

Investigation of metal deposition with ellipsometry

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INVESTIGATION OF METAL DEPOSITION WITH ELLIPSOMETRY

W. VISSCHER

Laboratory for Electrochemistry, Faculty of Chemical Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract—The underpotential and bulk deposition of a metal onto a foreign metal substrate was monitored with ellipsometry in combination with cyclic voltammetry. Deposit-substrate systems were investigated for which the refractive index of the bulk deposit is respectively larger, about equal and smaller than $N_{\text{substrate}}$, viz lead deposition on gold and platinum and copper deposition on platinum.

The refractive index of the Pb-UPD film on Au was found to be intermediate between N_{Pb} and N_{Au} . Bulk lead is deposited already when the coverage is about three monolayers; furthermore alloy formation was established at longer deposition times. Also for the Cu-UPD film on Pt, a refractive index was obtained in between the values of substrate and bulk deposit. Homogeneous deposition of bulk Cu occurs if $E < -0.60$ V vs *mse*. For the Pb-Pt system the refractive indices of the UPD layer and the bulk deposit do not differ much.

1. INTRODUCTION

Metal deposition onto a foreign metal substrate can be preceded by an underpotential deposition of adsorbate film. Kolb[1] has shown that the shift in potential increases with the difference in workfunction of deposit and substrate. The accommodation of the deposited atoms on the substrate surface affects the structure of the adsorbate layer. The nature of this adsorbate layer can thus be different from the bulk deposit even though the coverage is a monolayer or less.

Investigation of the underpotential deposited layer is of interest because it is a precursor to bulk deposition and also because the presence of an adsorbate film can alter the electrocatalytic properties of the substrate.

Cyclic voltammetry has been used extensively to establish the electrochemical properties of the adsorbate-substrate system. *In situ* monitoring of thin metal layer deposition with optical techniques can reveal structural changes during the process. Though the principles of these techniques are based on reflection and refraction at the interface between bulk homogeneous phases, it has been recognized that also (sub) monolayer films can be adequately detected with this technique. Ellipsometric measurements of Muller and Farmer[2] of underpotential deposition of Pb on Cu and Ag have shown that the fractional surface coverage can be best described with the model of superposition of polarization states resulting from reflection at bare and covered surface areas. Differential reflectance spectroscopy has been applied to several systems; changes in $\Delta R/R$ during deposition of Pb and Tl on Ag[3] indicate phase transformation of the adsorbed species to metallic-like layer. At substrates with a pronounced reflectance effect changes in the optical parameters can also be attributed to the substrate itself[4]. Takamura *et al.*[5] distinguish two

groups of adsorbate-substrate systems: group I involves systems for which the optical properties of the adsorbate layer are similar to the bulk metal, while in group II the reflectance spectra of the monolayer differs from that of bulk deposit and substrate.

This ellipsometric investigation of metal deposition was carried out at deposit-substrate systems with different and similar refractive indices viz: lead on gold ($N_{\text{Pb}} > N_{\text{Au}}$); lead on platinum ($N_{\text{Pb}} \approx N_{\text{Pt}}$); copper on platinum ($N_{\text{Cu}} < N_{\text{Pt}}$).

2. EXPERIMENTAL

The ellipsometer is the automatic Rudolph RR 2200, equipped with a tungsten iodine light source and a monochromatic filter for 546.1 and 450 nm.

The electrochemical equipment consisted of a Wenking potentiostat POS 73, controlled by a PAR Model 175 Universal Programmer. The measurements were carried out in a cylindrical Teflon cell with windows arranged for angle of incidence of 70° at the substrate electrode.

The substrates, polycrystalline Pt or Au, area 0.5 cm^2 , were polished with 0.05μ alumina before use.

