-ray diffraction are employed to monitor the two-dimensional growth and characterize the structure of up to 100 monolayers (ML) of Cu on Ag (111) and Au(111) substrates. The growth is carried out by multiple redox replacement of a layer of underpotentially deposited (upd) Pb used as a sacrificial metal. Open-circuit potential monitoring during the replacement reaction is used to control the completion of each deposition event. Anodic film stripping is performed to determine the film thickness and calculate the yield of the employed deposition strategy. The excellent surface quality of an epitaxially grown Cu film is manifested by a distinct Pb upd voltammetry and ascertained by in situ STM showing uniform surface morphology maintained during the entire growth process. High-resolution STM imaging of Pb upd layer deposited on as-grown Cu films reveals a structure identical to Pb on Cu(111). X-ray photoelectron spectroscopy analysis shows no traces of Pb into accordingly deposited Cu films.

Introduction

The growth of smooth, homo-, and heteroepitaxial metal layers has always been a major goal of electrodeposition. The reduced ohmic resistivity and electromigration of such layers renders them highly desirable for applications in electronics industry and low-metal loading catalysis. Aiming at epitaxial metal deposition, Sieradzki et al. developed the defect mediated growth (DMG)[1] and surfactant-mediated growth (SMG).[2] In both methods, potential controlled protocols ensure efficient, reversible manipulation of the deposition kinetics by mediating metal ions. This enables a continuous 2D growth mode in systems naturally growing in three dimensions (3D) at ambient temperature. The applicability of these methods was successfully demonstrated by growth of commercially thick metal deposits in the systems Ag/Au(111), Ag/Ag(111),[1,2] and Cu/Au(111)[3] with Pb^{2+} or Cu^{2+} as mediators. Recently a pioneering work of our group described the foundation of a new method (referred to as epitaxial growth by galvanic displacement) for epitaxial thin film growth.[4] Illustrated by the growth of Ag on Au(111), this method realizes a surface limited redox replacement (SLRR) as a "building block" reaction in the deposition of smooth and uniform thin-metal films.[4,5] The strategy employed is based upon multiple application of a protocol for submonolayer to monolayer surface modification proposed first by Brankovic et al.[6] and developed later on by Mrozek et al.[7] Thus, as a deposition protocol SLRR emphasizes unique decoupling of mutually dependent growth controlling factors typical for standard electrodeposition scenario.[4,5] Such decoupling associated with the electroless nature of the replacement reaction results in an "adlayer controlled" growth[6] that is so far seen only in

electrochemical atomic layer epitaxy.[8] Most recently, a detailed study of Stickney et al. at atomic level revealed preferential interaction between growing and sacrificial metal during the deposition of Pt on Au(111) by SLRR.[9] This result along with the preferential interaction between Ag and Pb in the SLRR growth of Ag on Au(111) observed in our earlier work[4,5] suggests a remarkable tunability of the proposed deposition scenario.

The study is aimed at employing the SLRR strategy in the epitaxial growth of Cu on Ag(111) and Au(111) (atomic mismatch of 11.1%). The emphasis in our effort is on the growth and characterization of relatively thick Cu films (beyond the first 2−4 atomic layers) where SLRR could be tested upon substantial stress accumulation. This research is justified by the industrial importance of the Cu deposition process and in particular the superior quality of smooth and continuous Cu films. In the longer run, epitaxial copper could be essential for the growth bimetallic multilayers with specific functionality.[10]

Without additional kinetic manipulation the systems Cu on Au(111) and Ag(111), both grow in a Stranski−Krastanov mode forming at most one wetting layer prior to 3D cluster formation.[3,11] The ability to underpotentially deposit on (111) faces of Cu, Ag, and Au[12] identifies Pb as an excellent candidate for a sacrificial metal in Cu homo- and heteroepitaxial growth. The distinct upd and surface sensitive voltammetry of Pb on those substrates enables efficient qualitative electrochemical monitoring during the growth.

