

Changes in Surface Stress of Gold Electrode during Underpotential Deposition of Pb

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The changes in surface stress of a gold film electrode during underpotential deposition (UPD) of lead in pH 3.0, 0.5 M NaClO₄ solution containing 10^{-4} M Pb(ClO₄)₂ or PbCl₂ were measured by a bending beam method to investigate the relation between surface stress and structural change of the Pb-UPD layer. A maximum in the surface stress *vs.* potential curve like an electrocapillary curve emerged at the onset of the UPD. Moreover, a hump in the surface stress *vs.* potential curve also emerged in the range of surface coverage of Pb from $\theta_{Pb} = 0.4$ to 0.8 during the UPD process. The changes in surface stress were plotted *vs.* cathodic charge required for Pb-UPD. Two linear and one plateau region appeared in the surface stress *vs.* the cathodic charge curve. The plateau region corresponded to the hump in the surface stress *vs.* potential curve is deduced from the comparison with the scanning tunnel microscopy, atomic force microscopy, and surface X-ray scattering spectroscopy results in the literature that the plateau region is associated with the change in rotation angle from $R = 0^{\circ}$ to 2.5° of incommensurate hexagonal close-packed Pb layer. Particularly, it was emphasized that the hump resulted from the release of compressive surface stress due to the change in rotation angle of the UPD surface stress of the UPD layer.

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Recent developments of scanning tunneling microscopy (STM), atomic force microscopy (AFM), and surface X-ray scattering spectroscopy (SXS) have revealed surface structural changes of singlecrystal metal electrodes in solution such as surface reconstruction.¹ However, explanations for the structural changes are not sufficient from the viewpoint of surface energetics because of the lack in experimental data of surface thermodynamics such as surface tension, γ , surface stress, g, and surface strain, ε . In general, surface stress and surface stress and surface strain become scalar and the following Shuttleworth equation² holds between surface stress, g, and surface tension, γ

$$g = \gamma + \frac{\partial \gamma}{\partial \varepsilon}$$
[1]

Moreover, the Gibbs adsorption isotherm for an isotropic solid electrode is given by

$$d\gamma = -q_{\rm m}dE - \sum_{\rm i} \Gamma_{\rm i}d\mu_{\rm i} + (g - \gamma)/d\varepsilon \qquad [2]$$

where $q_{\rm m}$ is the surface charge density of the electrode; *E*, the electrode potential; $\Gamma_{\rm i}$, the surface excess of *i*th species; and $\mu_{\rm i}$, the chemical potential of *i*th species. Lipkowski *et al.*³ have pointed out that the contribution of $(g - \gamma) d\varepsilon$ to $d\gamma$ is so negligibly small that the values of $d\gamma$ for an isotropic solid electrode can be obtained from a cyclic voltammogram. Seo *et al.*^{4,5} found from the measurement of changes in surface stress by a bending beam method that the second term in the right side of Eq. 1, *i.e.*, the difference between g and γ is significantly large in the case where iodide ions are adsorbed on gold and hydroxide ions are adsorbed on platinum accompanying a charge transfer. Gokhshtein⁶ and Haiss *et al.*⁷ derived the following equation between derivative of surface stress with surface-charge density and derivative of electrode potential with surface strain

$$\left(\frac{\partial g}{\partial q_{\rm m}}\right)_{\rm E} = \left(\frac{\partial E}{\partial \varepsilon}\right)_{\rm Q}$$
[3]

where $q_{\rm m}$ is the surface-charge density and Q is the total charge of the electrode surface. Haiss *et al.*⁷ have reported that the changes in

surface stress of the Au(111) electrode due to adsorption of electrolyte anions in various acid solutions are proportional to the surfacecharge density, q_m . Ibach⁸ suggested from the similarity of the linear relation between surface stress and surface coverage observed experimentally for adsorption of CO on Ni(100) in high coverage regime that the changes in surface stress of a solid metal electrode due to adsorption are attributed to an adsorbate-induced changes in the electronic structure of the substrate surface atoms. Furthermore, Ibach⁸ claimed that the changes in surface stress are not always proportional to the surface-charge density. Schmickler and Levia⁹ calculated the contribution of a metal side to surface stress and surface tension within the jellium model for a solid metal electrode and indicated the strong dependences of surface stress on adsorption energy and adsorbate interactions, supporting the results by Haiss *et al.*⁷

