An *in-situ* oblique-incidence optical reflectance difference study of Co electrodeposition on a polycrystalline Au(111) surface

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ABSTRACT

We studied submonolayer and multilayer deposition of Co on Au(111) using *in-situ* oblique-incidence optical reflectance difference (OI-RD). We show that the optical technique is highly sensitive and accurate in determining the electrodeposited film thickness and growth mode. We found that the optically determined thickness of the ultrathin Co film is in very good agreement with that deduced from the integration of the anodic current during cyclic voltammetry (CV). From a weak oscillatory behavior of the optical reflectance difference signal, it seems that the growth of electrodeposited Co on Au(111) under pulsed deposition condition proceeds by a combination of three dimensional island and quasi layer-by-layer growth modes.

INTRODUCTION

Electrochemically deposited Co layers on non-magnetic metal substrates are known to display perpendicular magnetic anisotropy [1]. This property, together with inherently high throughput of electrodeposition for film fabrication, has sparked a wealth of research to further understand the initial stage of Co electrodeposition on non-ferromagnetic systems [2-10]. Most of the emphasis has been placed on Co electrodeposition on single crystal Au [2-8]. Structural information during nucleation and the initial growth has been obtained by scanning tunneling microscopy (STM). The thickness of the electrodeposited Co films as a result of subsequent growth is usually determined *ex-situ* by Rutherford-Back-Scattering (RBS). Both the film structure (governed by the growth mode) and thickness govern the resulting magnetic anisotropy of an electrodeposited Co film. It is thus desirable that one monitors the electrodeposition *in-situ* so that the kinetics, such as growth mode and film thickness can be determined and controlled *during* growth.

We demonstrate that an oblique-incidence optical reflectance difference (OI-RD) technique can be used for such a purpose. This OI-RD technique is a special form of ellipsometry that is optimized to probe the change that takes place on a substrate surface or the interface between two condensed media. It has been used to characterize both growth mode and film thickness in vapor-phase epitaxy under ultra high vacuum (UHV) conditions [11-14]. In the present study we use this technique to follow and characterize the electrodeposition of Co on Au(111).

EXPERIMENT

Gold substrates were prepared by vacuum evaporation of 100nm thick gold films onto microscope slides. The polycrystalline gold exposes primarily (111) facets. Electrodeposition experiments were conducted in a conventional three-electrode cell with the gold film on the glass

substrate as the working electrode, a saturated mercury chloride electrode (SCE) as a reference, and a Pt counter-electrode. Two quartz windows form two opposite sides of the cell to allow for optical access. For each measurement the cell was filled with an aqueous solution containing controlled amounts of KCl, K_2SO_4, H_2SO_4, and $CoSO_4$ in ultrapure H_2O, and then deaerated by bubbling research grade N_2 in the final solution for 15 minutes. The working electrode potential was externally controlled using a potentiostat and a waveform generator. In this manner we were capable of controlling the deposition of Co with both cycled [for cyclic voltammetry (CV)] and single stepped potentials (for pulsed deposition).

