

Pb electrodeposition in the presence of chlorine ions on Cu(100): An in situ optical reflectivity difference study

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ABSTRACT

We studied the initial stages of the electrodeposition of Pb in the presence of chlorine ions on Cu(100), using an oblique-incidence optical reflectivity difference (OI-RD) technique. The OI-RD results reveal that immediately following the underpotential deposition (UPD) of the first Pb monolayer, two different types of bulk-phase films grow depending upon the magnitude of overpotential and cyclic voltammetry (CV) scan rate. At low overpotentials and/or slow scan rates, we propose that a bulk-phase Pb film grows on top of the UPD monolayer. At high overpotentials and/or fast scan rates, either a PbO, PbCl₂, or a rough Pb bulk-phase layer grows on top of the UPD layer such that the reflectivity difference signal from such a film has an opposite sign.

INTRODUCTION

Two separate steps can be identified in early stages of metal growth on a dissimilar substrate: the formation of an underpotential deposit (upd) and that of a bulk deposit [1]. The properties of these layers are extremely important, as they provide the initial steps of desirable crystal growth and govern the resultant structure of subsequently grown films. Consequently, to observe and control, in real time, the growth during the initial stages of electrodeposition is of great interest. Electrodeposition provides a convenient opportunity for studies of the effect of widely varying growth conditions through control of an externally applied overpotential, $v = E_{\text{dep}} - E_{\text{Me}/\text{Me}^{2+}}$. The latter enables not only dramatic changes in deposition rate, but also the on-sets of different kinetic processes that may take place at the interface between the electrolyte and the solid substrate. Recent electrodeposition studies by a number of groups using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and current transients, demonstrated over-potential dependent transitions between layer-by-layer growth to three-dimensional growth in metal-metal epitaxy [2-5]. In light of these recent findings, this work was undertaken to investigate the growth of a bulk-phase film (deposit) on an underpotential deposited first monolayer, and particularly to explore possible over-potential dependent growth mode changes, using an *in-situ* ellipsometry technique: oblique-incidence optical reflectivity difference (OI-RD).

We studied the deposition of Pb on Cu(100) in the presence of chlorine ions. The chlorine ions in the electrolyte have been shown in the previous studies to adsorb on a growth surface during electrodeposition. These surface chlorine atoms in turn enhance the kinetics of Pb deposition and affect the rates of surface kinetic processes such as step edge and terrace diffusion [6]. Brisard *et al.* show that chlorine ions exhibit a strong

effect on the step dynamics of immersed Cu(100) and Cu(111) surfaces [6]. The adsorbed Cl changed the mechanism of mass transport on the growth surface by reducing over-barrier hopping while facilitating atomic exchange. The cooperative nature of the exchange process is thought to favor interlayer diffusion and thereby layer-by-layer growth [7].

EXPERIMENTAL DETAILS

All experiments were carried out in a conventional three-electrode electrochemical cell equipped with 2 quartz windows to allow for optical probing at an incidence angle of 73.3° . The cell, with inner dimensions 80 mm x 14mm x 50mm, contains a saturated calomel electrode (SCE) and a Pt counter electrode facing a working electrode (the substrate). The latter was a 100nm-thick polycrystalline Cu(100) seed layer deposited on Si(100) at room temperature using electron-beam evaporation [8]. The structure of the polycrystalline Cu(100) layer was verified by X-ray diffraction (XRD). The polycrystalline Cu(100) grains have a preferred in-plane orientation as revealed by the azimuthal dependence of optical second harmonic generation (SHG) from the layer. Electrodeposition experiments were performed in deaerated solutions of 10 mM HCl and 1 mM $\text{Pb}(\text{ClO}_4)_2$ under potentiostatic control. Unless otherwise stated, the potentials of the working electrode are referenced to the SCE.

