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**Deposition of Gold** 

# Adsorption Processes during Electrochemical Atomic Layer

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Electrochemical atomic layer deposition (e-ALD) technique offers a simple and effective "wet chemistry" approach enabling highprecision monolayer-by-monolayer deposition of metal films. The process of e-ALD of Au involves lead underpotential deposition ( $Pb_{UPD}$ ) followed by its redox replacement by a Au monolayer. The time evolution of the deposit mass during "one-pot" Au e-ALD is known to exhibit a unique three-stage response that is presently not well understood. In this work, we probe this response using voltammetry, electrochemical quartz crystal microgravimetry (e-QCM), and chronoamperometry to unravel the underlying mechanistic events during Au e-ALD. The presence of adsorbed  $Au^{+3}$ -ligand complex(es) (Au-L) on the Au surface is established. In stage I of e-ALD, this Au-L adsorbed layer is reduced to Au while a  $Pb_{UPD}$  adlayer is formed. In stage II, the  $Pb_{UPD}$  adlayer undergoes spontaneous surface-limited redox replacement by nobler Au under open-circuit conditions. Finally, in stage III, readsorption of the Au-L occurs on the newly deposited Au. Quantitative analysis of the deposit mass transients obtained under a variety of conditions provides an estimate of the Au-L mass and its molecular weight.

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Deposition of thin metal films with atomic-scale precision is desired for various applications such as nano-electronics fabrication, corrosion protection, and fuel-cell catalysis.<sup>1-3</sup> Gold (Au) nano-films have promising potential applications in high-performance "hohlraums" (radiation cavities) for inertial confinement fusion (ICF) experiments. Here, Au coatings onto highly porous templates are required.4,5 Conventional vapor-phase ALD techniques have been investigated to achieve such coatings;<sup>6,7</sup> however, these techniques suffer from several drawbacks including the use of aggressive reaction conditions, lack of suitable precursor compounds (with good volatility and thermal stability), and the inability to produce conformal deposits (due to the recombination of radicals on the walls of complex structures).<sup>7</sup> Therefore, atomic layer deposition (ALD) of Au using electrochemical methods and liquid-phase precursors is attractive because of its potential for depositing uniform thin films inside porous structures. Electrochemical atomic layer deposition technique offers a simple and effective "wet chemistry" approach while enabling high degree of precision and control in thin film deposition.<sup>8,9</sup> The e-ALD approach involves two steps: (i) formation of a sacrificial monolayer, of a metal which is less noble than the e-ALD metal, onto the substrate typically via underpotential deposition (UPD),<sup>10</sup> followed by (*ii*) spontaneous surface-limited redox replacement (SLRR) of the sacrificial UPD metal monolaver by the nobler e-ALD metal monolayer.<sup>11,12</sup> These steps can be repeated to achieve multilayered deposits. Xie et al. have recently employed the e-ALD approach to synthesize Au-based alloy catalysts.<sup>13</sup> Also, Mitchell et al. and Fayette et al. have reported on epitaxial deposition processes for Au and Pt utilizing the e-ALD approach.<sup>14,15</sup> In their work, the Au deposition process was performed in a single electrochemical cell ("one-pot") containing both  $Pb^{+2}$  and  $Au^{+3}$  species. In step (*i*), a sacrificial Pb monolayer is deposited via UPD:

$$[Pb^{+2}]_{aq} + 2e^{-} \rightarrow Pb_{UPD}$$
<sup>[1]</sup>

In step (ii), spontaneous SLRR of the Pb monolayer by Au occurs:

$$3Pb_{UPD} + 2[Au^{+3}]_{aq} \rightarrow 2Au_{ALD} + 3[Pb^{+2}]_{aq}$$
 [2]

From Reaction 1, the formation of a  $Pb_{UPD}$  adlayer should cause a net increase in the electrode mass. However, from Reaction 2, stoichiometry dictates that every three atoms of Pb are replaced by two atoms of Au. Since the atomic mass of Au ( $M_{Au} = 197 \text{ g mol}^{-1}$ ) is only slightly lower than that of Pb ( $M_{\rm Pb} = 207 \text{ g mol}^{-1}$ ), this stoichiometry implies that the electrode mass should decrease during the SLRR step. Utilizing quartz crystal microgravimetry, experimental observations of the electrode mass change have been reported by Mitchell and coworkers.<sup>14</sup> These observations reveal a significantly more complex behavior. During the SLRR step, an initial mass decrease is followed by a mass gain of an even greater magnitude. The details of this behavior are provided below. A clear and convincing mechanism explaining this behavior is presently lacking. Here, we show how adsorption of  $Au^{+3}$ -ligand complexes (also refereed to here as "Au-L") quantitatively manifests in mass gain during step (i) as well as explains the mass transient (mass loss followed by mass gain) during step (ii) of e-ALD.

