# Ellipsometry of metal deposition

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# ELLIPSOMETRY OF METAL DEPOSITION

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**Abstract**—The initial stages during galvanic deposition were monitored by ellipsometry in combination with cyclic voltammetry for the growth of Bi, Cu and Ge films on polycrystalline Au, Pd and Pt substrates. The *upd* of Bi on Au, of Ge on Pt and of Cu on Au could be detected ellipsometrically but not for Bi on Pd or Pt. The refractive index of the *upd* film of Bi on Au changes with increasing coverage. The bulk deposit film of Bi on Au and of Cu on Au grows at constant refractive index.

## INTRODUCTION

The initial stages of metal deposition on a foreign metal substrate often involve the formation of a (sub)monolayer, which differs from the bulk layer as is indicated by its potential shift to more positive potentials with respect to the Nernst potential. This shift depends on the difference in work function of depositing metal and substrate metal and is affected by the crystallographic orientation of the substrate[1–5]. Adsorption of anions can induce lateral interaction effects and so cause a decrease in the *upd* shift, furthermore the *upd* can be influenced by an oxide film. The *upd* of metals can take place with partial charge transfer depending on the magnitude of the difference in electronegativity. Parameters which determine the structure of the *upd* layer are: the ratio of the atomic radii of the adsorbing metal and the substrate metal; the structure of the substrate itself and the adsorptive and lateral interactions of the adsorbate. In principle the accommodation of the *upd* layer on the substrate can be, in the case of 1/1 adsorption, epitaxial for $r_{dep} < r_{substr}$ and for 1/n or multisite adsorption, hexagonal close packed for $r_{dep} > r_{substr}$; in the latter case it is generally assumed that some superlattice structures are formed which are transformed to higher order phase transition with increasing coverage.

Bulk electrocrystallization proceeds *via* nucleation and growth; if an *upd* layer has been formed, the nucleation process takes place within the adsorption layer and involves a reorganization. The adsorbed layer in fact provides a modified substrate for the bulk metal deposition[6].

The presence of an *upd* layer also influences the electrocatalytic properties of the substrate by providing different acting sites and thus operating as a bifunctional catalyst or by modifying the electronic properties of the substrate. The activity of adatom-electrodes for oxidation of organic fuels is higher for oxygen adsorbing adatoms than for non oxygen adsorbing adatoms[7].

Optical reflection techniques can give information on the nature of the *upd* layer. These techniques are very sensitive *in situ* methods and can be used to monitor the substrate during deposition and/or dissolution of the adsorbate. Also the onset of bulk deposition can be measured up to some 10 nm, depending on the system; this can indicate whether the growth proceeds homogeneously or not. Determination of the true optical constants, however, can be difficult if the substrate properties are altered by the adsorbing species.

The galvanic deposition process was studied with cyclic voltammetry and ellipsometry for growth of Bi, Cu and Ge films on polycrystalline Au, Pt and Pd substrates. With $r(Ge) < r(Pt)$; $r(Bi) > r(Au, Pd, Pt)$ and $r(Cu) < r(Au)$ an epitaxial layer is expected at full coverage for *upd* of Cu on Au and Ge on Pt and a hexagonal close packed layer for Bi on Au, Pd and Pt.

## EXPERIMENTAL

All experiments were carried out in a cylindrical Teflon cell with windows arranged for an angle of incidence of 70° at the substrate. The substrate electrodes were discs (area 0.5 cm²) of Pt, Au and Pd; before each measurement they were polished with 0.05 $\mu$m alumina. The reference electrode is mercury-mercurous sulphate (*mse*), 0.65 V *vs nhe*, the counter electrode is a Pt foil.

The electrolyte, 0.5 M $H_2SO_4$ or 1 M $HClO_4$ with $x$ M Bi, Cu or Ge salts were prepared from AnalaR Chemicals and doubly distilled water and were deaerated with $N_2$.

The equipment consisted of a Wenking potentiostat POS 73 and an automatic ellipsometer, Rudolph RR 2200, with a tungsten iodine light source and monochromatic filters.

## RESULTS AND DISCUSSION

### Upd *of* Bi *on* Au

The *upd* of Bi on Au in 1 M $HClO_4 + 1$ mM $Bi(NO_3)_3$ is characterized by a number of peaks in the voltammogram; Fig. 1 represents the diagram at a

scan rate of 10 mV s⁻¹. The optical diagram, Fig. 2, shows inflections of Δ at −200, −300 and −410 mV during the cathodic scan. The total coulometric charge up to −410 mV corresponds to a monolayer. Due to the relatively small differences in Pauling's electronegativity, the adatoms are completely discharged and covalently bound[8]. For the Bi/Au system the adsorbed layer will be hexagonal close packed. The results indicate that the *upd* layer changes during deposition; calculation of the refractive index for the film at these potentials yields increasing n, k values with coverage. The data are summarized in Table 1; the high k value is typical for the metallic character of the *upd* film. Reflectivity measurements[9] also indicate a change during the formation of the *upd* layer. Similar behaviour has been found for the *upd* of Pb on Au[10, 11].