The working principles of an oblique-incidence optical reflectivity difference technique (OI-RD) have been described before [9,10]. The light source in our experiment is a 5-mW He-Ne laser. The laser beam is modulated between p- and s-polarization at a frequency of $\Omega = 50$ kHz with a photoelastic modulator. The polarization-modulated beam is reflected from the sample surface at an incidence angle of $\theta_i = 73.3^\circ$. The reflected beam is then passed through an analyzer before being detected with a photodiode. The detected laser intensity has terms that vary with time at various harmonics of the modulation frequency Ω . We measure the second harmonic, $I(2\Omega)$, with a lock-in amplifier. Let r_p and r_s be the reflectivity for p- and s-polarization components from the growth surface during electrodeposition. Let r_{p0} and r_{s0} be the corresponding reflectivity before the deposition. We define $\Delta_p = (r_p - r_{p0})/r_{p0}$ and $\Delta_s = (r_s - r_{s0})/r_{s0}$, and we measure $\Delta_p - \Delta_s$ as follows. Prior to electrodeposition, we adjust the transmission axis of the analyzer so that $I(2\Omega)$ is close to zero. The subsequent change in $I(2\Omega)$ is proportional to the real part of $\Delta_p - \Delta_s$, $\text{Re}\{\Delta_p - \Delta_s\}$ [9]. By separately measuring the proportionality constant, we extract $\text{Re}\{\Delta_p - \Delta_s\}$ directly. For an electrodeposited film with a thickness much less than the laser wavelength λ , $\Delta_p - \Delta_s$ as a function of the thickness d and dielectric constant ϵ_d of the film, is given by [9]:

$$\Delta_p - \Delta_s = i \frac{4\pi d}{\lambda} \sqrt{\epsilon_a} \cos \theta_i \sin^2 \theta_i \frac{\epsilon_{Cu}(\epsilon_a - \epsilon_d)(\epsilon_d - \epsilon_{Cu})}{\epsilon_d(\epsilon_{Cu}^2 \cos^2 \theta_i - \epsilon_a \epsilon_{Cu} + \epsilon_a^2 \sin^2 \theta_i)} \quad (1)$$

Here ε_a is the optical dielectric constant of the electrolyte. ε_{Cu} is the optical dielectric constant of the Cu substrate. Depending upon the composition of the electrodeposited Pb film, ε_d may be different from the optical dielectric constant ε_{pb} for a bulk-phase Pb.

RESULTS AND DISCUSSION

Figure 1(a) shows a cyclic voltammetry (CV) scan and the simultaneously measured reflectivity difference, $\text{Re}\{\Delta_p - \Delta_s\}$, over a potential range where both UPD and bulk-phase growth take place. The cycle begins at a rest potential of -0.2V where, according to previous LEED and STM studies, a stable $C(2 \times 2)$ chlorine overlayer is expected to cover the Cu(100) surface [11]. At a scan rate of 10mV/s , a well-defined cathodic wave at -0.4V indicates the formation of the UPD Pb monolayer. Upon closer inspection, we note that the cathodic wave is comprised of two distinct waves centered at $V = -0.38$ and -0.42V . The origin of the two waves in the upd cathodic current can be from two different processes. Since the polycrystalline Cu(100) contains many step facets, the two peaks could correspond to step adsorption for the first wave and subsequent terrace adsorption for the second. Alternatively, the origin of the two waves could correspond to the dissolution of the pre-adsorbed Cl overlayer at $V = -0.38\text{V}$, followed by the subsequent adsorption of the UPD Pb monolayer at -0.42V . Optically, we observe a large change in $\text{Re}\{\Delta_p - \Delta_s\}$ during the UPD of Pb. At the potentials of each cathodic current wave, we observe a noticeable kink in $\text{Re}\{\Delta_p - \Delta_s\}$. The plateau feature in $\text{Re}\{\Delta_p - \Delta_s\}$ at $t = 32\text{s}$ indicates the completion of the UPD Pb monolayer. To characterize the kinetics of the UPD, we varied the CV scan rate from 10mV/s to 100mV/s . We find that the numerical value of the plateau of $\text{Re}\{\Delta_p - \Delta_s\}$ is independent of scan rate, indicating that the process of forming the UPD monolayer is not a function of the surface diffusion properties of the Pb atoms, and is, therefore, an equilibrium process. As the potential is swept further to the overpotential region (more negative), a second cathodic wave appears, indicating that a bulk-phase film begins to grow. The corresponding change in $\text{Re}\{\Delta_p - \Delta_s\}$ is opposite in sign to the change in response to the first UPD monolayer Pb, and the magnitude of the change increases until the potential is reversed at -0.58V at $t = 48\text{s}$. As the potential is cycled back to -0.2V , two anodic waves, corresponding to dissolution of the bulk-phase film and the UPD Pb monolayer, coincide well with the complete reversal of the optical reflectivity difference signal. The latter shows a complete dissolution of the deposited film and re-adsorption of the Cl overlayer.