Au e-ALD electrolytes comprise Au<sup>+3</sup>-containing chloride salts dissolved in aqueous solutions. These undergo hydrolysis to form a variety of chloride complexes, e.g., AuCl<sub>3</sub>OH<sup>-</sup> or AuCl<sub>2</sub>(H<sub>2</sub>O)OH.<sup>16-20</sup> Previous reports have suggested that Au<sup>+3</sup>, Pt<sup>+4</sup>, and Ru<sup>+3</sup> complexes can undergo adsorption on Au and Pt surfaces under open-circuit conditions.<sup>14,21-23</sup> In the Au e-ALD process too, Au<sup>+3</sup>-ligand complexes may adsorb on the substrate surface during deposition. We show here that such adsorption quantitatively explains the observed features of the electrode mass transients during Au e-ALD.

#### Experimental

Electrochemical QCM, cyclic voltammetry (CV), and chronoamperometry were employed to characterize the Au e-ALD process. Details of these techniques are provided below.

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**Figure 1.** Electrode potential (*red*) and mass change (*blue*) during the Au e-ALD process performed on a Au-coated quartz crystal in an electrolyte containing 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> + 10  $\mu$ M AuCl<sub>3</sub>. Mass changes are defined as follows:  $\Delta m_{\rm I}$  = mass gain at the end of stage I (Pb<sub>UPD</sub>),  $\Delta m_{\rm II}$  = magnitude of mass loss at the end of stage II compared to stage I due to SLRR of Pb<sub>UPD</sub> by Au, and  $\Delta m_{\rm III}$  = mass gain in stage III compared to stage II.

*Electrochemical quartz crystal microgravimetry.*—A quartz crystal microbalance, QCM-200 (Stanford Research System), was used for gravimetric analysis of the Au e-ALD process. Au-coated quartz crystals (5 MHz, Fil-Tech) were used as substrates. The frequency change ( $\Delta f$ ) measured during Au e-ALD was converted to mass change ( $\Delta m$ ) using the Sauerbrey equation:  $\Delta f = -C_f \Delta m$ , where  $C_f$  is the sensitivity factor (=56.6 Hz  $\mu g^{-1}$ cm<sup>2</sup>).<sup>24</sup> In all e-QCM experiments, the electrode potential was applied and current was recorded using a VersaSTAT4 potentiostat (Princeton Applied Research). Details of the electrochemical cell setup are provided below.

Cyclic voltammetry.--CV was utilized to characterize the Pbupp behavior on polycrystalline Au. First, the Au-coated quartz crystal was rinsed in 18 M $\Omega$ -cm deionized (DI) water, then in acetone and again in DI water, and finally dried under a stream of nitrogen (N<sub>2</sub>) gas. CV measurements were performed in an electrochemical cell with a three-electrode configuration. The Au-coated quartz crystal was the working electrode, while a Pt wire and a Ag/AgCl/Saturated KCl (Fisher Scientific) served as the counter electrode and the reference electrode, respectively. The electrolyte used for Pb<sub>UPD</sub> was prepared using DI water, and contained 10 mM perchloric acid (HClO<sub>4</sub>, Fisher Scientific) and  $400 \,\mu\text{M}$  lead perchlorate (Pb(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O, Acros Organics). The pH of the electrolyte was measured to be 2. The electrochemical cell was capped with a Teflon lid. The electrolyte was de-aerated with argon (Ar) gas for 30 min prior to electrochemical measurements to lower the concentration of dissolved oxygen in the electrolyte, and kept under de-aeration during experimentation. All potentials reported in this work are with respect to the standard hydrogen electrode (SHE). The potential was scanned from 0.50 V to -0.23 V to underpotentially deposit an adlayer of Pb, followed by stripping of the Pb<sub>UPD</sub> layer during the reverse scan (anodic scan direction). Scan rate was 20 mV s<sup>-1</sup>. For comparison, a background scan was also obtained under the same conditions but in the absence of  $Pb(ClO_4)_2$  in the electrolyte.