The electrochemical cell and the optical set up are shown in Figure 1. For the optical reflectance difference measurement, we use a 5mW 632.8nm TEM_{00} He-Ne laser as the probe light beam. We alternate the polarization of the beam between s- (transverse electric) to p-polarization (transverse magnetic) using a photoelastic modulator (PEM90, Hinds Instrument) at a frequency of $\Omega = 50$ kHz. The polarization-modulated beam enters the electrochemical cell and is incident on the gold surface obliquely. The reflected beam exits the cell and passes through an analyzing polarizer before it is detected with a photodiode detector. The reflected laser beam intensity has terms that vary at various harmonics of the modulation frequency. We measure the magnitude of the second harmonic, $I(2\Omega)$, with a Stanford Research SR850 digital Lock-in amplifier. Let $r_{p0} = |r_{p0}|\exp(i\varphi_{p0})$ and $r_{s0} = |r_{s0}|\exp(i\varphi_{s0})$ denote the reflectivities for the p- and s-polarized light from the gold surface before electrodeposition, and let $r_p=|r_p|\exp(i\varphi_p)$ and $r_s=|r_s|\exp(i\varphi_s)$ during the electrodeposition of Co on the gold surface. We define $\Delta_p=(r_p - r_{p0})/r_{p0}$ and $\Delta_s=(r_s - r_{s0})/r_{s0}$. By adjusting the analyzer, we nullify the magnitude of $I(2\Omega)$ before the deposition. During the subsequent electrodeposition, $I(2\Omega)$ is then simply proportional to the real part of $\Delta_p - \Delta_s$, namely, $Re\{\Delta_p - \Delta_s\}$. In our experiment, we separately determine the proportionality constant so that we extract $Re\{\Delta_p - \Delta_s\}$ directly from $I(2\Omega)$. It has been shown by Zhu and coworkers that [15]

$$\Delta_p - \Delta_s = i\frac{4\pi d}{\lambda}\sqrt{\varepsilon_a}\cos\theta_i\sin^2\theta_i \frac{\varepsilon_{Au}(\varepsilon_a - \varepsilon_{Co})(\varepsilon_{Co} - \varepsilon_{Au})}{\varepsilon_{Au}(\varepsilon_{Au}^2\cos^2\theta_i - \varepsilon_a\varepsilon_{Au} + \varepsilon_a^2\sin^2\theta_i)} \tag{1}$$

d is the averaged film thickness, λ is the laser wavelength, θ_i is the angle of incidence, ε_a is the dielectric constant of the electrolyte in the cell, ε_{Co} is the dielectric constant of the deposited Co, and ε_{Au} is the dielectric constant of the Au(111) sample. Utilizing this equation, we can compute the film thickness, d, from the experimental value of $Re\{\Delta_p - \Delta_s\}$ for compact films. We can also find qualitative information about the growth mode from the dielectric response of the adsorbed layer. In a layer-by-layer growth, the effective ε_{Co} that includes the responses from step edge atoms, oscillates with the increasing film thickness and as a result $\Delta_p - \Delta_s$ is also oscillatory. For three dimensional growth the effective ε_{Co} varies monontonically as the surface density step edge atoms increase with the thickness [11], and the resultant $\Delta_p - \Delta_s$ changes monotonically with ε_{Co} as well as the average thickness, d.

RESULTS AND DISCUSSION

Cyclic Voltammetry

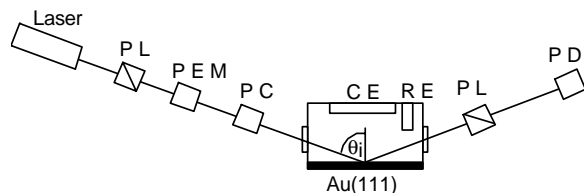Figure 2 shows a representative cyclic voltammagram from the Au(111) surface in

Figure 1. Sketch of electrochemical cell and the optical setup for the oblique-incidence reflectance difference technique. PL: Glan-Thompson polarizers; PEM: photoelastic modulator (Hinds Instruments, OR); PC: Pockel Cell; CE: Pt counter electrode; RE: SCE reference electrode; and PD: biased silicon photodiode.