Experimental

Mechanically polished, and then either electropolished and flame annealed Au(111) or chemically polished Ag(111) single crystals (both provided by Monocrystals Co.), 2 mm thick and 1 cm in diameter, were used as working electrodes (WE). The mechanical polishing for both crystals down to 0.05 μm was

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done using water-based, de-agglomerated alumina suspensions (Buehler). The gold surface was then electropolished by anodization in 3:2:1 ethylene glycol, hydrochloric acid, and glacial acetic acid for 10−15 s at dc current density of 2.5 A.cm^{-2} with a platinum cathode. After a thorough rinsing with Barnsted Nanopure water (>18 MΩ), the Au crystal was annealed to "red heat" in a propane flame for 10 min and cooled rapidly in N$_2$ atmosphere. The silver single crystal was prepared using a slightly modified procedure developed originally by Smolinski et al.[13] After the preparation, the electrode (Ag or Au) was terminated by a water droplet to prevent contamination and mounted on a holder for work at a "hanging meniscus" configuration.[14] Finally, the holder with the crystal was placed in a state-of-the-art, controlled environment, three-compartment electrochemical setup, which allows for multiple immersion of the WE[4] in different electrolytes. In this sealed setup allowing for thorough de-oxygenation (more details in[4]), the static, quartz glass Petri dish containing 0.003 M Pb(ClO$_4$)$_2$ (Sigma Aldrich, 99.995+%) + 0.100 M NaClO$_4$ (Sigma Aldrich, 99.99%) + 0.010 M HClO$_4$ (GFS Chemicals, double distilled) solution serves as a three-electrode cell where upd experiments are carried out using a Pb wire as a pseudo-reference electrode (pre) and a Pt wire serving as a counter electrode. The mobile quartz glass compartments contain 0.010 M Cu(ClO$_4$)$_2$ (Alfa Aesar, 99.999%) + 0.010 M HClO$_4$ solution for the redox replacement and Barnsted Nanopure water for rinsing, respectively. In another version of the replacement growth method ("one pot" deposition) that will be described in details later in this paper, the deposition was performed in a sealed, standard three-electrode cell containing both Cu^{2+} and Pb^{2+} ions, albeit at different concentration. Ultrahigh purity N$_2$ with less than 1 ppb oxygen, CO, CO$_2$, and moisture content was used for de-oxygenation of all working solutions. Cyclic voltammetry experiments were performed with a Cypress Systems "66-OMNI-101B" potentiostat equipped with "66-Acquire101" software package allowing communication with a PC to collect experimental data. All solutions were made with Barnstead Nanopure water and high-purity grade chemicals (as detailed while introducing working solutions) used as received from vendors. For the sake of clarity, all potentials are measured and quoted with respect to Pb/Pb^{2+} pre that features a potential of −0.200 V versus normal hydrogen electrode under the existing experimental circumstances.

In situ STM characterization experiments (to prevent surface oxidation in air) were performed right after the growth. A Molecular Imaging (MI) Pico Scan 300S scanner, MI Pico Scan 2100 controller, and MI Pico Scan software were used for monitoring the Cu layer surface morphology. The experiments were controlled by MI 300S Pico bi-potentiostat and carried out in a custom-made Teflon cell of 1 cm^3 in volume that exposed 0.3 cm^2 of the electrode surface. A Pb pre and Pt counter electrode were used in a working solution containing 0.003M Pb(ClO$_4$)$_2$ + 0.100M NaClO$_4$ + 0.010M HClO$_4$ for the in situ experiments. Tunneling tips were made by etching of Pt80%-Ir20% wire in a 1:2 mixture of saturated CaCl$_2$ solution and water at 25 V (ac). A tip coating with Apiezon wax was performed after the etching in order to minimize the background current to values less than 20pA.

X-ray diffraction results were obtained on a Scintag XDS2000, θ−θ configuration powder diffractometer equipped with a Ge-(Li) solid-state detector (Cu Kα radiation). X-ray Photoelectron Spectroscopy (XPS) experiments were carried out at the Center for Nanoscale Systems (CNS) at Cornell University. The instrument used was Surface Science SSX-100 (X-ray source,
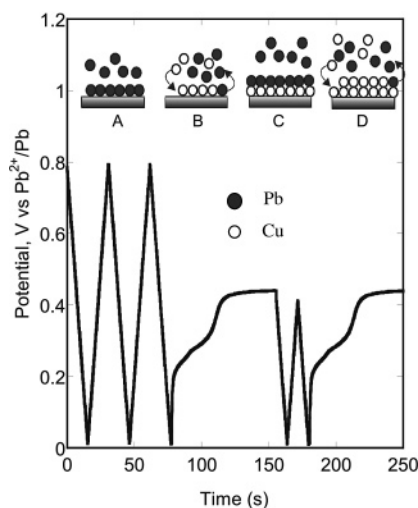

Figure 1. Schematic, illustrating the time−potential protocol employed for a growth by surface limited redox replacement.