The reference electrode is mercury-mercurous sulphate (*mse*), 0.65 V vs *nhe*, and the counter electrode is a Pt-foil. The electrolytes, $1 \text{ M HClO}_4 + x \text{ M Pb}(\text{ClO}_4)_2$ or $1 \text{ M H}_2\text{SO}_4 + x \text{ M CuSO}_4$ were prepared from AnalaR chemicals and doubly distilled water and were deaerated with N_2 .

3. RESULTS AND DISCUSSION

3.1. Lead deposition on gold

The cyclic voltammogram of Au in $1 \text{ M HClO}_4 + 3.4 \times 10^{-3} \text{ M Pb}(\text{ClO}_4)_2$ is given in Fig. 1a for the

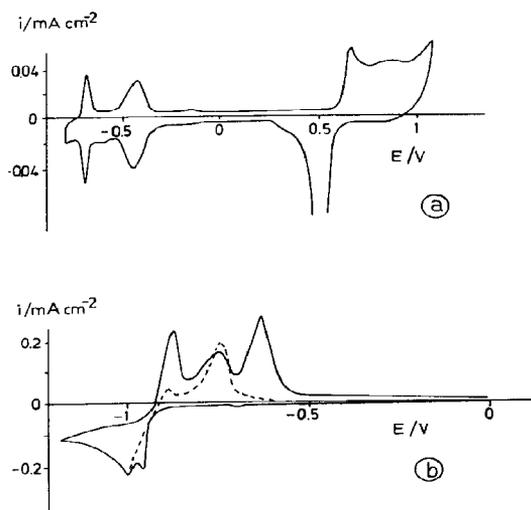


Fig. 1. Cyclic voltammogram of Au in 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$. Scan rate: 20 mV s^{-1} . Scan range: (a) 1.1 to -0.8 V vs mse ; (b) 0 to -1.2 V vs mse .

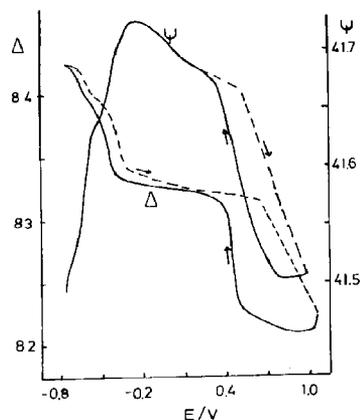


Fig. 2. Ellipsometric changes during potential scan 1.1 to -0.8 V vs mse of Au in 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$. Scan rate 20 mV s^{-1} ; wavelength 546.1 nm .

potential range 1.1 V to -0.8 V vs mse , at scan rate 20 mV s^{-1} ; the UPD peaks are observed at -0.45 and -0.69 V . Figure 2 shows the optical response to this potential scan at wavelength 546.1 nm : both Δ and ψ change in the UPD range and the kink at -0.6 V coincides with the onset of the second peak in the voltammogram. Measurements at $\lambda = 450 \text{ nm}$ show a similar change of Δ and ψ in the UPD range. The coulometric charge corresponding with the deposited Pb film up to $E = -0.8 \text{ V}$ was found to be a monolayer (0.4 mC cm^{-2}) and hence the thickness of the UPD film is 3.5 \AA . Calculation of the refractive index of this layer is given in Table 1. At potentials $< -0.9 \text{ V}$ bulk lead is deposited (Fig. 1b), the anodic scan exhibits

three peaks which characterize [6] bulk Pb, AuPb_3 and AuPb_2 respectively. The ellipsometric results during potential sweep to more negative potential (0 to -1.2 V), depicted in Fig. 3, show a rapid increase of Δ and decrease of ψ with potential.