## Upd *of* Bi *on* Pd *and* Pt

In the system Bi/Pd and Bi/Pt the presence of an oxide film interferes with *upd*. Figure 3 shows the
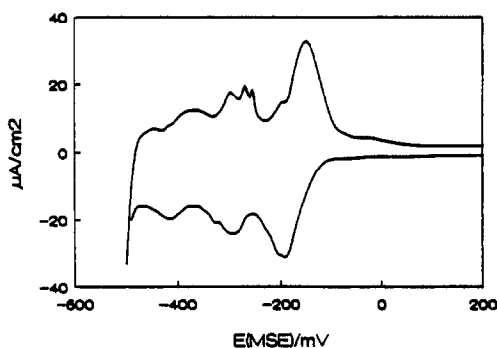
Fig. 1. Voltammogram of Au in 1 M HClO₄ + 1 mM Bi(NO₃)₃; scan rate, 10 mV s⁻¹.
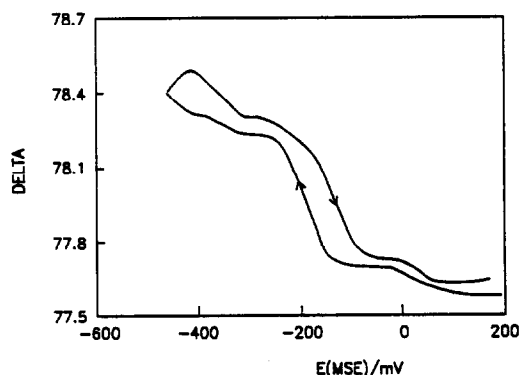
Fig. 2. Ellipsometric change during potential scan of Au in 1 M HClO₄ + 1 mM Bi(NO₃)₃; wavelength, 546.1 nm; scan rate, 10 mV s⁻¹.

Table 1. Change of refractive index of Bi *upd* film on Au at indicated potentials in 1 M HClO₄ + 1 mM Bi(NO₃)₃; wavelength, 546.1 nm

| Peak/mV | θ | n | k |
|---|---|---|---|
| −200 | 0.52 | 0.83 | 4.77 |
| −300 | 0.85 | 1.15 | 4.30 |
| −410 | 1.0 | 1.27 | 4.25 |
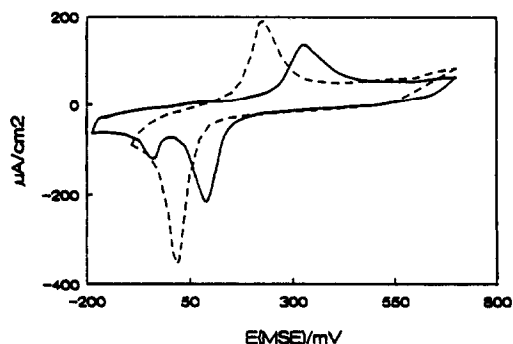
Fig. 3. Voltammogram of Pd in 0.5 M H₂SO₄ + 0.2 mM Bi(NO₃)₃ (dashed line) and in 1 M HClO₄ + 0.7 mM Bi(NO₃)₃ (full line); scan rate, 20 mV s⁻¹.
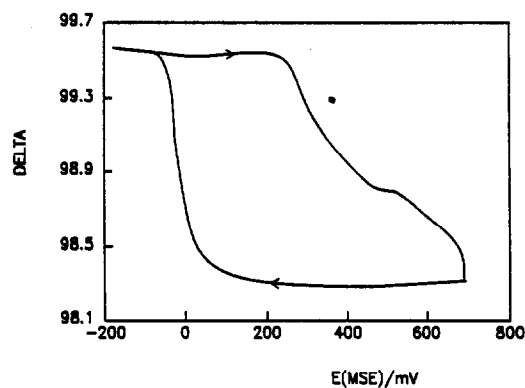
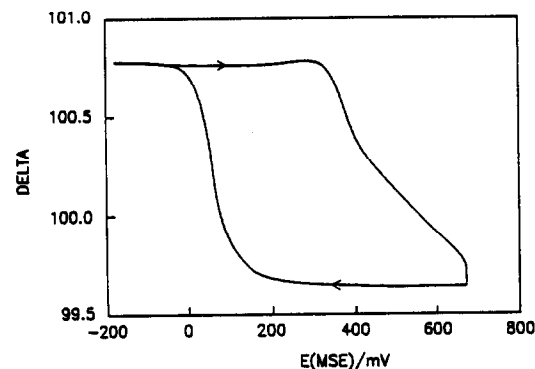Fig. 4. Ellipsometric change during potential scan of Pd/Bi system in 0.5 M H₂SO₄; scan rate, 20 mV s⁻¹; wavelength, 546.1 nm.