Al Kα, 1486.6 eV) spectrometer operating at base pressure of 1 × 10^{-9} Torr with both incident beam and detector angle set to 55°. The spot size was 1000 μm.

Results and Discussion

Multiple Immersion. The time-potential protocol employed for Cu deposition is schematically illustrated in Figure 1 that represents real potential time dependence in the course of the growth. Before the deposition, the substrate (Ag or Au) surface was subjected to a potential cycle in the Pb upd range until a stable voltammogram, consistent with previously reported in the literature for which Pb on either Ag(111)[15] or Au(111)[16] was registered. After cycling, the substrate surface was covered by a upd layer of Pb (sketch A), and upon discontinuing the potential control, it was transferred into a solution containing 0.010 M Cu^{2+} ions. Then a redox replacement reaction was ensuing (sketch B) owing to a substantial difference in the formal potentials of lead and copper. The optimal immersion time of 20s to complete the stoichiometric redox exchange between Pb and Cu was established on the basis of our previously reported study of upd layer stability at open circuit potential (OCP).[17] After the replacement, the surface was thoroughly rinsed by de-oxigenated Nanopure water to avoid Cu oxidation/dissolution and next the electrode was transferred back to the Pb upd cell. There, a new Pb upd layer was formed (sketch C) by holding the potential after a single-potential sweep was registered. This encompasses the "building block" reaction that could be employed as many times as desired to grow an epitaxial copper film with variable thickness.

The equation below represents in detail the redox replacement reaction in shown in Figure 1, sketch B, D as follows:[4]

$$Pb_s^0 + k\left(\frac{2}{2}\right)Cu_{aq}^{2+} \rightarrow Pb_{aq}^{2+} + k\left(\frac{2}{2}\right)Cu_s^0$$
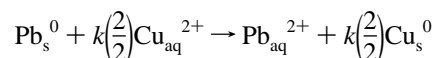
Here, the factor k taking into account the size difference between Pb and Cu atoms has a value in the range of 0.56 to 0.59 based on data for the fcc copper lattice parameter and the nearest-neighbor distance of Pb upd layer on Cu(111) surface.[17] This suggests that it is theoretically impossible to deposit more than 0.6 monolayers of Cu per one "building block" reaction. Unfortunately, regardless of the substrate (Ag(111) or Au(111)), this low theoretical yield turned out to be even lower when the "multiple immersion" replacement strategy was employed for
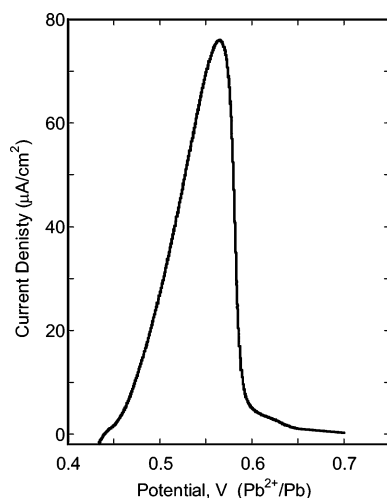
Figure 2. Anodic stripping voltammetry of Cu on Ag(111) after 30 replacements events in multiple immersion configuration showing stripping of 10 ML of copper. Sweep rate 1 mV/s.

the growth of Cu. Subsequent stripping of accordingly grown copper layer on Ag(111) suggested yields rarely exceeding 0.3 monolayers per one building block reaction (50% efficiency). This could be illustrated by the stripping charge obtained by integration of the anodic curve (Figure 2) that manifests the stripping of ten equivalent Cu monolayers grown in "multiple immersion" configuration by 30 replacement events. Most likely the reason of such low yield is associated with an insufficient oxygen evacuation from the working solution. It is known that the oxygen reduction reaction (ORR) is the main competitor of the growing metal in the oxidation of the upd layer during the replacement reaction.[17] The "multiple immersion" amplifies the oxygen effect as each electrode transfer assumes new contact with insufficiently de-oxygenated solution. At the same time, this effect is not that pronounced during Ag growth by multiple immersion replacement protocol owing to the considerably lower rate of ORR on Pb covered Ag(111)[18] in comparison to Pb covered Cu(111).[20]