Underpotential deposition (UPD) of foreign metal atoms on a noble metal electrode is one of the interesting subjects in relation to surface energetics since the structural changes of an adlayer have been often observed for many UPD systems¹⁰⁻¹⁷ by SXS and STM. However, there are few studies of the changes in surface stress during the UPD process.¹⁸ In this study, the changes in surface stress of a gold electrode during Pb-UPD were measured by a bending beam method to investigate the relation between surface stress and the structural change of Pb-UPD layer. Moreover, the kinetics of the structural changes of Pb-UPD layer was discussed from the changes in surface stress.

Experimental

Preparation of the gold electrode and electrolytes.—One side of a thin glass plate (thickness, $t_s = 150 \,\mu$ m; width, 5.0 mm; length, 60 mm; Young's modulus, $E_s = 70.9$ GPa; Poisson's ratio, $v_s = 0.23$) was precoated with a titanium film at a thickness of 15 nm for a good adhesion by evaporation, and then a gold film with a thickness of 220 nm was evaporated on the glass plate. The gold film thus prepared on the thin glass plate was mainly oriented to the (111) plane and used as a working electrode.

The electrolyte used in this experiment was 0.5 M NaClO₄ solution with or without 10^{-4} M PbCl₂ or 10^{-4} M Pb(ClO₄)₂, the pH of which was adjusted to 3.0 by adding 10^{-3} M HClO₄. This electrolyte was prepared from guaranteed reagent grade chemicals with ultrapure water supplied through a super Millipore Milli Q filter system. Before introduction to the electrochemical cell, the electrolyte was deaerated with ultrapure argon gas in solution reservoirs.

Measurements of changes in surface stress of the gold electrode.—The principle and apparatus of a bending beam method

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for measurement of changes in surface stress of a solid electrode were described elsewhere.^{4,5,19} A laser beam of He-Ne was irradiated perpendicular to the glass plate side of the working electrode which was placed into an electrochemical cell with an optical window. The irradiated beam also passed the liquid-air interface through the optical window at a normal incidence angle. The reflected beam was directed toward a position-sensitive photodetector (PSD, Hamamatsu, Inc., S1300) located at a distance of W = 0.60 m from the working electrode. The distance between the solution level and reflection point of the laser beam, *L*, was 40 mm. The changes in dc output signals of the PSD were converted into the changes in position, Δa , of the reflected beam on the PSD.

The changes in reflection angle, $\Delta \phi$, of the laser beam due to bending of the glass plate caused by the changes in surface stress are given by

$$\Delta \varphi = \Delta a / n_{\rm s} W$$
[5]

where n_s is the refractive index of the solution. The term of n_s in Eq. 5 has not been so far taken into consideration for most of the studies on changes in stress by using a bending beam method. As claimed by Láng and Seo,¹⁹ the insertion of n_s into Eq. 5 is indispensable because the reflected beam is refractive at the solution/air interface. Otherwise, the omission of n_s would produce 20-30% errors in the final calculation of Δg . The changes in reciprocal to the curvature radius of bending of the glass plate, $\Delta(1/R)$, are directly related to the changes in reflection angle, $\Delta \varphi$, as follows

$$\Delta(1/R) = \Delta \varphi/2L$$
 [6]

In the case where the thickness of the metal film electrode, t_f , is sufficiently less than that of the glass plate, t_s , the changes in surface stress, Δg , can be calculated by using Stoney's equation.²⁰

$$\Delta g = [E_{\rm s} t_{\rm s}^2 / 6(1 - v_{\rm s})] \Delta(1/R)$$
[7]