Fig. 5. Ellipsometric change during potential scan of Pd/Bi system in 1 M HClO₄; scan rate, 20 mV s⁻¹; wavelength, 546.1 nm.

voltammogram for the *upd* of Bi on Pd: in 0.5 M H₂SO₄ the *upd* is detected only in the anodic scan; in 1 M HClO₄, the oxide peak is shifted to higher potential and a Bi *upd* peak is now also noticed in the cathodic voltammogram. The Bi *upd* layer is indirectly detected in the optical potential scans of Figs 4 and 5: its presence prevents the oxidation of Pd; once Bi is oxidized and dissolved, the substrate oxidation starts as indicated by the kink in the anodic scan at 230 mV (H₂SO₄) and 300 mV (HClO₄) respectively.

The Bi/Pt system shows similar behaviour in 1 M $HClO_4$: the cathodic voltammogram reveals a small peak following the reduction of the platinum oxide and a steep peak at 220 mV in the reverse scan, in agreement with Refs [9, 12, 13]. The optical response (Fig. 6) indicates the disappearance of the *upd* film and the start of oxidation in the anodic scan at about 350 mV. Cadle and Bruckenstein[12] concluded that the initial Bi(III) reduction occurs simultaneously with the reduction of the Pt oxide; Bi(0) is only partially removed in the anodic scan.

The Bi *upd* layer on Pd and Pt does not reach full coverage[12, 13]; the ellipsometric results imply that the resulting optical constants of the film are close to those of the substrate. These results differ somewhat from reflectivity measurements of Takamura et al.[9] for Bi/Pd and Bi/Pt; this may be due to a difference in potential range and scan rate.

## Upd of Ge on Pt

Figures 7 and 8 show the voltammogram and optical response in the potential range 700 to $-650$ mV for Pt in 0.5 M $H_2SO_4 + 1$ mM $GeO_2$. Both the onset of *upd* of Ge and the dissolution are clearly observed by the change of $\Delta$ at $-350$ mV in the cathodic scan and at $-30$ mV in the anodic scan (Fig. 8).

At potentials $< -600$ mV bulk and alloy formation occurs. With repeated scanning the electrode
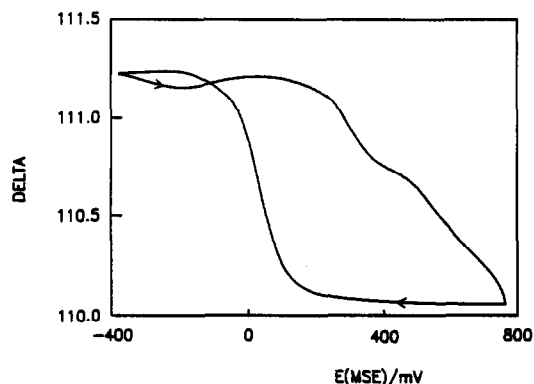


Fig. 8. Ellipsometric change during potential scan of Pt in 0.5 M $H_2SO_4 + 1$ mM $GeO_2$; scan rate, 5 mV s$^{-1}$; wavelength, 546.1 nm.



Fig. 9. Voltammogram of Au in 0.5 M $H_2SO_4 + 1$ mM $CuSO_4$; scan rate, 200 mV s$^{-1}$.



Fig. 6. Ellipsometric change during potential scan of Pt in 1 M $HClO_4 + 1$ mM $Bi(NO_3)_3$; scan rate, 20 mV s$^{-1}$; wavelength, 546.1 nm.