"One-Pot" Deposition—Cu on Ag(111). The low yield registered for growth of Cu by "multiple immersion" raises the need to modify the deposition protocol in such way so that it meets the requirements for an "adlayer controlled" deposition[6,9] and at the same time would allow work at minimum oxygen concentration. Such a protocol could be carried out in a standard three-electrode cell configuration in a solution with high enough concentration of the upd metal ions so that the sacrificial layer would form upon a very short potential pulse. The solution should also contain low enough concentration of the growing metal ions so that only a negligible amount would plate during the potential pulse. Yet the growing metal concentration should be at least 1 order of magnitude higher than the steady-state oxygen concentration in the electrolyte. Under these circumstances, once the upd layer is formed, the potential control is discontinued, and the metal layer grows as its more noble ions oxidize the sacrificial metal atoms without interference from side oxidative processes such as ORR.

To employ the "one-pot" strategy in our growth experiments, we used electrolyte with a composition of 0.010 M $Pb(ClO_4)_2$ + 0.0003 M $Cu(ClO_4)_2$ + 0.010 M $HClO_4$. In this solution, a Pb upd layer forms for less than a second while the Cu deposition rate does not exceed 1.5 to 2 ML/min so virtually no Cu would deposit upon upd layer formation. Also, the oxygen concentration in the near electrode vicinity under "hanging meniscus" configuration is expected to be at least 2 orders of
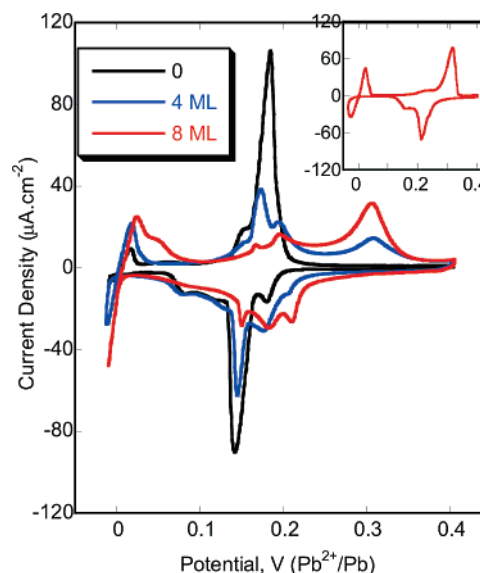

Figure 3. Cyclic voltammetry of Ag(111) covered with different number of Cu ML in 0.003 M $Pb(ClO_4)_2$ + 0.100 M NaClO$_4$ + 0.010 M HClO$_4$ solution at sweep rate of 10 mV/s. Inset: Cyclic voltammetry of Cu(111) electrode under the same experimental condition.

magnitude lower than the concentration of Cu^{2+} ions as shown in our earlier work.[17] Following the step sequence described in Figure 1, our experiments in "one pot" configuration need approximately 20s for carrying out one building block replacement reaction. This timing is established by monitoring the open circuit potential during each replacement event. Results for the growth of Cu on Ag(111) by redox replacement of Pb upd layer in "one pot" configuration are presented in Figure 3, where voltammetry curves are registered on pure Ag(111) (black line and on Cu deposits with different thickness (blue and red curves) in a separate cell with Pb containing solution. The copper layers are obtained by repeating the "building block" procedure for 6 and 12 times. As it could be seen in Figure 3, a continuity of the Cu layer is achieved after deposition of eight equivalent Cu monolayers on the Ag surface (as confirmed by subsequent stripping analysis). This conclusion is ascertained by a typical voltammetry for the Pb/Cu(111) system (inset in Figure 3). A close similarity between the inset curve and the curve obtained after 12 replacement events suggests indirectly a layer-by-layer growth mode. Also, according to earlier findings of Pauling et al.,[20] the comparison between the red curves suggests that at least two of these eight layers are continuous and uniformly cover the silver surface. However, following the same argument, we can conclude that four equivalent layers of Cu are not enough for deposition of two continuous copper layers. X-ray diffraction spectrum obtained on ~100 ML thick Cu layer grown by SLRR on Ag(111) is presented in Figure 4. The presence of a peak typical exclusively for a Cu(111) face and absence of other features in the presented diffraction spectrum (the broad weak peak at $2\theta = 52.5$ cannot be associated with the Cu layer) suggest no evidence for polycrystallinity and thus rule out the possibility for 2D to 3D transition.