*Electrochemical atomic layer deposition of Au.*—As described above, Au e-ALD consists of two steps that are repeated cyclically:

(*i*) UPD of a sacrificial monolayer of Pb on the Au surface at a constant applied potential of -0.2 V for 50 s, followed by (*ii*) SLRR of Pb by the more noble Au under open-circuit conditions. A cut-off potential ( $E_{\rm cut-off}$ ) was used in step (*ii*) to terminate the Au e-ALD cycle and transition to the next cycle.  $E_{\rm cut-off}$  was chosen to be 1.2 V or 0.275 V to study the effect of cut-off potential on mass transients during e-ALD. The electrolyte used for Au e-ALD contained 10 mM HClO<sub>4</sub>, 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> and 10  $\mu$ M gold trichloride (AuCl<sub>3</sub>, Sigma-Aldrich). Other aspects of the three-electrode configuration used during Au e-ALD studies were analogous to those used for CV studies (detailed above). Note that the concentration of Pb<sup>+2</sup> ions was significantly higher compared to the concentration of Au<sup>+3</sup> species in the Au e-ALD electrolyte. This minimized Au co-deposition in step (*i*).<sup>25</sup>

#### The Three Stages of Au e-ALD

Figure 1 represents the mass and electrode potential transient typically observed for a single cycle of Au e-ALD performed in an electrolyte containing 10 mM HClO<sub>4</sub>, 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub>, and  $10 \,\mu\text{M}$  AuCl<sub>3</sub>. To characterize the e-ALD process, we categorize the mass transient into three distinct stages. Stage I involves Pbupp adlayer formation at -0.2 V for 50 s. Stages II and III comprise SLRR of Pb<sub>UPD</sub> by Au under open-circuit conditions until the potential reaches  $E_{\text{cut-off}} = 1.2 \text{ V}$ . The mass changes corresponding to stages I, II and III are labelled in Fig. 1 as  $\Delta m_{\rm I}$ ,  $\Delta m_{\rm II}$ , and  $\Delta m_{\rm III}$ , respectively. As observed in Fig. 1, the mass gain due to Pb<sub>UPD</sub> at the end of stage I was  $\Delta m_{\rm I} = 208 \text{ ng cm}^{-2}$ . It is important to note that this mass gain is lower than the mass of a  $Pb_{UPD}$  adlayer on Au  $(\sim 290 \text{ ng cm}^{-2})$  that is expected to be deposited at -0.2 V. In stages II and III, the electrode potential gradually drifted from -0.2 V towards 1.2 V. In stage II, the mass change is most likely attributed to the replacement of Pb<sub>UPD</sub> by Au, which per the stoichiometry represented in Eq. 2 should result in net mass loss. As seen in Fig. 1, the mass decreased by  $\Delta m_{\rm II} \approx 100 \text{ ng cm}^{-2}$  by the end of stage II. Theoretically, assuming  $\Delta m_{\rm I}$  represents the mass of Pb<sub>IIPD</sub>,  $\Delta m_{\rm II}/\Delta m_{\rm I}$  should be about 0.37; however, the observed ratio in Fig. 1 is considerably different ( $\Delta m_{\rm H}/\Delta m_{\rm I} = 0.48$ ). The mass decrease is halted as the open-circuit potential of 0.275 V is reached at the end of stage II. Interestingly, stage II is followed by a dramatic gain in mass of  $\Delta m_{III} \sim 160 \text{ ng cm}^{-2}$  by the time the electrode potential reaches the cut-off value of 1.2 V. The cause of this mass gain is not presently known although some have speculated the role of adsorptive processes.<sup>14</sup> Here, we attempt to characterize the Au e-ALD process and provide answers to the following key questions:

•Why does  $\Delta m_{\rm I}$  have a value (= 208 ng cm<sup>-2</sup>) that is significantly lower than that expected for a full Pb<sub>UPD</sub> monolayer?

- •Why is the ratio  $\Delta m_{II}/\Delta m_{I}$  about 0.48 instead of 0.37 expected based on stoichiometry?
- •What process causes mass gain  $\Delta m_{\rm III}$  of ~160 ng cm<sup>-2</sup> during stage III, and how does this affect subsequent Au e-ALD cycles?

