Electrodeposition of Epitaxial Cu(111) Thin Films on Au(111) Using Defect-Mediated Growth

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Thin films of various materials are deposited onto the surface of bulk materials (substrates) to achieve properties unattainable in the substrates alone.[1] Among the various types of thin films, those with single crystal quality and in registry with the crystallographic orientation of the substrate are called epitaxial films. They have enormous importance especially in the semiconductor industry, because they exhibit reduced or inhibited side reactions with their surroundings, improved metal properties (e.g., the reduced resistivity and electromigration), and atomically smooth layer.[2]

Compared to the conventional methods for thin film growth in ultrahigh vacuum (UHV), metal deposition in electrochemical environments has such advantages as remarkably low cost and easy handling. However, electrochemical deposition at room temperature often results in a rough polycrystalline film, making it difficult to adapt the electrodeposition to situations that demand high-quality metal films. One strategy to obtain a smoother film has been the use of additives such as thiourea.[3] Although the additives make the film flatter and brighter, the resulting film typically takes the form of a polycrystalline film, sometimes with the void inside the deposit, and the additives may contaminate the film during the course of electrodeposition.[4]

In their pioneering work, Sieradzki et al. proposed a new and general method to perform metal epitaxy in electrochemical environment, which was named the defect-mediated growth (DMG).[5] In their scheme, the metal of interest is co-deposited with a reversibly deposited mediator metal (Pb^{2+} or Cu^{2+}). The mediator is periodically deposited and stripped from the surface by appropriate cycling of the electrode potential, which spawns a high density of metal clusters on a growing layer and leads to layer-by-layer growth. For Ag/Au(111) and Ag/Ag(111) systems with Pb^{2+} or Cu^{2+} as mediators, they could obtain epitaxial films with considerable thickness (250 ML or more).

While the lattice mismatch between Ag(111) (metallic radius 0.288 nm) and Au(111) (0.288 nm) is negligibly small, that between Cu(111) (0.256 nm) and Au(111) is as large as 11%; thus, the electrodeposition of Cu on Au(111) generally results in rough polycrystalline films. Hence, we were motivated by the question whether the DMG method would also produce a heteroepitaxial film for the film/substrate system with large lattice mismatch. In this paper we present a study on Pb-mediated Cu electrodeposition on Au(111) using various surface tools such as cyclic voltammetry (CV), in situ scanning tunneling microscopy (STM), X-ray diffraction (XRD), and Auger electron spectroscopy (AES).

Cu deposition solution was made from ultrapure water (Modulab, U.S. Filter, > 18 MΩ cm), 1 mM $Cu(NO_3)_2$ (Aldrich, 99.999%), 0.1 M $HClO_4$ (Aldrich, double-distilled), and 0.1 M $Pb(ClO_4)_2$ (Aldrich, 99.995%). Electrodeposition of Cu was performed on a Au(111) working electrode (Metallhandel Schröer GmbH), which was annealed with the H_2 flame, by pulse cycles of the electrode potential between 0.050 and 0.400 V versus $Pb^{2+/0}$ using an Autolab potentiostat. STM images were obtained in constant current mode with a Topometrix TMX1000 while an electrochemically etched Pt/Ir wire (Molecular Imaging) coated with Apiezon wax was used as the STM tip. All images are presented unfiltered. For the ex situ measurements, Cu thin film was prepared as above, rinsed with ultrapure water, and dried in air. The XRD measurement was carried out using a D/Max-IIIc (Rigaku), and the AES was measured using a PHI4300 (Perkin-Elmer).

Figure 1 shows a temporal sequence of STM images for the Cu electrodeposition on Au(111) using the DMG method. The electrode potential was manually pulsed between 0.050 and 0.400 V (vs Pb/0.1 M Pb^{2+}). Initially at 0.600 V, which is the just negative of the Cu upd, Figure 1a exhibits the typical Au(111) terrace on which a number of Cu upd islands are deposited. The Cu upd takes the form of an island because its deposition is extremely slow in perchlorate, where the formation of a full monolayer takes 10−20 min.[6] After Figure 1a is acquired, the voltage was changed to 0.400 V. During the acquisition of Figure 1b, a 1-sec potential pulse to 0.050 V is applied to the electrode, which deposits the Pb upd adlayer that acts as a mediator. Then, a potential step back to 0.400 V induces the stripping of the Pb upd adlayer and the continued growth of the Cu adlayer. It is seen that the Cu island density is fairly increased by the deposition and stripping of the mediating Pb upd adlayer. Figure 1b shows that the first Cu adlayer is almost completely deposited and the second one begins to nucleate after another 1-s potential pulse to 0.050 V followed by the Cu deposition at 0.400 V. After application of several more pulses, the Cu adlayers enlarge and grow layer by layer. (Figure 1c) Thicker Cu film is grown, after retracting the STM tip from the surface to minimize tip shielding effect, by repetitive potential pulse cycles (0.050 V for 0.5 s and 0.400 V for 2 s). In Figure 1d, the STM image after 2000 potential pulse cycles shows that the Cu film has grown layer-by-layer with a terrace size of ca. 80 nm. Note the triangular shape of the Cu terraces which is as expected from the three-fold symmetry of the epitaxial Cu(111) thin film.

The overall STM observation indicates that the role of the mediating Pb upd adlayer is to spawn a large density of Cu islands,[7] which then enlarge and merge together to construct the full Cu adlayer. This is similar to the layer-by-layer growth of Ag on Au(111) with a Pb mediator, in which it was proposed that the deposited Ag atom undergoes interlayer exchange with the underlying upd Pb atom and, after stripping off the Pb upd adlayer, myriads of small Ag clusters remain and continue to grow.[5] Also, in the UHV analogue of the surfactant-mediated growth, the homoepitaxy of Cu on Cu(111) surface which is covered with a full layer of Pb resulted in nucleation of a large density of Cu islands on the terrace and layer-by-layer growth.[8]

To confirm the formation of the epitaxial Cu(111) thin film on the Au(111) substrate, XRD measurements are carried out.