1mM $CoSO_4$ with a supporting electrolyte consisting of 10 mM K_2SO_4 + 0.1 mM KCl + 1mM H_2SO_4.The resulting current, I_{dep}, is shown in Figure 2(b). The cycle begins at a positive electrode potential of 0.4V vs. SCE, where the Au surface does not contain any Co. Ramping the potential downward at a rate of 20mV/s initially results in a cathodic current at –0.6V vs. SCE. As the potential becomes more negative, two distinct current features appear. The feature at –0.75V vs. SCE corresponds to a reduction of protons [3]. The feature at –1.0V vs. SCE corresponds to the reduction of Co^{2+}. The positive peak in anodic current at - 0.35V vs. SCE is related to dissolution or stripping of Co from the gold surface. Time integration of this peak gives a direct measurement of the total Co deposition. If we assume that each Co ion is doubly ionized and that deposition of 1 ML of Co corresponds to one Co atom for one surface Au atom with a density of $1.85 \times 10^{15}/cm^2$, then the charge per monolayer is $Q_{ML} = 0.59$ mC/cm^2 [3]. For the annodic peak in Figure 2(b) the time-integrated current is 2.98 mC/cm^2, which corresponds to a total deposition of 5.1 ML of Co. Figure 2(c) shows the optical reflectance difference signal in response to the potential cycle of Figure 2(a). The optical signal shows no significant change until the potential reaches –0.87V. At this potential a strong optical response indicates the onset of Co growth. The signal continues to rise until the potential is cycled from –1.23V back to –0.87V. The net change in the total optical signal, $Re\{\Delta_p - \Delta_s\}$, during this part of the cycle is 0.05. This value remains constant until the potential reaches –0.5V where the dissolution of Co begins. This is also where the current crosses zero and becomes positive, which is in good agreement with the value for the Nernst potential for Co/Co^{2+} [4]. Upon returning the potential to positive values, the optical signal returns to its original value, indicating a complete dissolution of the adsorbed Co layer.

From Eq. (1) we calculated the expected optical signal change $Re\{\Delta_p - \Delta_s\}$ for 1 ML of Co deposited on Au(111). The dielectric constants for the three level system are $\varepsilon_a = 1.33$, $\varepsilon_{Au} = -9.98 + 0.85i$ [17] and $\varepsilon_{Co} = -11.62 + 18.47i$ [17]. The angle of incidence of the laser beam is $\theta_i = 72.5^o$, and the thickness, d, of 1ML of Co on Au is 2.5Å. Using these values, we calculate $Re\{\Delta_p - \Delta_s\}$/ML = 0.01. Therefore, the optical response indicates a total thickness of the electrodeposited Co film of 5.0 ML. This is in excellent agreement with the value of 5.1ML obtained by the time-integrated current of the anodic current.

Figure 3 shows the CV results as a function of the potential (E_{SCE}/V). Since the optical signal is a direct measure of the amount of Co charge deposited on the sample, we use $d(Re\{\Delta_p - \Delta_s\})/dt$ as a qualititative measure of the *local* Co deposition current [16]. In Figure 3(c) we show
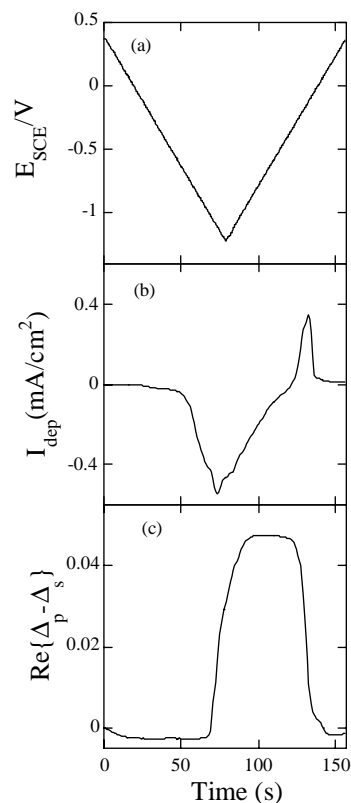
Figure 2. (a) Potential cycled from 0.4V to –1.23V at a rate of 20mV/s in 1mM $CoSO_4$ + 10mM K_2SO_4 + 0.1 mM KCl + 1mM H_2SO_4. (b) Deposition current for the potential cycle in (a). (c) Optical reflectance difference signal, $Re\{\Delta_p - \Delta_s\}$, for the same cycle.