Evaluation of these results yields values of the refractive index which are virtually the same for both wavelengths. In Table 1 the data are summarized for potential scans up to -1.35 V ; measurements with higher Pb^{2+} concentration are also included. The data agree well with literature data for bulk Pb (7, 8). The results show that bulk values are already obtained for a thickness of 10 \AA (about 3 monolayers). The optical constants for the UPD film differ from the bulk data indicating a change of properties. A further analysis of the UPD film is provided by the ψ - Δ plot of Fig. 4 which shows a linear relationship over the potential range -0.8 to -0.4 V for the anodic scan data and from -0.55 to -0.8 V for the cathodic scan. This indicates that during the initial deposition, corresponding with the first cathodic peak, the refractive

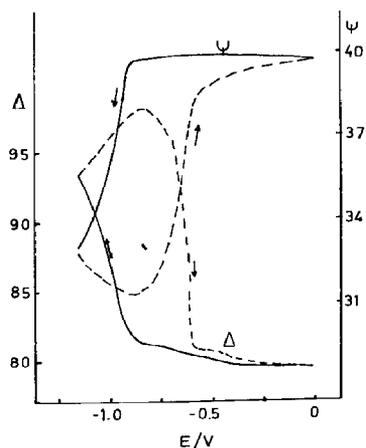


Fig. 3. Ellipsometric changes of Pb-Au system of Fig. 2 during potential scan 0 to -1.2 V vs mse .

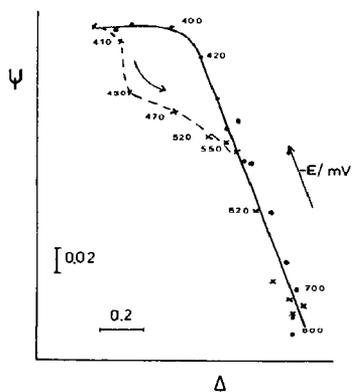


Fig. 4. ψ - Δ plot of data of Fig. 2 in UPD range; numbers indicate potential values.

Table 1. Refractive index and thickness of Pb layers on Au formed during potential scanning to $E = -0.8$ V *vs mse* (underpotential deposition) and to E_{scan} (bulk deposition). Electrolyte: 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$.

	Thickness/Å	n	k	Wavelength/nm
UPD film	3.5	1.15	4.67	546.1
		1.46	3.82	450
$E_{scan}/\text{V vs mse}$				
-0.95	10	2.13	5.00	450
-0.975	24	2.05	4.54	450
-1.05	39.5	2.02	3.90	450
-1.2	75	2.08	4.15	546.1
-1.35	96	2.08	4.15	546.1
-1.0 (*)	266	2.16	4.00	546.1
Au-substrate		0.47	2.61	546.1
		1.37	2.23	450

* Concentration Pb^{2+} : 3.4×10^{-2} M.

index of the film changes, *eg* at -0.45 V, $n=0.63$, $k = 5.33$ was obtained for $\lambda=546.1$ nm. With the onset of the second cathodic peak the refractive index reaches a constant value. Using the three parameter ellipsometric transient technique Horkans *et al.*[8] found for the first cathodic peak virtually the same values as reported here for the complete UPD layer. It was argued[8-10] that the primarily deposited film undergoes a transition to a metallic type adlayer at the potential of the second cathodic peak. However our results indicate that a transition of adsorbed layer to metallic bulk layer occurs around -0.9 V *ie* after completion of the monolayer.

The refractive index of the UPD layer is wavelength dependent. Takamura *et al.*[5] also concluded from reflectance measurements that the optical properties of the lead adsorbate layer shows a similarity with the gold substrate. Prolonged deposition of Pb results in noticeably smaller changes of Δ and ψ . In Fig. 5 Δ and ψ transients are given for galvanostatic deposition at 0.04 mA cm^{-2} . The optical constants calculated at different times during the deposition are presented in Table 2. The values are wavelength dependent in contrast to the data obtained for lead deposited during potential scanning. The values are more close

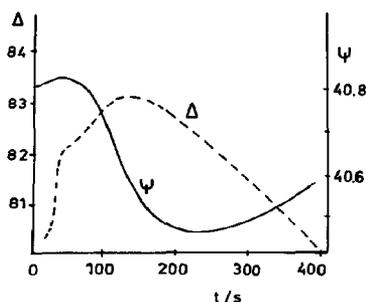


Fig. 5. ψ - and Δ -time curves during Pb deposition on Au at $i=0.04$ mA cm^{-2} . Electrolyte 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$; wavelength 546.1 nm.