A gold plate was used as the counter electrode. The electrode potential was measured with an Ag/AgCl electrode in a saturated KCl solution and referred to the standard hydrogen electrode (SHE). The cyclic voltammogram (CV) was measured at a potential sweep rate of 5 mV s⁻¹ in the potential region between -0.24 and 0.8 V (SHE) and simultaneously the dc output signals of the PSD were recorded on a personal computer. The anodic limit was chosen at 0.8 V to avoid the onset of the surface oxygenation reaction on gold, while the cathodic limit was chosen at -0.24 V, corresponding to the equilibrium potential of Pb/Pb²⁺(10⁻⁴ M). The potential step from 0.8 V to a certain potential in the UPD region was also performed to follow the transient of the surface stress. The temperature of solution in the electrochemical cell was kept at 25°C.

Results and Discussion

Cyclic voltammogram and surface stress vs. electrode potential curve.-Figure 1a and b show the CV and the surface stress vs. electrode potential ($\Delta g \ vs. E$) curve measured at a potential sweep rate of 5 mV s⁻¹ for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10^{-4} M Pb(ClO₄)₂. The surface stress, Δg , was referred to zero at the anodic limit of 0.8 V. The sign of change in surface stress to the tensile direction was taken to be positive as is usually defined. The blank Δg vs. E curve measured in pH 3.0, 0.5 M NaClO₄ solution without Pb^{2+} is also shown in Fig. 1b for comparison. This blank curve was shifted to positive by $\Delta g = 0.4 \text{ J m}^{-2}$ to avoid the overlapping of both curves. The blank Δg vs. E curve changes monotonously in both cathodic and anodic potential sweeps while the Δg vs. E curve in the presence of Pb²⁺ has maxima at about 0.2 V and humps at about -0.05 V in both cathodic and anodic potential sweeps. These maxima and humps correspond to the cathodic and anodic current peaks in the CV of Fig. 1a associated with underpotential deposition and desorption of Pb. The main cathodic and anodic current peaks at about -0.05 V in



the CV of Fig. 1a are consistent with those observed for the singlecrystal gold(111) electrode in the same electrolyte solution,²¹ indicating that the evaporated gold thin-film electrode used in this experiments is mainly oriented to the (111) plane. In the cathodic potential sweep from the anodic limit, the increase in Δg down to 0.2 V responds to the decrease in positive surface charge density or desorption of perchlorate ion from the electrode surface, whereas the decrease in Δg at potentials lower than 0.2 V is brought about by UPD of Pb. The humps at about -0.05 V in the Δg vs. *E* curve of Fig. 1b may be associated with the structural change of the UPD phase as discussed later.

Figure 2a and b show the CV and the surface stress *vs.* electrode potential ($\Delta g \ vs. E$) curve measured at a potential sweep rate of 5 mV s⁻¹ for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10⁻⁴ M PbCl₂. There are no significant differences between Fig. 1 and 2, except for that $\Delta(\Delta g)$ between 0.2 V and anodic limit (0.8 V) in Fig. 2b is larger by 0.2 J m⁻² than that in Fig. 1b. This difference may result from the strong specific adsorption of chloride ion as compared to perchlorate ion in the potential region between 0.2 and 0.8 V. Although there is some hysteresis in CV and the Δg *vs. E* curve between cathodic and anodic potential sweeps in Fig. 1 and 2, in this paper the discussion is focused on the results obtained in the cathodic potential sweep in which Pb-UPD proceeds.