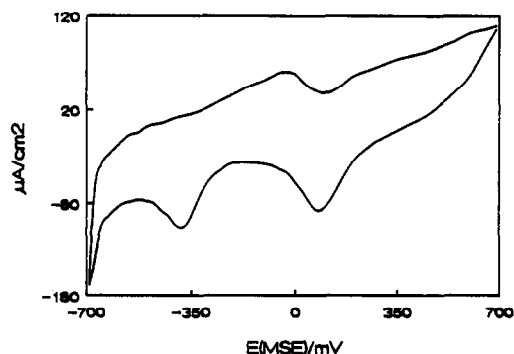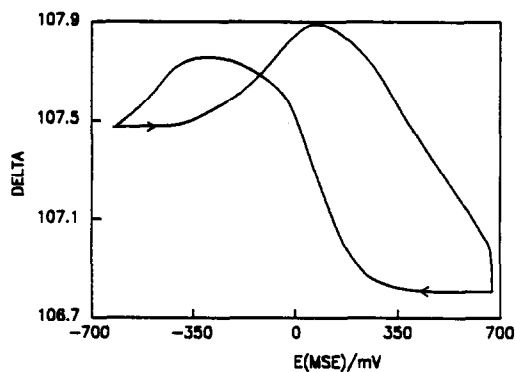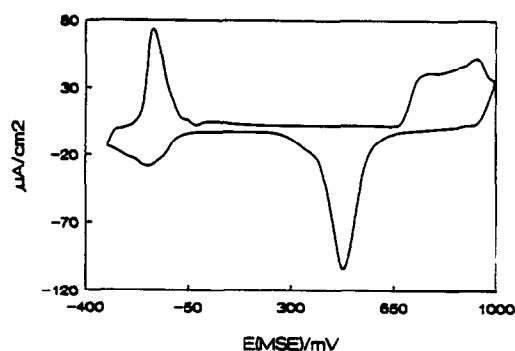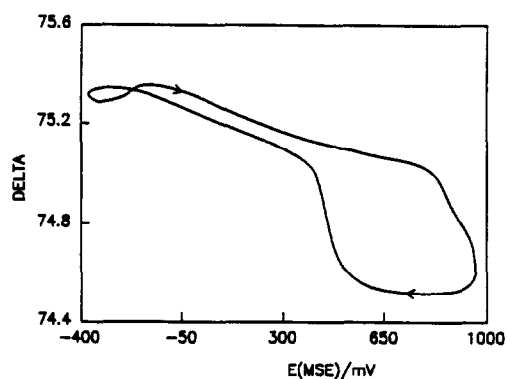Fig. 10. Ellipsometric change during potential scan of Cu/Au system; scan rate, 20 mV s$^{-1}$; wavelength, 546.1 nm.

becomes more active. Furuya and Motoo[14] have shown that the Ge adatoms adsorb oxygen in the potential region corresponding with the double layer region. Further evaluation of the data was therefore not performed.

## Upd of Cu on Au

The *upd* of Cu on Au in 0.5 M $H_2SO_4 + 1$ mM $CuSO_4$ corresponds with a monolayer and the voltammogram (Fig. 9) shows a distinct peak, as was investigated by Lorenz et al.[15]. The optical changes, however, were found to be very small (Fig. 10); this was observed at all wavelengths in the range



Fig. 7. Voltammogram of Pt in 0.5 M $H_2SO_4 + 1$ mM $GeO_2$; scan rate, 20 mV s$^{-1}$.

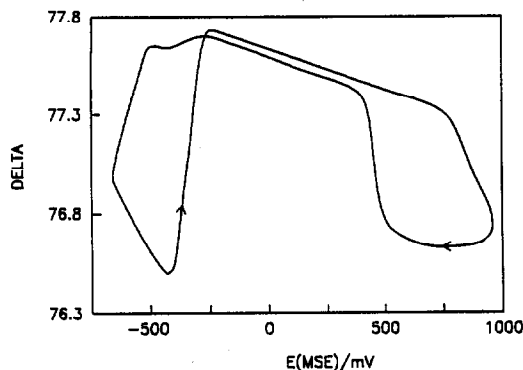Fig. 11. Ellipsometric change during potential scan (20 mV s$^{-1}$) with onset of bulk deposition of Cu on Au; wavelength, 546.1 nm.
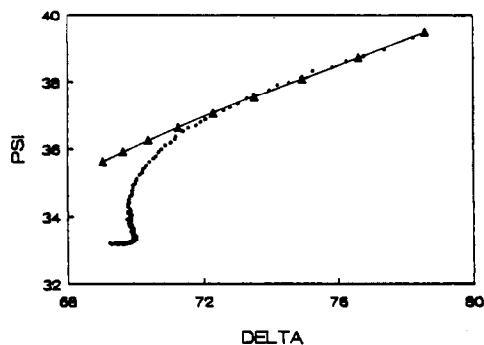


Fig. 12. Change of $\Psi$-$\Delta$ during deposition of Bi on Au at $i = 0.1$ mA cm$^{-2}$; electrolyte, 1 M HClO$_4$ + 2 mM Bi(NO$_3$)$_3$; wavelength, 546.1 nm. Full line: calculated for film growth with $n = 1.18$; $k = 1.85$; (▲) points indicate thickness increase of 30 Å.