Table 2. Refractive index and thickness of Pb film during deposition at $i=0.04$ mA cm^{-2} on Au. Electrolyte: 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$.

Thickness/Å	n	k	Wavelength/nm
11	0.41	3.30	546.1
27	0.45	3.30	
50	0.55	3.20	
73	0.57	3.05	
103	0.57	2.80	
140	0.55	2.70	
27	1.47	2.60	450
58	1.49	2.60	
89	1.47	2.60	

to the substrate value and it must therefore be concluded that these optical results indicate alloy information. Though alloy peaks are also observed in the voltammogram of Fig. 1b there was no indication of such formation in the ellipsometric results of Fig. 2.

If larger amounts of lead are deposited, the anodic voltammogram recorded afterwards showed increased bulk and alloy peaks, and a film is obtained with a refractive index which differs from the bulk value of Pb. The results do not allow a further evaluation as to what kind of alloy is deposited and the refractive index as obtained here is therefore to be considered as an effective value for the deposited layer.

3.2. Lead deposition on platinum

On Pt the underpotential deposition of Pb is observed at 0.1 V *vs mse*. Figure 6a gives the voltammogram of Pt in 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$ recorded for the potential range $+0.90$ to -0.65 V and $+0.20$ to -0.65 V at scan rate 20 mV s^{-1} . The UPD charge obtained from the anodic peak amounts to a coverage of $\Theta = 0.41$. Likewise Kolb *et al.*[11] concluded that no complete monolayer is formed during UPD of Pb on Pt (110).

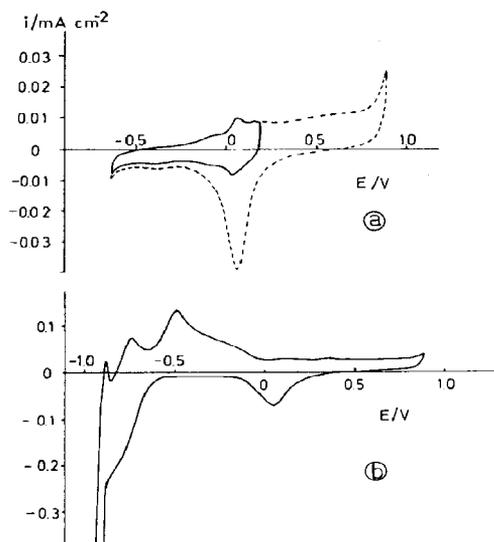


Fig. 6. Cyclic voltammogram of Pt in 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$. Scan rate 20 mV s^{-1} . Scan range: (a) dashed curve 0.9 to -0.65 V vs mse , full curve 0.2 to -0.65 V vs mse ; (b) 0.9 to -0.95 V vs mse .

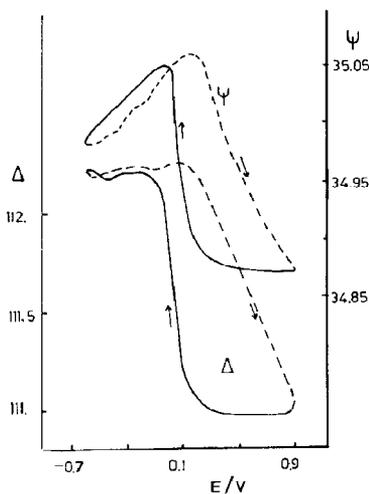


Fig. 7. Ellipsometric changes during potential scan 0.9 to -0.65 V vs mse of Pt in 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$ at scan rate 20 mV s^{-1} ; wavelength 546.1 nm .

In Fig. 7 the optical monitoring of the Pb–Pt system is shown for the potential scan 0.9 to -0.65 V at $\lambda = 546.1 \text{ nm}$. For the UPD layer at -0.65 V a refractive index $n = 2.05$, $k = 4.95$ is found with thickness 1.5 \AA .