"One-Pot" Deposition—Cu on Au(111). The copper deposition on Au(111) electrodes provides better opportunity for morphological characterization using STM. It is known that a typical value for the average terrace width of Ag(111) single crystal is 5−50 nm.[22] At the same time, a well-prepared Au-(111) crystal features average terrace size of 200−500 nm.[23] This identifies gold as an excellent substrate for deposits that need to be characterized morphologically. A key advantage here is the flat surface appearance that allows easier and more
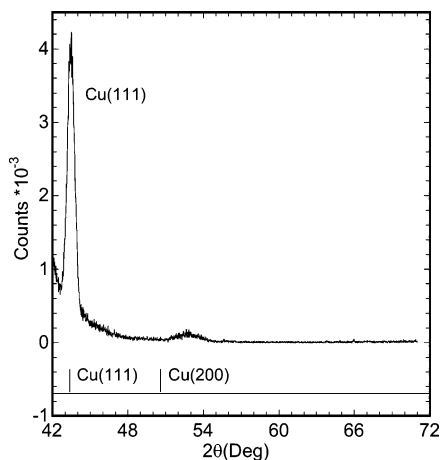
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Figure 4. X-ray diffraction spectrum of a Cu thin film (100 ML) deposited on Ag(111) by surface limited redox replacement in "one pot" configuration.
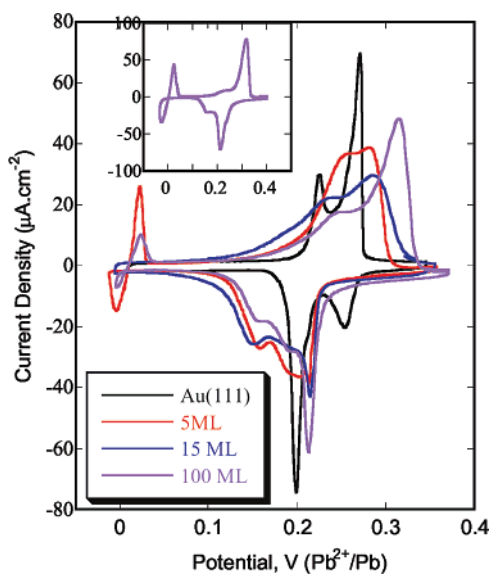

Figure 5. Cyclic voltammetry of Au(111) covered with different number of Cu ML in 0.003 M Pb(ClO$_4$)$_2$ + 0.100 M NaClO$_4$ + 0.010 M HClO$_4$ solution at sweep rate of 10 mV/s. Inset: Cyclic voltammetry of Cu(111) electrode under the same experimental condition.

Figure 6. STM micrographs showing the morphology evolution of a Cu thin film deposited in "one pot" configuration by redox replacement of Pb upd layer on Au(111): A (Z-range 3 nm), 5 ML thick; B (Z-range 3.5 nm), 15 ML thick; C (Z-range 5 nm), 50 ML thick; and D (Z-range 6.5 nm), 100 ML thick. The scan size for all images is 250 × 250 nm.