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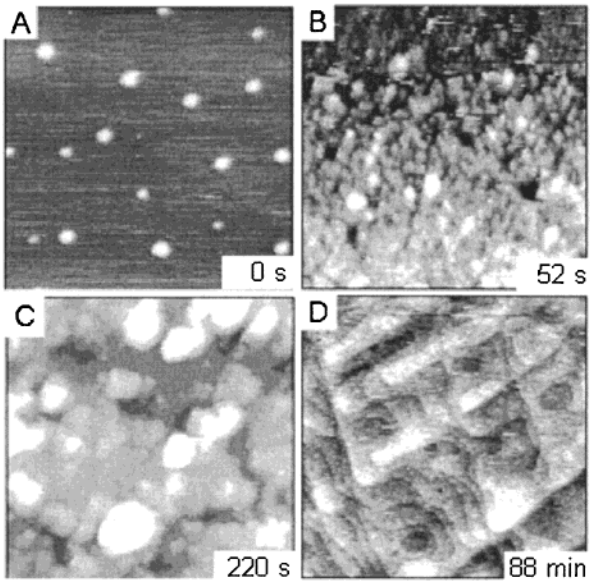

Figure 1. A temporal sequence of in situ STM images of Cu electrodeposition on Au(111) with Pb mediator. (a) 149 nm × 149 nm image of the initial stage of Cu upd on Au(111) terrace. Growth of Cu adlayers after (b) two 1-s pulses to 0.050 V and (c) 6 pulses. Acquisition time of (a−c) was 42 s. (d) Thicker Cu film (ca. 100 ML which was measured by stripping voltammetry) after 2000 pulses. (380 nm × 380 nm) At the lower right corner is shown the time at which scan started. In all images, the *y*-scan direction is downward.

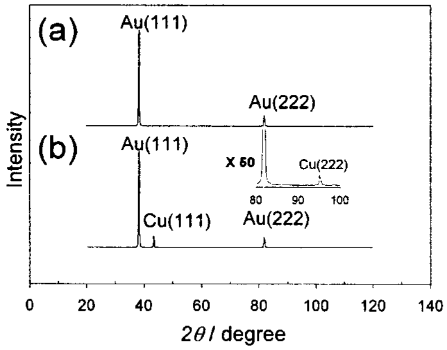

Figure 2. XRD of (a) a bare Au(111) and (b) the one deposited with epitaxial Cu(111) thin film (100 ML) using the DMG method.

The XRD of the bare gold evaporated on glass and annealed in the H_2 flame shows only two peaks,[9] (Figure 2a) which is in good agreement with that for Au(111) single crystal.[10] After the Cu thin film is deposited onto the Au(111) using the DMG method, more XRD peaks appear. (Figure 2b) The peak at 43.46° is assigned to Cu(111) and the smaller one at 95.31° to Cu(222).[11] Epitaxial growth of Cu(111) with respect to Au(111) is confirmed by the Cu (111) and (222) peaks and by the absence of peaks from other planes such as (200) and (220).[12]

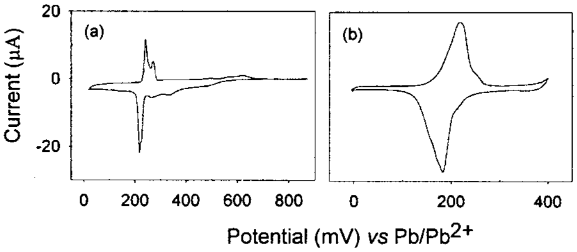

Figure 3. CV in 5 mM PbO + 0.1 M $HClO_4$ at 10 mV/s of (a) a bare Au(111) and (b) the one with epitaxial Cu(111) thin film (100 ML).

Additionally, the Cu(111) thin film is electrochemically characterized by the Pb upd, the CV of which is sensitive to the identity and the face of the electrode surface. Thus, it can be used as a fingerprint for a specific surface. Figure 3a shows the current−potential curve for the Pb upd on bare Au(111), which is in good agreement with those previously reported.[13] After the deposition of the Cu thin film (100 ML), the CV for the Pb upd is entirely changed (Figure 3b), which is in good agreement with previously reported studies on the Pb upd on Cu(111) electrode.[14]

Auger electron spectroscopy (AES) is performed to assess any remaining mediator Pb. The AES of the Cu thin film shows a strong peak for Cu and no peak for Pb and indicates that the mediator Pb is not incorporated into the Cu thin film during the DMG process.

In the present study, the most remarkable finding is that the layer-by-layer growth can be accomplished using the DMG method even for the Cu/Au(111) system, in which epitaxial growth has been impossible due to the large lattice mismatch. At the present stage, however, the mechanism by which the interface strain is relaxed remains unclear yet. A more detailed investigation of the interface structure by the surface X-ray scattering is required to verify this. Compared to the surfactant-assisted epitaxy in the UHV environment, the DMG method has a couple of advantages. While the remarkably low cost and easy handling are obvious merits, the DMG method does not suffer from the remaining mediator material because it can be reversibly stripped from the film. We expect that this DMG method can find its applications in various fields of thin film fabrication.

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Supporting Information Available: The AES graph proving that the mediating Pb metal is not incorporated into the Cu thin films and the STM images of Cu deposition without mediator (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] After flame annealing, the Au/glass sample shows a bunch of ca. 300-nm Au crystallite grains. The (111) direction of each grain is aligned with the surface normal, while the azimuthal angle of the grain might be randomly oriented.

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