The underpotential deposition begins after the oxide has been reduced; this was established by comparing the magnitude of the Δ and ψ changes during the oxide reduction in a solution without Pb^{2+} ions.

Amadelli and Yeager[12] assumed that in presence of Pb^{2+} a destabilization and/or hindrance of the oxide layer occurs, but the optical results indicate that the growth of the oxide layer is not influenced by the presence of lead ions. The refractive index of the UPD layer points to a strong metallic character. Its value is close to that of bulk Pb[7]. This is in contrast with the findings of Takamura *et al.*[5] who concluded that the optical properties of the adsorbate layer are different.

Bulk lead deposition takes place at potential scans to values $< -0.7 \text{ V}$. Figures 6b and 8 show the diagrams for a scan $+0.9$ to -0.95 V . The sudden changes in Δ during the anodic scan correspond with the peaks in Fig. 6b characterizing bulk and alloy formation. Evaluation of the refractive index of the film is given in Table 3 for potential scans up to -1.0 V . Some experiments were carried out at constant deposition potential and these results are also presented in Table 3. The optical constants of these

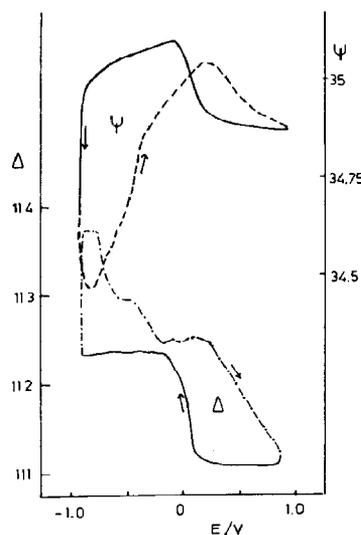


Fig. 8. Ellipsometric changes of the Pb–Pt system of Fig. 7 for potential scan 0.9 to -0.95 V vs mse .

Table 3. Refractive index and thickness of Pb films on Pt deposited during potential scan and at constant potential; wavelength 546.1 nm . Electrolyte: 1 M $\text{HClO}_4 + 3.4 \times 10^{-3}$ M $\text{Pb}(\text{ClO}_4)_2$.

$E_{\text{scan}}/\text{V vs mse}$	Thickness/ \AA	n	k
-0.65 (UPD-film)	1.5	2.05	4.95
-0.85	8.6	1.90	4.00
-0.95	22	2.40	4.82
-1.00	37	2.50	4.82
$E_{\text{const. during: t/s}}$			
-0.95 60	100	2.44	2.80
-0.95 120	210	2.41	2.83
-1.00 60	115	2.35	3.94
Pt-substrate		1.95	4.48

films are also close to bulk lead values[7]. The ellipsometric results (*cf.* Fig. 8) show a drastic change for $E < -0.90$ V, however the refractive index values do not differ much from the UPD data.

Though Fig. 6b shows both bulk and alloy peaks in the anodic voltammogram, the ellipsometric data do not reveal a distinct difference; it is only noted that k tends to decrease with prolonged deposition.