#### Gravimetric and Coulometric Analysis of PbUPD and Au e-ALD

Underpotential Deposition of Pb on Au.—CV was performed on a Au-coated e-QCM electrode in electrolytes containing 10 mM HClO<sub>4</sub> with and without 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> at a scan rate of 20 mV s<sup>-1</sup>. During the cathodic scan, the electrode potential was scanned from 0.5 V to -0.23 V vs SHE. The cathodic potential limit was set to -0.23 V to avoid electrodeposition of Pb. As seen in Fig. 2a, several reduction peaks were observed corresponding to underpotential deposition of Pb on Au. The splitting of the cathodic UPD peaks is likely due to the polycrystalline nature of the Au-coated quartz crystal electrode, as observed in other UPD systems.<sup>26–28</sup> During the reverse scan (anodic direction), the corresponding Pb<sub>UPD</sub> stripping peaks were observed. The mass change during CV is shown in Fig. 2b. The mass increased and nearly reached saturation



**Figure 2.** (a) Cyclic voltammograms (CVs) for a Au-coated e-QCM electrode in 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> (*red*) and 10 mM HClO<sub>4</sub> only (*blue*). The scan rate was 20 mV s<sup>-1</sup>. (b) Mass change measured by e-QCM during the CVs. At -0.23 V, the mass gain due to Pb<sub>UPD</sub> on Au was measured to be 311 ng cm<sup>-2</sup>. At -0.2 V, the Pb<sub>UPD</sub> mass was ~290 ng cm<sup>-2</sup>.

at  $\Delta m_{\rm Pb} = 311$  ng cm<sup>-2</sup> during the cathodic scan. This mass gain corresponds to the deposition of a near-complete monolayer of Pb<sub>UPD</sub> on Au.<sup>29</sup> Based on this CV, -0.2 V was chosen as the applied potential for facilitating Pb<sub>UPD</sub> during step (*i*) of Au e-ALD. At -0.2 V, the Pb<sub>UPD</sub> mass is ~290 ng cm<sup>-2</sup> from Fig. 2b. Figure 2b also confirmed that the Pb<sub>UPD</sub> adlayer was completely stripped during the reverse scan (anodic scan direction).

Hypothesis of Au<sup>+3</sup>-ligand (Au-L) Adsorption during Au e-ALD.—The plots shown in Figs 3a and 3b contain the electrode potential transient and corresponding mass transient for four consecutive cycles of Au e-ALD with  $E_{\rm cut-off} = 1.2$  V (blue curves). The mass changes in each stage (I, II and III) of the Au e-ALD process were reasonably consistent. The  $\Delta m_{\rm I}$ ,  $\Delta m_{\rm II}$ , and  $\Delta m_{\rm III}$ values and the associated charge densities recorded in stage I ( $Q_{\rm I}$ ) for the four cycles of Au e-ALD can be found in Table I (columns for  $E_{\rm cut-off} = 1.2$  V). The average values for  $\Delta m_{\rm I}$ ,  $\Delta m_{\rm II}$  and  $\Delta m_{\rm III}$  are 212 ng cm<sup>-2</sup>, 90 ng cm<sup>-2</sup> and 167 ng cm<sup>-2</sup>, respectively. As also seen in Fig. 1,  $\Delta m_{\rm I}$  in all the four cycles in Fig. 3 is considerably lower than the expected mass gain due to Pb<sub>UPD</sub> adlayer on Au (290 ng cm<sup>-2</sup> at -0.2 V, Fig. 2). Also,  $\Delta m_{\rm III}$  is 167 ng cm<sup>-2</sup> consistent with Fig. 1.

It is worthwhile to note that the average charge density during  $Pb_{UPD}$  ( $Q_I = 426 \ \mu C \ cm^{-2}$  in Table I) is substantially greater than the value expected for the deposition of  $\Delta m_{\rm I} = 212 \, {\rm ng} \, {\rm cm}^{-2}$ equivalent of Pb on the Au surface. For 212 ng cm<sup>-2</sup> of Pb<sub>UPD</sub>, a charge density of  $\sim 200 \ \mu \text{C cm}^{-2}$  would be reasonable.<sup>30</sup> Parasitic electrodeposition of Au via reduction of Au<sup>+3</sup> aquo-species cannot explain this excess charge density, because although Au deposition would increase the measured charge it would also increase (not decrease as observed) the deposit mass above that of a Pbupp adlayer. Instead, the higher-than-expected value of  $Q_{\rm I}$  can be explained by hypothesizing that Au<sup>+3</sup>-ligand complexes (Au-L) are adsorbed on the Au electrode before stage I of Au e-ALD and these undergo reduction during stage I. As mentioned in the introduction section, hydrolysis of Au<sup>+3</sup>-containing chloride salts leads to formation of complexes and such complexes are known to exhibit adsorption on Au.<sup>16–20</sup> The hypothesis of Au-L adsorption on pristine Au allows us to explain the apparent discrepancies in gravimetry and coulometry described above:

- (a) During stage I, measured  $Q_{\rm I}$  of 426  $\mu$ C cm<sup>-2</sup> comprises the charge density due to Pb<sub>UPD</sub> and an excess charge density corresponding to the reduction of the adsorbed Au-L to Au.
- (b) In stage I,  $\Delta m_{\rm I} = 212 \text{ ng cm}^{-2}$  is lower than the expected value for a complete Pb<sub>UPD</sub> coverage (Fig. 2), because, despite the mass gain caused by Pb<sub>UPD</sub> adlayer formation, the concurrent reduction of adsorbed Au-L causes a mass loss due to the discharge of ligands. We use the term "discharge of ligands" to describe the process where ligands from adsorbed Au-L are returned to the electrolyte upon Au-L reduction. Thus, the net mass gain  $\Delta m_{\rm I}$  is lowered.
- (c) If we assume that SLRR is completed by the end of stage II, then in stage III,  $\Delta m_{\rm III}$  of 167 ng cm<sup>-2</sup> is the mass gain due to re-adsorption of the Au-L on the surface of the newly formed Au in stage II. The re-adsorption of Au-L in stage III implies that such an adsorbed layer exists at the beginning of the subsequent e-ALD cycle.

Figure 3 also shows the coulometric and gravimetric response during Au e-ALD, when it is practiced at a lower cut-off voltage of  $E_{\text{cut-off}} = 0.275 \text{ V}$  (red curves). This cut-off potential was chosen so that Au e-ALD is terminated at the end of stage II and stage III is eliminated. Given our hypothesis of Au-L adsorption during stage III, this lower cut-off potential also ensures that such complex adsorption does not proceed on the newly deposited Au surface. Mass transients corresponding to  $E_{\text{cut-off}} = 0.275 \text{ V}$  are shown in red in Figs. 3b and 3c (3rd cycle), and the values of  $Q_{\rm I}$ ,  $\Delta m_{\rm I}$ , and  $\Delta m_{\rm II}$  are provided in Table I (columns for  $E_{\rm cut-off} = 0.275$  V). First, the average value of  $\Delta m_{\rm I}$  is now 292 ng cm<sup>-2</sup>, which is larger than that measured for  $E_{\text{cut-off}} = 1.2 \text{ V}$ . This supports the ligand discharge mechanism in stage I hypothesized in point (b) above. Second,  $\Delta m_{\rm I} = 292 \,\mathrm{ng \, cm^{-2}}$  for  $E_{\rm cut-off} = 0.275 \,\mathrm{V}$  is very close to the expected value for complete Pb<sub>UPD</sub> adlayer coverage (Fig. 2). The charge density value  $Q_{\rm I}$  for  $E_{\rm cut-off} = 0.275$  V is lower than that for  $E_{\rm cut-off} = 1.2$  V too as seen in Fig. 3d. Average  $Q_{\rm I}$  for  $E_{\rm cut-off} = 0.275$  V is 317  $\mu$ C cm<sup>-2</sup>, lower than 426  $\mu$ C cm<sup>-2</sup> for  $E_{\rm cut-off} =$ 1.2 V suggesting that reduction of Au-L complexes during Pb<sub>UPD</sub> contributes to the  $Q_{\rm I}$  value only at the higher cut-off potential. This supports the Au-L reduction process hypothesized in point (a) above for  $E_{\text{cut-off}} = 1.2$  V. A quantitative analysis of the effect of cut-off



**Figure 3.** (a) Electrode potential transient during 4 Au e-ALD cycles performed on a Au-coated quartz crystal in an electrolyte containing 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> + 10  $\mu$ M AuCl<sub>3</sub>. Two cut-off potentials where stage III is terminated were selected: 1.2 V vs SHE (*blue*) or 0.275 V vs SHE (*red*). (b) Mass change during 4 Au e-ALD cycles with  $E_{\text{cut-off}} = 1.2$  V (*blue*) or 0.275 V (*red*). (c) Mass change during the 3rd Au e-ALD cycle with  $E_{\text{cut-off}} = 1.2$  V (*blue*) or 0.275 V (*red*). (c) Mass change during the 3rd Au e-ALD cycle with  $E_{\text{cut-off}} = 1.2$  V (*blue*) or 0.275 V (*red*). (c) Mass changes during the three stages in each Au e-ALD cycle are shown in Table I. No  $\Delta m_{\text{III}}$  was recorded at  $E_{\text{cut-off}} = 0.275$  V because Au-L adsorption was disabled. (d) Charge density during stage I of a typical Au e-ALD cycle with  $E_{\text{cut-off}} = 1.2$  V (*blue*).