Relation between surface stress, Δg , and cathodic charge density, Δq_c .—Figures 3 and 4 show the relation between surface stress, Δg , and cathodic charge density, Δq_c for the gold electrodes in pH 3.0, 0.5 M NaClO₄ solutions with 10^{-4} M Pb(ClO₄)₂ and PbCl₂, respectively. In Fig. 3 and 4, the surface stress, Δg , was obtained in the cathodic potential sweep from the anodic limit while the cathodic charge density, Δq_c , was obtained with integration of the corresponding CV, referred to zero at the anodic limit. The cathodic charge density, Δq_c , thus defined is different from the surface charge density, $\Delta \sigma_M$, which is obtained with integration of CV from the potential of zero charge (pzc). The pzc can be determined by capacitance or impedance measurement. As pointed out by Seo





Figure 2. (a) CV and (b) surface stress vs. electrode potential ($\Delta g \ vs. E$) curve measured at a potential sweep rate of 5 mV s⁻¹ for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10⁻⁴ M PbCl₂.

et al. for Cu-UPD on Au²² and by Conway *et al.* for Pb-UPD on Au,²³ the pzc likely shifts with surface coverage of the metal adatom. Therefore, it seems difficult to determine the pzc during Pb-UPD on Au. However, if the CV has no significant hysteresis in anodic and cathodic directions, the relative change of Δq_c would not deviate from that of $\Delta \sigma_M$ except for the opposite sign (positive or negative) of charge. In Fig. 3 and 4, the sign of Δq_c was taken to be negative. Here, by the above reasons, we deal only with the relative change in Δq_c in place of surface charge density, $\Delta \sigma_M$. The Eq. 3 may be applicable to discuss the relation between Δg and Δq_c . It is



Figure 3. Relation between surface stress, Δg , and cathodic charge density, Δq_c , (or surface coverage of Pb, θ_{Pb}) for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10⁻⁴ M Pb(ClO₄)₂.



Figure 4. Relation between surface stress, Δg , and cathodic charge density, Δq_c (or surface coverage of Pb, θ_{Pb}) for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10^{-4} M PbCl₂.

seen from Fig. 3 and 4 that the relation between Δg and Δq_c consists of three linear (a), (c), and (e), and two plateau (b) and (d) domains. In the linear (a) domain, no UPD of Pb but adsorption of perchlorate ions or chloride ions proceeds. The slopes of the linear (a) domain are -1.19 V in Fig. 3 and -1.24 V in Fig. 4, respectively. According to Haiss *et al.*,⁷ the slopes derived from the linear relation between changes in surface stress and surface charge density for the evaporated gold film electrode in 0.1 M HClO₄ and 0.1 M HClO₄ + 5 \times 10⁻³ M CsCl solutions were -0.91 V for ClO_4^- and -0.67 V for Cl⁻. The discrepancy in slope between the present result and Ref. 7 may come from the differences in potential sweep rate, solution pH, electrolyte species, and concentration. The plateau (b) domain corresponds to the transition from the anion adsorption phase to the Pb-UPD phase. The slopes of the linear (c) domain are 0.55 V in Fig. 3 and 0.36 V in Fig. 4. The difference between coadsorption of ClO₄⁻ and Cl⁻ with Pb atoms may reflect on the difference in slope of the linear (c) domain. Coadsorption of metal atoms and anion species has been well studied for the UPD of Cu on Au(111) in the presence of SO_4^{2-} and Cl^{-} .^{24,25} Shi *et al*.²⁵ estimated the surface concentration of Cl⁻ coadsorbed with copper atoms during Cu-UPD on Au(111) by measuring the CV in perchlorate solutions with different Cl⁻ and Cu²⁺ concentrations and using the Gibbs adsorption isotherm, and reported that the maximum surface concentration of coadsorbed Cl⁻ is about 10% of the concentration of Cl⁻ in the close-packed monolayer of Cl⁻. The coadsorption of Cl⁻ may occur during Pb-UPD on Au as well as Cu-UPD. However, there have been few studies on coadsorption of Cl⁻ for UPD of Pb on Au.^{23,26} Vicente *et al.*²⁶ by using a rotating-disk electrode found that Cl⁻ apparently enhances the adsorption of Pb on Au.