accurate detection of possible 2D to 3D transition in the growth mode during metal deposition. Similar to the Cu deposition on Ag(111), we employed cyclic voltammetry as a relevant tool for monitoring the deposit quality. Figure 5 shows voltammetric curves registered on pure gold and on Cu deposits with a thickness of 5, 15, and 100 equivalent monolayers. In addition to that, a cyclic voltammogram for Pb upd on pure Cu (111) is presented in the inset. Bearing in mind the substrate sensitivity of the CV curve in the system Pb^{2+}/Cu(111),[24] the comparison between the purple curves undoubtedly demonstrates the crystallographic identity of both substrates. This suggests that a 100 ML thick copper deposit on Au (111) accommodates a Pb upd layer in identical way as a Cu (111) does. The latter finding hints generally at a highly single-crystalline, flat and uniform copper surface. Figure 6 shows the surface morphology of representative 250 nm × 250 nm spots (from 5 separate locations) on 5, 15, 50, and 100 ML thick Cu films. It is clearly seen that there are no evidence of 3D growth mode at thickness as high as 100 ML. It is apparent from the presented results that the copper surface consists only of flat terraces separated by atomically high growth steps. It is to be noted that the flat and uniform appearance of the surface remains unchanged in
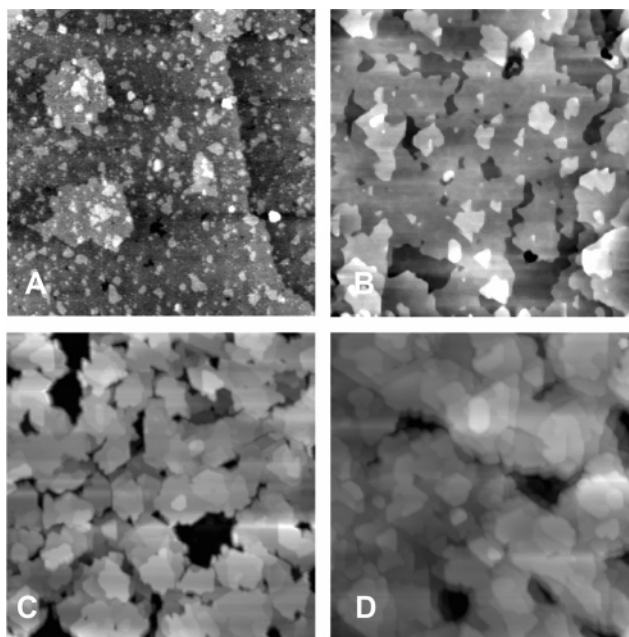
comparison with the starting gold substrate (representative morphology of Au(111) shown in[4]) up to thickness of 15 ML. Images C and D display certain morphology evolution as suggested by the higher Z range values. This implies that a multinuclear multi-layer-by-layer growth mode operates in this system after the deposit reaches certain critical thickness. Similar morphology evolution was also registered at thickness of 40 ML in the growth of Ag on Au(111) by SLRR of Pb and Tl sacrificial layers.[5]

A detailed morphological and crystallographic analysis could be found in Figure 7 that represents the morphology of 15 ML thick copper film examined in situ in presence of Pb^{2+} ions into the solution. It is evident from the cross-section analysis in image A (inset) that the step height of 0.210−0.220 nm corresponds to the theoretical value of 0.208 nm for monatomic step on Cu(111) (fcc) face. The lack of vacancy clusters deeper than 1 ML (Figure 7, images A) and the relatively constant surface roughness after growth of 15 Cu layers suggests a "quasi-perfect" layer-by-layer growth mode.[5] The higher resolution image B illustrates the 4 × 4 Moiré atomic structure typical for Pb upd layer on Cu(111).[25] This suggests smooth transition from Au(111) to Cu(111) crystallographic structure and confirms the finding based upon the voltammetry results discussed earlier in this paragraph.