Table I.  $Q_1$ ,  $\Delta m_1$ ,  $\Delta m_{II}$ , and  $\Delta m_{III}$  measured on a Au-coated quartz crystal electrode in an electrolyte containing 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub> + 10  $\mu$ M AuCl<sub>3</sub> with  $E_{cut-off}$  = 1.2 V or 0.275 V vs SHE. The average values of  $Q_1$  and  $\Delta m_1$  at  $E_{cut-off}$  = 0.275 V are calculated using the 2nd, 3rd and 4th cycles only.

Cycle Number	$E_{ m cut-off} = 1.2 \  m V$				$E_{ m cut-off}=0.275~ m V$		
	$Q_{\rm I} ~(\mu {\rm C~cm^{-2}})$	$\Delta m_{\rm I} \ ({\rm ng} \ {\rm cm}^{-2})$	$\Delta m_{\rm II} \ ({\rm ng} \ {\rm cm}^{-2})$	$\Delta m_{\rm III} \ ({\rm ng} \ {\rm cm}^{-2})$	$Q_{\rm I} ~(\mu {\rm C~cm^{-2}})$	$\Delta m_{\rm I} \ ({\rm ng} \ {\rm cm}^{-2})$	$\Delta m_{\rm II} \ ({\rm ng} \ {\rm cm}^{-2})$
1	429	208	102	159	433	219	88
2	433	208	84	163	314	290	106
3	422	216	99	177	317	293	116
4	422	212	74	170	320	293	130
Average	426	212	90	167	317	292	110

potential on the recorded mass changes, also addressing point (c) is presented below.

Quantitative analysis of  $Au^{+3}$ -ligand complex adsorption effects.—Based on the discussion above, we assume that the Au surface contains a pre-adsorbed layer of Au-L before the commencement of stage I of Au e-ALD. Mass is added in stage I via  $Pb_{UPD}$  adlayer formation ( $m_{Pb}$ ), but mass is lost due to ligand discharge ( $m_L$ ). Assuming all Au deposited in stage I is through reduction of the adsorbed Au-L complex:  $[Au^{+3}-L]_{ads} + 3e^- \rightarrow Au_{ads} + L$ , the Au co-deposition does not contribute to mass change  $\Delta m_I$  in stage I. Thus, we write:

$$\Delta m_{\rm I} = m_{\rm Pb} - m_{\rm L} \tag{3}$$

At a cut-off potential of 1.2 V, and referring to Table I:

$$\Delta m_{\rm I}|_{1.2\rm V} = m_{\rm Pb} - m_{\rm L} = 212 \text{ ng cm}^{-2}$$
[4]

Similarly, at a cut-off potential of 0.275 V where Au-L adsorption does not occur ( $m_L = 0$ ):

$$\Delta m_{\rm I}|_{0.275\rm V} = m_{\rm Pb} - 0 = 292 \,\,\mathrm{ng}\,\mathrm{cm}^{-2}$$
<sup>[5]</sup>

From Eqs. 4 and 5, we calculate the mass of the ligands to be  $m_{\rm L} = 80 \text{ ng cm}^{-2}$ .

In stage II, the magnitude of mass loss ( $\Delta m_{\rm II}$ ) compared to  $m_{\rm Pb}$  is determined by stoichiometry of reaction (2):

$$\frac{\Delta m_{\rm II}}{m_{\rm Pb}} = 1 - \frac{2M_{\rm Au}}{3M_{\rm Pb}}$$
[6]

Knowing the atomic weights of Au and Pb, we calculate this ratio to be 0.37. Since  $m_{\rm Pb}$  is reliably known from Eq. 5 for the case of  $E_{\rm cut-off} = 0.275$  V ( $m_{\rm Pb} = 292$  ng cm<sup>-2</sup>), we can now calculate  $\Delta m_{\rm II}$ from Eq. 6. This provides  $\Delta m_{\rm II}$  of 108 ng cm<sup>-2</sup>, which is very close to the value of 110 ng cm<sup>-2</sup> seen in Table I for  $E_{\rm cut-off} = 0.275$  V.