The plateau (d) domain coincides with the potential region of the hump in Δg vs. *E* curves of Fig. 1b and 2b. The emergence of hump in Δg vs. *E* curve may be associated with the structural change of surface phase. Therefore, it is suggested that the structural change of UPD phase takes place at the plateau (d) domain. The slopes of the linear (e) domain are 0.58 V in Fig. 3 and 0.52 V in Fig. 4, respectively. The difference in slope at the linear (e) domain between Fig. 3 and 4 is very small as compared to that at the linear (c) domain, which may be associated with the structure of Pb-UPD phase after the structural change at the plateau (d) domain.

If the intersection point of two extrapolated lines in the linear (a) and (c) domains is regarded as onset of Pb-UPD, *i.e.*, $\Delta q_c = -0.94 \text{ Cm}^{-2}$ in Fig. 3 and $\Delta q_c = -1.06 \text{ Cm}^{-2}$ in Fig. 4, the cathodic charges, $\Delta (\Delta q_c)_m$ required for completion of the



Figure 5. Transients of cathodic current density, i_c , and of surface stress, Δg , by a potential step from 0.8 to -0.24 V for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10^{-4} M Pb(ClO₄)₂.

first UPD monolayer at the cathodic limit are -3.72 C m⁻² in Fig. 3 and -4.20 C m⁻² in Fig. 4, respectively. The atomic density of an atomically flat Au(111) surface without reconstruction is 1.38×10^{19} atom m⁻². Assuming the sorption valency of Pb, $\gamma = 2$ and the hexagonal close-packed monolayer of Pb and taking the difference in radius between Pb (r = 0.175 nm) and Au (r = 0.144 nm) atoms into account, the cathodic charge required for the completion of the first UPD monolayer on an atomically flat Au(11) surface is $\Delta(\Delta q_c)_m = 3.02 \text{ Cm}^{-2}$. Therefore, the surface roughness of the Au electrode can be estimated by dividing $|\Delta(\Delta q_c)_m| = 3.72 \text{ Cm}^{-2}$ in Fig. 3 and 4.20 cm⁻² in Fig. 4 by $\Delta(\Delta q_c)_m = 3.02 \text{ Cm}^{-2}$. The surface roughness thus estimated is in the remer of 1.2 to 1.4 Eact burgers of the surface of 1.2 to 1.4 Eact burgers of 1.2 to the range of 1.2 to 1.4. Furthermore, the surface coverage of Pb, $\theta_{\rm Ph}$, can be estimated by dividing $\Delta(\Delta q_{\rm c})$ by $\Delta(\Delta q_{\rm c})_{\rm m}$ required for completion of the first UPD monolayer. The estimated surface coverage of Pb in the plateau (d) domain ranges from $\theta_{Pb} = 0.41$ to 0.83 in Fig. 3 and from θ_{Pb} = 0.47 to 0.83 in Fig. 4, which are consistent with the coverage isotherms of the Au(111)/Pb²⁺, ClO₄⁻ system obtained by Engelsmann *et al.*²¹ According to the SXS study of UPD of Pb on Au(111) by Toney *et al.*,²⁷ the Pb-UPD layer forms a compressive, incommensurate, hexagonal structure and its average near-neighbor spacing changes from 0.35 to 0.34 nm as the UPD proceeds. Even if the lattice constant of the UPD layer changes due to compression, the surface coverage of Pb estimated from $\Delta(\Delta q_c)$



Figure 6. Transients of cathodic current density, i_c , and of surface stress, Δg , by a potential step from 0.8 to -0.24 V for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10^{-4} M PbCl₂.

would not provide the considerable errors (at most 6%). Vicente *et al.*²⁶ showed that the cathodic charge during Pb-UPD on Au increased with Cl⁻ concentration. It should be noted that the value of $|\Delta(\Delta q_c)_m|$ in perchlorate solution containing Cl⁻ (Fig. 4) is larger by 0.5 C m⁻² than that of $|\Delta(\Delta q_c)_m|$ in perchlorate solution without Cl⁻ (Fig. 3), which is consistent with the results obtained by Vicente *et al.*²⁴