3.3. Copper deposition on platinum

The deposition of Cu on Pt was investigated in 0.5 M $\text{H}_2\text{SO}_4 + 6 \times 10^{-5}$ M CuSO_4 . Figure 9 shows the cyclic voltammogram, recorded at 200 mV s^{-1} for three different potential ranges. The underpotential deposition is manifested by the anodic peaks at 0.0 and 0.08 V *vs mse*, at -0.45 V bulk deposition begins. The optical results are given in Fig. 10 for the scan range $+0.9$ to -0.5 V at scan rate 20 mV s^{-1} for wavelength 546.1 nm; they indicate a decrease of Δ and ψ when the underpotential deposition starts. For the UPD film a coulometric charge corresponding with $\Theta = 0.6$ was found, which implies a thickness of 1.5 Å. For the refractive index of the film $n = 2.5$, $k = 3.3$ was obtained. Figure 11 shows the ellipsometric results for the potential range 0.9 to -0.7 V. It is noticed that Δ and ψ pass through a minimum at -0.45 V and at -0.65 V reach about the same values as at 0.1 V, at which potential the substrate is bare. Since full coverage, $\Theta = 1$, is obtained at about -0.70 V it must be concluded from this Δ , ψ behaviour that a rearrangement of the surface atoms takes place prior to the actual bulk deposition. This could imply a change-over of top layer atoms with underlying atoms such that optically more substrate area is seen than absorbed film. Using reflectance spectroscopy Kolb and Kötzt[13] also concluded that a structural change took place in the adsorbate layer at $\Theta = 0.6$. It has been discussed[14, 15] whether or not a

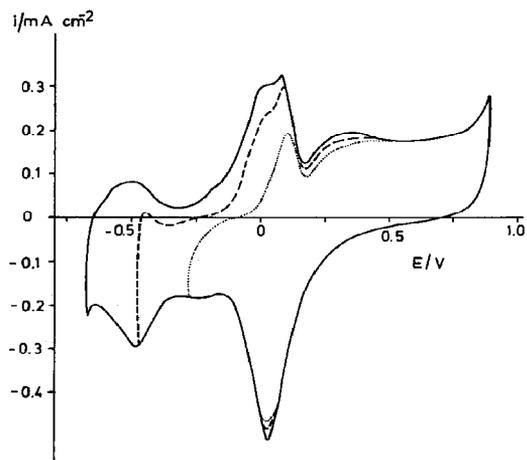


Fig. 9. Cyclic voltammogram of Pt in 0.5 M $\text{H}_2\text{SO}_4 + 6 \times 10^{-5}$ M CuSO_4 . Scan rate 200 mV s^{-1} . Scan range: (—) 0.9 to -0.7 V; (---) 0.9 to -0.5 V; (···) 0.9 to -0.30 V *vs mse*.

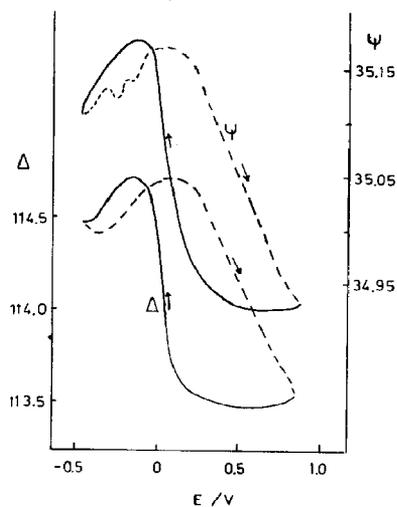


Fig. 10. Ellipsometric changes of Pt in 0.5 M $\text{H}_2\text{SO}_4 + 6 \times 10^{-5}$ M CuSO_4 during potential scan 0.9 to -0.5 V *vs mse*; scan rate 20 mV s^{-1} ; wavelength 546.1 nm.

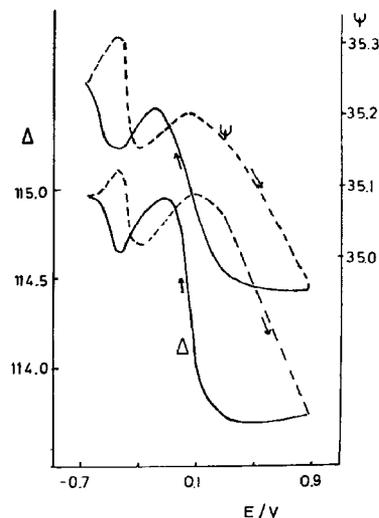


Fig. 11. Ellipsometric changes of the Cu-Pt system of Fig. 10 during potential scan 0.9 to -0.7 V *vs mse*.

complete monolayer must be formed before bulk deposition can start. The ellipsometric results provide evidence that bulk layer formation is preceded by reorientation of the initial surface layer which occurs when a coulometric charge equivalent to about a monolayer, has passed through. The different nature of the UPD layer is also expressed by its refractive index which differs from the value[7]. These results are in good agreement with UPD experiments[16] on large Pt electrodes.