Now,  $\Delta m_{\rm III}$  in cycles with  $E_{\rm cut-off} = 1.2$  V corresponds to the mass of the re-adsorbed Au-L. Assuming that the adsorbed complex solely contains Au (of mass  $m_{\rm Au}$ ) and ligands (of mass  $m_{\rm L}$ ), we write:

$$\Delta m_{\rm III} = m_{\rm Au} + m_{\rm L}$$
 [7]

From Table I, we know that the average value of  $\Delta m_{\rm III}$  is 167 ng cm<sup>-2</sup>. Also, from the preceding discussion, we have established that  $m_{\rm L} = 80$  ng cm<sup>-2</sup>. Thus, from Eq. 7, we estimate  $m_{\rm Au}$  to be 87 ng cm<sup>-2</sup>. If such a Au<sup>+3</sup>-ligand complex is reduced in stage I of the subsequent e-ALD cycle, the charge required for its reduction would

be 127  $\mu$ C cm<sup>-2</sup>. This number is very close to the excess charge density (Fig. 3d) in stage I for  $E_{\text{cut-off}} = 1.2$  V (*blue*) compared to  $E_{\text{cut-off}} = 0.275$  V (*red*). This explains why  $Q_{\text{I}}$  is larger by 109  $\mu$ C cm<sup>-2</sup> for  $E_{\text{cut-off}} = 1.2$  V compared to  $E_{\text{cut-off}} = 0.275$  V.

If each Au is assumed to bound to one ligand in the adsorbed layer, then the following relation holds:

$$\frac{m_{\rm L}}{M_{\rm L}} = \frac{m_{\rm Au}}{M_{\rm Au}}$$
[8]

 $M_{\rm L}$  is the molecular weight of the ligand. Knowing  $m_{\rm L}$  (= 80 ng cm<sup>-2</sup>),  $m_{\rm Au}$  (= 87 ng cm<sup>-2</sup>), and  $M_{\rm Au}$  (= 197 g mol<sup>-1</sup>), we find that the molecular weight of the ligand is:  $M_{\rm L}$  = 181 g mol<sup>-1</sup>. Thus, the molecular weight of the Au<sup>+3</sup>-ligand complex is estimated to be (197 + 181) = 378 g mol<sup>-1</sup>. This weight is within range of many possible Aucomplexes: AuCl<sub>3</sub>OH<sup>-</sup> (320 g mol<sup>-1</sup>) and AuCl<sub>3</sub>(ClO<sub>4</sub>)<sup>-</sup> (403 g mol<sup>-1</sup>). Given the limitations of the methods employed here, conclusive identification of the adsorbed complex is not feasible at the present moment. Also, it is likely that multiple complexes are present, and that our estimate of the complex molecular weight (378 g mol<sup>-1</sup>) represents only an average value. Advanced high-resolution imaging<sup>23</sup> or first-principles simulations<sup>31</sup> may aid in determination of the structure of the adsorbed Au-complexes.

**Demonstrating the presence of Au-L adsorbed layer.**—Here, we employ gravimetry during Pb<sub>UPD</sub> to conclusively demonstrate the presence of an adsorbed Au<sup>+3</sup>-containing layer on the Au electrode. Three experiments were performed sequentially: (*i*) Pb<sub>UPD</sub> on a pristine Au-coated quartz crystal (Fig. 4a); (*ii*) Pb<sub>UPD</sub> on a Au-coated quartz crystal that was pre-treated by immersion in an aqueous solution of 10 mM HClO<sub>4</sub> + 10  $\mu$ M AuCl<sub>3</sub> for 5 min at open-circuit conditions (Fig. 4b); and (*iii*) Pb<sub>UPD</sub> on the same substrate as (*ii*) after it was cleaned (Fig. 4c). In each step, Pb<sub>UPD</sub> was performed at -0.2 V vs SHE for 50 s. After each step, the Pb<sub>UPD</sub> adlayer was stripped by applying a potential of 0.5 V vs SHE for 100 s. Surface cleaning of Au prior to each experiment involved thorough rinsing with DI water and blow-drying in a stream of N<sub>2</sub> gas. The electrolyte for Pb<sub>UPD</sub> was the same as above: 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub>.