A stripping of the Cu deposit reveals a morphology typical for Au(111) surface after lifting of the thermal reconstruction. Figure 8 shows stripping of Cu deposit grown by SLRR with 25 replacements of Pb upd on Au(111) registered at a scan rate of 1mV/s. Based upon theoretically calculated charge density of one ML of Cu on Au(111), the amount of experimentally stripped Cu is equal to about 15 ML. Stripping experiments of thicker films (100 ML) suggest 2−3% excess of Cu in comparison with the theoretically calculated. This could be attributed to a limited Cu deposition during the potential pulses to form a sacrificial layer. While such deposition has virtually no contribution per cycle, it could accumulate to a measurable level upon large number of replacement events. The complete
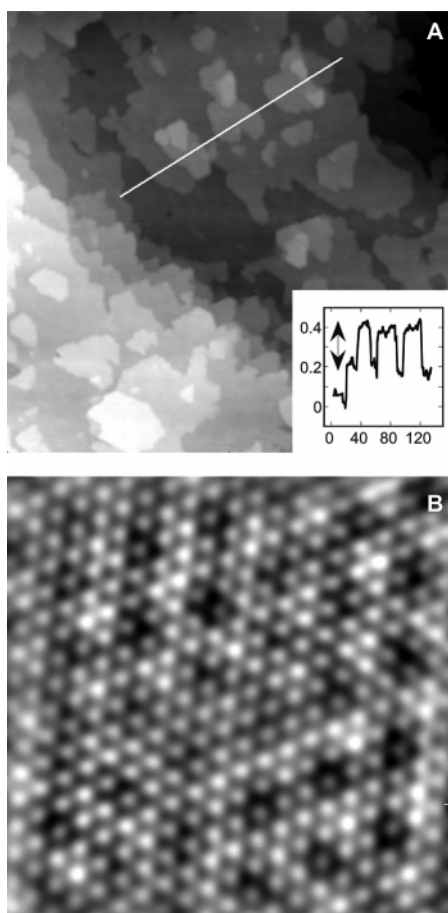
Figure 7. (A) STM image 240 × 240 nm with cross-sectional analysis (inset) illustrating the morphology evolution after 25 displacement events with fifteen grown Cu layers. (B) High-resolution STM image 6 × 6 nm illustrating the (4 × 4) Moiré atomic structure of a Pb upd layer on Cu(111) grown by SLRR.

striping of the copper layer growth revealing bulk terminated Au(111) surface was proven by high magnification atomic structure (Figure 8, inset B). Identical morphological appearance of Au(111) surface could be seen in our earlier work where Au(111) is used as a substrate and Pb is the upd metal.[4,5]

XPS Characterization. The elemental composition of Cu films grown by SLRR of Pb upd layers was also analyzed. A two-point, depth-profile XPS analysis (Figure 9) with a limit of detection (LOD) 0.1 atom % found no traces of Pb incorporated into the deposit. This result is in concert with the elemental analysis of layers grown by DMG where traces of mediating metals were also not found.[3] Even though no surface alloying has been reported for the system Pb/Cu(111) in electrolyte, the "one pot" configuration addresses the issue associated with a general possibility for alloying by both (i) termination of the displacement step strictly at a positive enough potential (the stability of a surface alloy depends upon the applied potential[26]) and (ii) selection of optimal experimental parameters that assume a fast displacement reaction (the surface alloying is typically a slow process[27]). Such strict control makes virtually impossible the inclusion of any upd metal participating in the displacement reaction. The latter is warranted by the typically considerable difference between the formal potentials of upd and growing metals. Recent compositional analysis of similarly grown ultrathin Cu layers reported by Stickney et al. also suggests no presence of Pb.[28]

Proposed Mechanism of Deposition by SLRR. No strict quantitative view of the SLRR method is yet available. However,
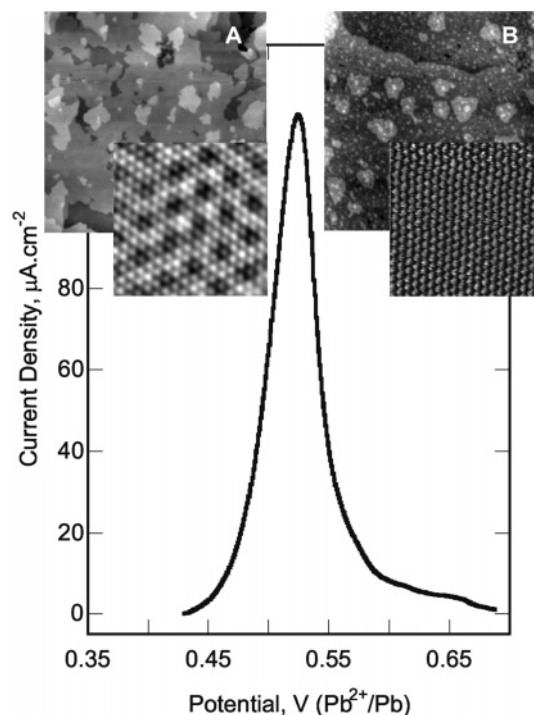