STM²⁸ and AFM²⁹ studies showed that on reconstructed Au(111) surfaces Pb deposition initially takes place at the step edges. Afterwards, small Pb islands are formed on the terrace, and these islands coalesce to form the full monolayer at about -0.05 V. It was confirmed that the Pb island consists of the closed-packed hexagonal structure with an atom-atom spacing of 0.35 ± 0.02 nm. Moreover, the SXS study of UPD of Pb on Au(111) (Ref.27) indicated that the Pb monolayer with compressive, incommensurate hexagonal structure rotated from the gold substrate $[01\overline{1}]$ direction by $R = 2.5^{\circ}$ at the potential lower than -0.11 V, but not rotated (*i.e.*, $R = 0^{\circ}$) at the potential higher than -0.08 V. It is deduced from comparison of our present results with STM, AFM, and SXS results that the initial Pb deposition at the step edge and followed by formation of small islands on the terrace take place in the linear (c) domain, while the coalesce of Pb island proceeds in the plateau (d) domain, accompanying the change in rotation angle of the incommensurate hexagonal structure from $R = 0^{\circ}$ to 2.5°, and, eventually, the linear (e) domain responds to the formation of the full monolayer with $R = 2.5^{\circ}$.



Figure 7. Transients of cathodic current density, i_c , and of surface stress, Δg , by a potential step from 0.8 to 0.0 V for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10⁻⁴ M PbCl₂.

The surface stress measurement for the solid/gas interfaces such as Ni(111)/O, C, or S and Ni(100)/C showed that the changes in surface stress have plateaus in certain surface coverage range.³⁰ The presence of the plateau means the relaxation of surface stress due to the reconstruction of the surface at certain surface coverage which was revealed in the solid/gas interface. For example, in case of the Ni(111)/C interface, the change in surface stress to the compressive direction increased with increasing coverage for carbon adsorbed on Ni(111) and took a plateau at $\theta = 0.4$.³¹ This stress relaxation was attributed to the reconstruction of the surface which involves the formation of a (100)-type surface layer of atoms with carbon atoms in the fourfold hollow site as have been revealed by Gardin et al.³² and by Kink et al.³³ The compressive surface stress in this structure is reduced because of the less dense packing of the surface atoms. In the case of Pb-UPD on Au(111), however, the situation may be different from the Ni(111)/C system because no reconstruction of the second surface atomic layer consisting of gold atoms takes place in spite of the structural change of the Pb-UPD layer from $R = 0^{\circ}$ to 2.5°. According to Toney *et al.*,²⁷ although an average near-neighbor spacing of the incommensurate hexagonal Pb monolayer decreased as Pb-UPD proceeded, the decrease in the average near-neighbor spacing was suppressed in the potential region lower than -0.1 V at which the structural change in Pb-UPD layer from $R = 0^{\circ}$ to 2.5° took place. The suppression of the decrease in the average near-neighbor spacing may correspond to the release of



Figure 8. Transients of cathodic current density, i_c , and of surface stress, Δg , by a potential step from 0.8 to 0.3 V for the gold electrode in pH 3.0, 0.5 M NaClO₄ solution with 10^{-4} M PbCl₂.

compressive surface stress. The potential (-0.05 V) at which the hump of Δg appears in the present study may deviate slightly from the potential (-0.1 V) at which the structural change in Pb-UPD layer from $R = 0^{\circ}$ to 2.5° takes place, because the pH and concentration (Pb²⁺ or ClO₄⁻) of the electrolyte solutions used for experiments are different between the present and SXS²⁷ studies.