$d(Re\{\Delta_p - \Delta_s\})/dt$ during the entire potential cycle. The qualitative features of $d(Re\{\Delta_p - \Delta_s\})/dt$ follow the CV current of Figure 3(a) very closely. In fact, the time derivative of the optical signal is only sensitive to the *in-situ* or *local* Co deposition current and is therefore a better monitor of Co electrodeposition and dissolution. It is noteworthy that the signal-to-noise ratio of the time derivative is extremely high for a local deposition probe.

Pulsed deposition

In a pulsed electrodeposition experiment, we instantaneously drop the working electrode potential from a 0.4V vs. SCE to –0.9V vs. SCE, and measure the temporal behavior of the subsequent deposition of Co. In this way, we control the Co deposition to a desired amount. Figure 4 displays the optical signal $Re\{\Delta_p - \Delta_s\}$ during a pulse deposition at –0.9V. At this potential, the signal increases monotonically with increasing Co deposition, a signature of three dimensional or island growth [11]. This is in contrast to the deposition during CV scans, where the potential is slowly ramped, resulting in a more compact film. Island growth has been found for Co on Au(111) using *in situ* STM [3-5]. By subtracting the envelope of the optical signal during the pulsed deposition we found a reproducible oscillatory component. This is shown in
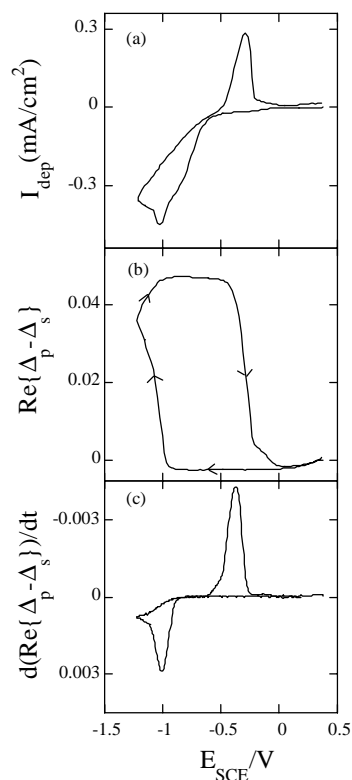
Figure 3. (a) Current while the potential is cycled from 0.4V to –1.23V at a rate of 20mV/s in 1mM $CoSO_4$ + 10mM K_2SO_4 + 0.1 mM KCl + 1mM H_2SO_4. (b) Optical reflectance difference signal, $Re\{\Delta_p - \Delta_s\}$, for the same cycle. (c) Time derivative of the optical signal. The vertical axis is reversed for comparison with Figure 3(a).

the insert of Figure 4. The amplitude of the oscillation is on the order of 1% of the total amplitude corresponding to one Co monolayer. This weak oscillatory component suggests that the three dimensional growth is accompanied by a very small component of a layer-by-layer growth. This means that on the terraces of three dimensional Co islands, nucleation, growth, and eventual coalescence in two dimensions takes place as the islands grow primarily in three dimension [11]. Cagnon et al, using STM on the same electrolyte and $CoSO_4$ concentration, also suggest that a quasi perfect layer-by-layer epitaxy exists in the initial growth mechanism for Co on Au(111) [3].

CONCLUSION

We show that the optical reflectance difference technique provides a quantitative measure of thin film thickness for CV deposition of Co on Au(111). Additionally, the optical results
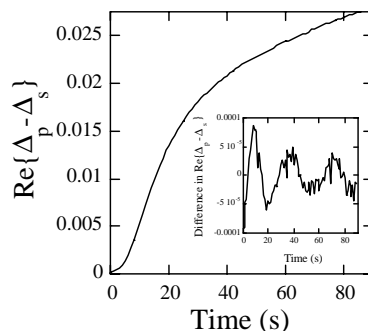
Figure 4. Re$\{\Delta_p$-$\Delta_s\}$ as a function of time for a pulsed potential of –0.9V. Inset: subtraction of the envelope.

suggests that during pulsed deposition, Co deposits on Au(111) by a combination of three dimensional island growth and a weak quasi layer-by-layer growth component.

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