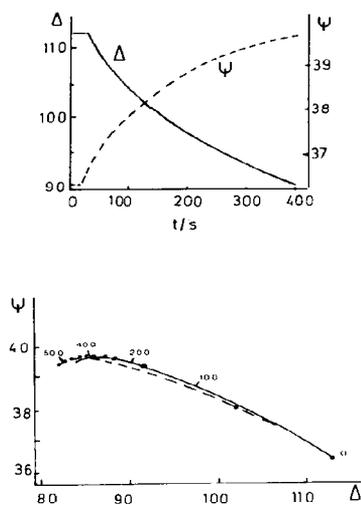


Fig. 12. Ellipsometric changes during Cu deposition on Pt at $E = -0.6$ V *vs mse*. Electrolyte $1\text{ M H}_2\text{SO}_4 + 3.4 \times 10^{-3}\text{ M CuSO}_4$. (a) Δ - and ψ -time curves; (b) ψ - Δ plot; (●): experimental data; full curve: calculated for $N=0.65 - 2.8 i$; dashed curve: calculated for $N=0.65 - 2.7 i$, numbers indicate thickness values in Å.

A further investigation involved multilayer deposition at constant potential or current density. The growth of Cu film at -0.60 V *vs mse* in $0.5\text{ M H}_2\text{SO}_4 + 3.4 \times 10^{-3}\text{ M CuSO}_4$ was monitored optically and the results are shown in Fig. 12a. In Fig. 12b the data are presented as a ψ - Δ plot together with calculated ψ - Δ curves with refractive index $n=0.65$, $k=2.60$ and 2.70 . The close agreement implies that the copper film grows homogeneously and its refractive index is very close to the bulk value[7]. Similar results were obtained for deposition at potentials < -0.60 V.

However, at less negative potentials (or at small current densities) the Δ - and ψ -transients indicate a non-homogeneous growth. This can be explained by the initial nucleation and growth process. If the overvoltage is high enough, instantaneous nucleation occurs followed by three dimensional growth, thus the film growth proceeds homogeneously. At low overvoltage however the initial film is gradually filled with metallic deposit with the result that the composition of this layer changes with time; hence a layer growth is observed with a varying refractive index.

4. CONCLUSIONS

For the deposit-substrate systems with different refractive indices, Cu-Pt and Pb-Au, the refractive index of the UPD film was found to be intermediate between the values of the substrate and the bulk

deposit. It is of interest to note that the refractive index of the Pb-UPD film on Au has about the same value as the Pb adsorbate film on Cu and Ag[2] *viz* $n=1.285$, $k=4.080$ for Ag(111) and $n=1.225$ resp. 0.952 , $k=3.520$ respectively 3.898 for Cu(111) at $\lambda=514.5$ nm. At each of these metals Au, Ag and Cu the coulometric charge related to UPD corresponds with full coverage. Since the atomic radius of Pb is larger than that of Au, Ag and Cu the adatoms will form a hexagonal close packed layer independent of substrate symmetry[17]. The Pb-UPD films on these metals are thus structurally alike and this explains the similarity in refractive indices.

In the Pb-Pt system both deposit and substrate have about the same refractive index and the value of the UPD film was found to be close to that of the bulk metal.

It was established that homogeneous growth of bulk deposit of Cu or Pt occurs if the deposition potential is < -0.6 V *vs mse*; bulk values are already obtained for a deposited layer of about three monolayer thickness. Alloy formation could also be detected by ellipsometry. The optical response during prolonged deposition of Pb on Au is quite different from that during potential scanning and the refractive index of the deposited layer shows a similarity with the substrate value.

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