Figure 1(b) shows a CV scan in the same range as in figure 1(a) but at a higher scan rate of 30mV/s . The CV diagram is qualitatively the same as in figure 1(a). However, after completion of the first UPD Pb monolayer, the change in $\text{Re}\{\Delta_p - \Delta_s\}$ is in the same direction as that in response to the first UPD monolayer Pb. This means a different bulk-phase film grows under the condition of a faster scan rate. Figure 2 shows overpotential (in magnitude). $\text{Re}\{\Delta_p - \Delta_s\}$ shows that after completion of the first a CV

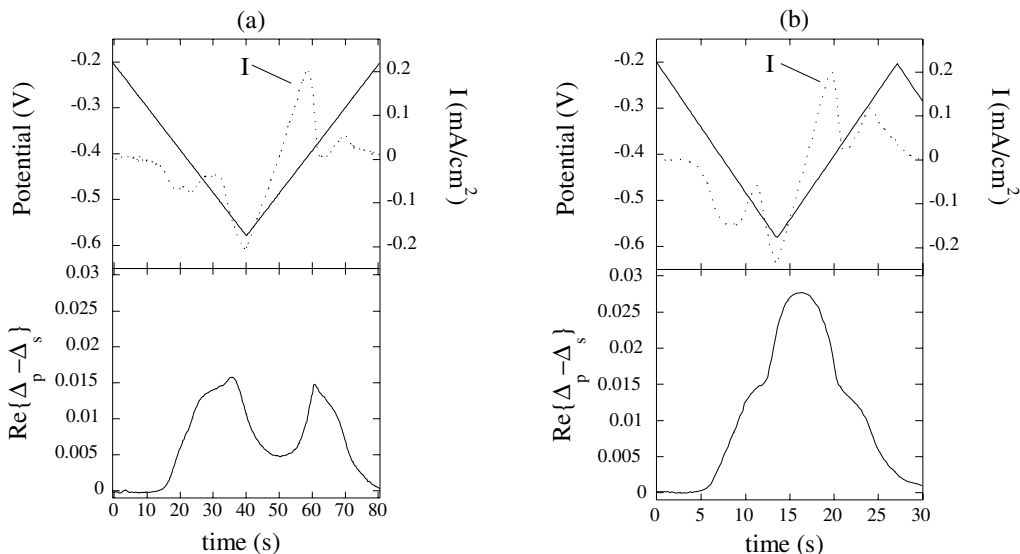


Figure 1. (a) CV for potential cycled from -0.2 to -0.58 V at a scan rate of 10 mV/s (top) and resulting optical signal, $\text{Re}\{\Delta_p - \Delta_s\}$ (bottom). (b) CV for potential cycled from -0.2 to -0.58 V at a scan rate of 30 mV/s (top) and resulting optical signal, $\text{Re}\{\Delta_p - \Delta_s\}$ (bottom).

scan at the same low scan rate of 10 mV/s as in figure 1(a), but to a larger UPD Pb monolayer, the same type of bulk-phase film as shown in figure 1(a) grows first. At a potential of -0.58 V at $t = 39$ s, the second type of bulk-phase film as in Figure 1(b), begins to grow instead. As the potential is cycled back to -0.2 V, $\text{Re}\{\Delta_p - \Delta_s\}$ traces the same path in the reverse direction, indicating that the two types of film dissolve sequentially in the reverse order. This means that a different bulk-phase film grows under the condition of a large overpotential.

Figure 3 shows a typical pulsed deposition result. Immediately after pulsing the potential to -0.52 V, $\text{Re}\{\Delta_p - \Delta_s\}$ rises above the level corresponding to the first UPD Pb monolayer on Cu(100), indicating the formation of bulk-phase film as in figure 1(b). At $t = 20$ s, $\text{Re}\{\Delta_p - \Delta_s\}$ changes direction in response to the formation of a bulk-phase like that in figure 1(a). When we switch the potential to -0.48 V at $t = 35$ s, where only the UPD Pb monolayer is stable, the second bulk-phase dissolves continuously until the signal reverses direction at $t = 90$ s, then the first bulk-phase dissolves in sequence, as indicated by the resulting OI-RD signal that traces the deposition path almost exactly, until the level for the UPD Pb monolayer alone.