As shown in Fig. 4a,  $Pb_{UPD}$  on a pristine Au-coated quartz crystal resulted in a net mass gain of 299 ng cm<sup>-2</sup>, comparable to that obtained for a near-complete  $Pb_{UPD}$  adlayer (Fig. 2). However, pretreatment of the Au surface by first immersing in an aqueous solution of 10 mM HClO<sub>4</sub> + 10  $\mu$ M AuCl<sub>3</sub> followed by  $Pb_{UPD}$  in a separate cell changed the mass gain during  $Pb_{UPD}$  considerably. As seen in Fig. 4b, the mass gain was reduced to 219 ng cm<sup>-2</sup>. This is 80 ng cm<sup>-2</sup> less than that seen in Fig. 4a—a difference that is



**Figure 4.** Mass change measured during  $Pb_{UPD}$  on a Au-coated quartz crystal at -0.2 V vs SHE in an electrolyte containing 10 mM HClO<sub>4</sub> + 400  $\mu$ M Pb(ClO<sub>4</sub>)<sub>2</sub>. (a) Substrate was pristine Au; (b) Substrate was Au pre-treated in 10 mM HClO<sub>4</sub> + 10  $\mu$ M AuCl<sub>3</sub> for ~5 min causing adsorption of a Au<sup>+3</sup>-ligand (Au-L) layer; (c) Substrate in (b) but after removal of the Pb<sub>UPD</sub> and Au-L layers. The net mass gain during Pb<sub>UPD</sub> was lowered by 80 ng cm<sup>-2</sup>, which represents the mass loss due to ligand discharge.



Figure 5. Schematic representation of the Au e-ALD mechanism highlighting Au-L adsorption and reduction steps.

precisely equal to the mass of ligands  $(m_{\rm I})$  determined above. This suggests that a species which discharged during Pb<sub>UPD</sub> had already adsorbed on the electrode when it was pre-treated. Stripping of the Pb<sub>UPD</sub> followed by thorough cleaning of the Au electrode returned the mass gain during a subsequent  $Pb_{UPD}$  test back to 298 ng cm<sup>-2</sup>. This experiment indirectly confirms the presence of an adsorbed Au-L layer on the Au surface that is immersed in Au<sup>+3</sup>-containing electrolyte.

#### Conclusions

Analysis of "one-pot" Au e-ALD is reported using CV, e-QCM and chrono-coulometry. Analysis reveals the following findings:

- (i) A  $Au^{+3}$ -ligand complex is conclusively shown to adsorb on the Au surface in contact with AuCl<sub>3</sub>-containing aqueous solutions used for Au e-ALD. Molecular weight of this adsorbed complex is about 378 g mol<sup>-1</sup>, but its molecular formula or structure is not discernable using methods employed herein.
- During the process of Pb<sub>UPD</sub> (stage I of Au e-ALD), the (ii) adsorbed Au<sup>+3</sup>-ligand complex undergoes reduction via the reaction:  $[Au^{+3}-L]_{ads} + 3e^- \rightarrow Au_{ads} + L$ . The mass of discharged ligands  $m_L = 80 \text{ ng cm}^{-2}$  is detected in the mass transient recorded during Au e-ALD.
- After the Pb<sub>UPD</sub> is redox-replaced by Au during stage II of Au (iii) e-ALD, the Au<sup>+3</sup>-ligand complex re-adsorbs on the deposited Au in stage III if a sufficiently positive cut-off potential is chosen. This manifests as a mass gain of  $\sim 167$  ng cm<sup>-2</sup> during stage III. The adsorbed layer is the cause of the lower-thanexpected mass gain  $(\Delta m_{\rm I})$  in stage I of the subsequent e-ALD cycle because the adsorbed layer is reduced during Pb<sub>UPD</sub> once again triggering ligand discharge.

These findings lead us to deriving the Au<sup>+3</sup>-ligand adsorptionmediated mechanism of Au e-ALD depicted schematically in Fig. 5. While this is an advancement in understanding of Au e-ALD over and above the simplistic model of reactions 1 and 2 accepted in literature, several new questions emerge from our work. For example, the nature of the ligand, its adsorption characteristics ( i.e., potential-dependent adsorption), and its modulation of the Pb<sub>UPD</sub> coverage, impurity incorporation if any and displacement kinetics during stages I and II presently remain unknown. We will attempt to address these aspects in future work. Also, we plan to apply our methods to understanding adsorption behavior of  $Pt^{+4}$  and Ru<sup>+3</sup> complexes in relevant e-ALD systems.

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