Kinetics of structural change of the Pb-UPD phase evaluated from the response of surface, stress by a potential step.—Figures 5 and 6 show the transients of cathodic current density, i_c , and of surface stress, Δg , by a potential step from 0.8 to -0.24 V for the gold electrodes in pH 3.0, 0.5 M NaClO₄ solutions with 10^{-4} M Pb(ClO₄)₂ and PbCl₂, respectively. The i_c and Δg rise rapidly after the potential step and then decrease gradually. Afterward Δg takes a maximum and decreases again, while i_c decreases continuously, accompanying an inflection point. The emergences of a maximum of Δg and an inflection point in i_c , correspond to the structural change of the UPD phase from $R = 0^{\circ}$ to 2.5° and the completion of the Pb monolayer with $R = 2.5^{\circ}$, respectively. After passing through the inflection point, however, i_c does not drop to zero. This may result from the reduction of oxygen which remained slightly in solution in spite of removal of dissolved oxygen by ultrapure argon gas. The times required for the emergences of a maximum of Δg and an inflection point in i_c are shorter in Fig. 6 by about 4 s than those in Fig. 5, suggesting that the structural change of Pb-UPD phase and the completion of the UPD monolayer are promoted by the presence of the chloride ion. It is known that the coadsorption of Cl⁻ and SO₄²⁻ or HSO₄⁻ take place during Cu-UPD on Au (111).^{24,25} It seems that the coadsorption of anion species stabilizes the UPD phase due to the decrease in surface energy. The coadsorption of Cl⁻ during Pb-UPD on Au should promote the structural changes of the UPD phase. More quantitative studies on coadsorption of anion species during Pb-UPD on Au, however, are needed to understand the kinetics of the structural changes of the UPD phase and their anion effects. Figures 7 and 8 show the transients of cathodic current density, $i_{\rm c}$, and of surface stress, Δg , by potential steps from 0.8 to 0.0 V and 0.3 V for the gold electrode in pH 3, 0.5 M NaClO₄ solutions with 10^{-4} M PbCl₂, respectively. At the potential step from the anodic limit to 0.0 V which is higher by only 50 mV than the potential (-0.05 V) of hump emergence, no maximum of Δg except for the initial stage and no inflection point of i_{c} are observed, indicating that any structural changes of the Au(111) surface do not proceed at a potential higher than -0.05 V. At the potential step from the anodic limit to 0.3 V, the potential of which is prior to the onset of the Pb-UPD, Δg increases rapidly and then attains a steady state, indicating that desorption of Cl^- or $ClO_4^$ proceeds without Pb-UPD. In pH 3.0, 0.5 M NaClO₄ solutions with 10^{-4} M Pb(ClO₄)₂, results similar to Fig. 7 and 8 were obtained.

Conclusions

The surface stress of gold-film electrode during underpotential deposition (UPD) of Pb was measured by a bending beam method to investigate the relation between surface stress and structural change UPD phase. The following conclusions were drawn.

The surface stress *vs.* potential curve took a maximum at the potential of the transition from anion adsorption to Pb adsorption. Moreover, the hump in the surface stress *vs.* potential curve emerged in the range of Pb surface coverage, θ_{Pb} , from 0.4 to 0.8, indicating the structural change of the Pb-UPD layer.

Two linear relations separated with a plateau region held between surface stress and cathodic charge during Pb-UPD. The plateau region corresponded to the hump in the surface stress *vs.* potential curve. It was deduced from the comparison with the STM, AFM, and SXS results in the literature that the plateau region is associated with the change in rotation angle from $R = 0^{\circ}$ to $R = 2.5^{\circ}$ of incommensurate hexagonal close-packed Pb layer.

The kinetics of the structural changes of Pb-UPD layer was investigated from the response of surface stress by a potential step from the anodic limit to the cathodic limit (monolayer deposition). It was found that it took 20-30 s for structural changes in the Pb-UPD layer. The coadsorption of Cl^- seems to promote the structural changes of the UPD phase.

It was emphasized that the compressive surface stress induced in Pb-UPD layer was released by the change in rotation angle from $R = 0^{\circ}$ to 2.5° of Pb-UPD layer.

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