From figures 1-3 we arrive at the conclusion that two types of bulk-phase films grow on the first UPD Pb monolayer, depending upon the CV scan rate and the magnitude of the overpotential. From equation (1), $\text{Re}\{\Delta_p - \Delta_s\}$ is a function of the thickness and the optical dielectric constant of a film. The latter depends on the composition of the film. Since Morin and coworkers recently reported the observation of potential-controlled transition from a 2-D step flow growth (resulting in a smooth Pb

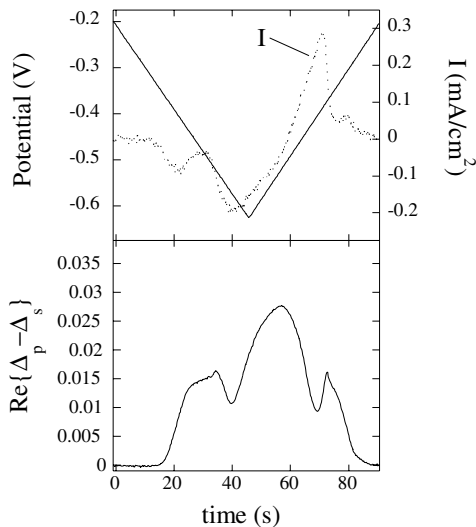


Figure 2. CV for potential cycled from -0.2 to -0.62 V at a scan rate of 10 mV/s (top) and corresponding optical signal, $\text{Re}\{\Delta_p - \Delta_s\}$ (bottom).

film) to 3-D decoration transition (resulting in a rough Pb film) for Ni electrodeposition on Ag(111) [2], it is conceivable that one of the films is a compact, smooth Pb film and the other is simply a rough or even porous Pb film. To understand the optical reflectivity difference signal in terms of the compositions of the bulk-phase films, we employed a Bruggeman effective medium theory to find the effective optical dielectric constant for a material that is mixture of two different bulk-phase materials. We determined the thickness of the bulk-phase films by integration of the anodic peak of the CV with respect to time. Using the measured thickness and equation 1, we calculated the expected $\text{Re}\{\Delta_p - \Delta_s\}$ from a smooth Pb film with $\epsilon_d = \epsilon_{pb}$ and from a rough film with the effective optical dielectric constant calculated using an effective medium comprised of a mixture of Pb and H_2O . The calculated value of $\text{Re}\{\Delta_p - \Delta_s\}$ for a rough Pb film is opposite in sign from that of a smooth Pb film, if the rough film consists of 20% Pb and 80% H_2O . From this model, 2-D Pb growth corresponds to slow scan rates and/or low overpotentials, while a 3-D film results at fast scan rates and/or high overpotentials.

Another possibility for the sign reversal in $\text{Re}\{\Delta_p - \Delta_s\}$, is the formation of a new film consisting of a Pb compound such as PbO or PbCl_2 . Using ellipsometry, Kruger [12] studied the oxidation of Cu substrates in water and observed an abrupt change in the sign of the ellipsometric signal that was attributed to the formation of CuO instead of expected CuO_2 . In our case, a strong candidate for the second bulk-phase film is PbO. We calculated the expected $\text{Re}\{\Delta_p - \Delta_s\}$ for a bulk-phase film consisting of Pb using equation 1 and the optical dielectric constant of a mixture of Pb and PbO. The calculated value predicts a sign reversal for a film consisting of between 50 and 100% PbO. From this model, 2-D Pb growth corresponds to slow scan rates and/or low overpotentials, while a new bulk-phase film, PbO, results at fast scan rates and/or high overpotentials.

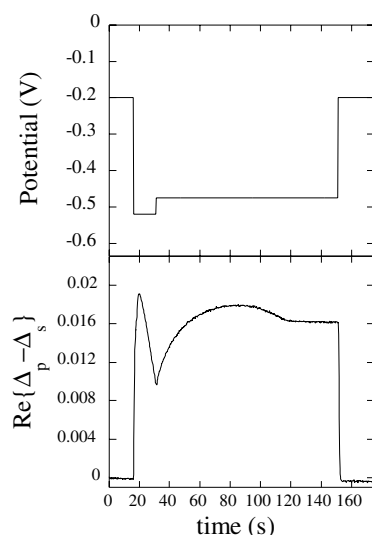


Figure 3. Applied pulse potential (top) and corresponding optical signal, $\text{Re}\{\Delta_p - \Delta_s\}$ (bottom).

CONCLUSION

The initial stages of the electrodeposition of Pb in the presence of chlorine ions on Cu(100), have been studied using an OI-RD technique. The OI-RD results suggest that two types of bulk-phase films grow depending upon the magnitude of overpotential and the CV scan rate. At low overpotentials and/or slow scan rates, we propose that a bulk-phase Pb film grows on top of the UPD monolayer. At high overpotentials and/or fast scan rates, either a PbO, PbCl₂ or a rough Pb bulk-phase layer grows on top of the UPD layer such that the reflectivity difference signal from such a film has an opposite sign.

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