Figure 8. Anodic stripping voltammetry of Cu on Au(111) after 25 replacements events in one pot configuration showing stripping of 15 ML Cu. (A): STM image (220 × 220 nm) of Cu(111) layer (15 ML thick) registered at a potential of 0.03 V Pb2+/Pb prior to stripping. Inset A: High-resolution STM image 6 × 6 nm illustrating the (4 × 4) Moiré atomic structure of a Pb upd layer on Cu(111) grown by SLRR (B) STM image (220 × 220 nm) of Au(111) surface registered at a potential of 0.70 V Pb2+/Pb after the stripping. Inset B: High-resolution STM image 6 × 6 nm illustrating a bulk terminated Au-(111) surface. Sweep rate 1 mV/s.
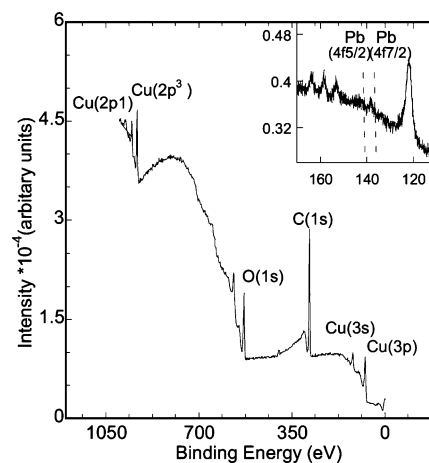

Figure 9. Characteristic XPS survey spectrum of 100 ML thick Cu layer grown on Au(111) by SLRR (main graph). The inset represents a high-resolution spectrum of the same sample where black markers indicate the expected peak positions presence of Pb exceeding 0.1 atom%.

experimental results of this work along with previous experience summarized elsewhere[4,5] allow for building a working hypothesis. According to our view, the displacing metal ions driven by the potential established by the sacrificial metal (Pb) tend to arrange in a way that will warrant a uniform coverage of the predeposited upd layer. Such flat layer arrangement scenario satisfies the general requirement for lowering of the surface free energy as interpreted for a general upd process in EC ALE.[9] Key arguments explaining the surfactant mediation role of various upd layers in ultrahigh vacuum and in solution[2,29] also

suggest the likelihood for 2D growth. Last, the most recent results for the very beginning of Cu deposition by SLRR of Pb upd provide experimental support to our hypothesis suggesting that Cu was depositing only on spots where Pb was originally present.[9] Continuing with our description, we expect a stoichiometric redox exchange, initialized mainly on the flat terraces (it is easier to replace a upd atom from a terrace site than from a step and/or kink site[12]), to facilitate the formation of large clusters that grow laterally and eventually merge to yield a continuous epitaxial deposit. Let us assume now a direct exchange, suggesting that every displacing atom will take the deposition site of the sacrificial one. In the system of interest where displacing and sacrificial metals manifest equal state of oxidation (2:2), the odds to obtain a layer that perfectly reproduces the substrate morphology are substantially higher. Apparently, following these arguments we should expect to obtain an ideal layer-by-layer growth. In our view such growth does take place to a large extent in the experiments reported in this work. At the same time, the departure from the ideality registered at later stages of the deposition process could be attributed to both, size difference between growing and sacrificial metal not allowing completion prior to next nucleation event and also to a stress accumulation with the increasing layer thickness. A mathematical modeling and numerical simulations of the replacement event accumulation could help to quantitatively address this matter.

Conclusions

This paper reports for the first time on the growth of Cu on Ag(111) and Au(111) by SLRR of Pb upd used as a sacrificial layer. The "multiple immersion" strategy used successfully in the deposition of Ag on Au(111) is found to provide low yield when employed in the growth of Cu. The "one pot" strategy proposed as an alternative herein serves to address the "yield" issue by carefully chosen composition of a solution containing both Cu^{2+} and Pb^{2+} ions. Cyclic voltammetry, XRD, and in situ STM characterization experiments provide direct evidence for an epitaxial 2D growth of up to 100 ML of Cu on Ag(111) and Au(111). XPS analysis finds no trace of Pb metal within the limits of 0.1 atom %.

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