450–650 nm and indicates that the optical constants of the *upd* layer are close to the values of the substrate. Reflectivity measurements also reveal only small effects[9, 16].

*Bulk deposition of* Cu *on* Au

The onset of bulk deposition of Cu on Au is observed as a steep change in the optical diagram during potential scan, Fig. 11. The results, obtained at 546.1 and 450 nm, for potentials −500 to −800 mV are given in Table 2; the data show a constant refractive index for layers with thickness up to 6 nm. The same values were found for deposition of Cu on Pt[11], and agree with literature data for bulk Cu[17].

*Bulk deposition of* Bi *on* Au, Pt *and* Pd

Deposition of Bi on Au was followed with time at constant current of 0.1 mA cm$^{-2}$ in 1 M HClO$_4$ + 2 mM Bi(NO$_3$)$_3$; the optical data are plotted as a $\Psi$-$\Delta$ graph in Fig. 12. The full line represents calculated data for film growth with refractive index $n = 1.18$ and $k = 1.85$ at 546.1 nm. The results imply that the growth proceeds homogeneously to about 120 Å.

The deposition of a Bi film onto Pd or Pt does not appear to grow at constant refractive index; measurements at constant current or potential indicate an initially varying composition. The refractive index measured for a bulk layer deposit of about 120 mC cm$^{-2}$ is for Bi on Pt: $n = 1.22$; $k = 1.91$; for Bi on Pd: $n = 1.76$; $k = 3.17$.

The refractive index values of Bi on Au and on Pt are the same; for Bi on Pd a higher $n,k$ value is obtained. This might indicate some alloy formation as well[12]. Literature data for Bi are scarce and depend strongly on the crystallographic orientation[17].

Table 2. Refractive index and thickness of Cu film deposited on Au in 1 M HClO$_4$ + 1 mM CuSO$_4$ during potential scanning in the potential range −500 to −800 mV

| Thickness/Å | $\lambda = 546.1$ nm | | $\lambda = 450$ nm | |
|---|---|---|---|---|
| | $n$ | $k$ | $n$ | $k$ |
| 8 | 0.70 | 2.25 | | |
| 25 | | | 1.00 | 2.10 |
| 33 | 0.69 | 2.05 | | |
| 44 | 0.69 | 2.20 | 1.02 | 2.05 |
| 54 | | | 1.05 | 2.07 |
| 58 | 0.70 | 2.30 | | |

## SUMMARY

Optical monitoring of *upd* is possible if the refractive index of the layer differs from the substrate. Ellipsometric changes were observed for *upd* of Bi on Au and for Ge on Pt, for Cu on Au a marginal change was seen; *upd* of Bi on Pd and Pt does not give rise to an optical change. The start of bulk deposition of Cu on Au and of Bi on Au was found to proceed at constant refractive index; due to the presence of the *upd* layer, sufficient nuclei have been created to enable homogenous growth.

## REFERENCES

1. D. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering* (Edited by H. Gerischer and Ch. W. Tobias), Vol. 11, p. 125, Wiley, New York (1978).
2. K. Jüttner, *Electrochim. Acta* **31**, 917 (1986).
3. K. Jüttner and W. Lorenz, *Z. phys. Chem. NF* **122**, 163 (1980).
4. R. R. Adzic, in *Advances in Electrochemistry and Engineering* (Edited by H. Gerischer), Vol. 13, p. 159, Wiley, New York (1984).
5. G. Kokkinidis, *J. electroanal. Chem.* **201**, 217 (1986).
6. H. Bort, K. Jüttner, W. J. Lorenz, G. Staikov and E. Budevski, *Electrochim. Acta* **28**, 985 (1983).
7. M. Shibata and S. Motoo, *J. electroanal. Chem.* **202**, 137 (1986).
8. S. M. Sayed and K. Jüttner, *Electrochim. Acta* **28**, 1635 (1983).
9. K. Takamura, F. Watanabe and T. Takamura, *Electrochim. Acta* **26**, 979 (1981).
10. J. Horkans, B. D. Cahan and E. Yeager, *J. electrochem. Soc.* **122**, 1585 (1975).
11. W. Visscher, *Electrochim. Acta* **34**, 1169 (1989).
12. S. H. Cadle and S. Bruckenstein, *Anal. Chem.* **44**, 1993 (1972).
13. R. R. Adzic, D. N. Simic, A. R. Despic and D. M. Drazic, *J. electroanal. Chem.* **65**, 587 (1975).
14. N. Furuya and S. Motoo, *J. electroanal. Chem.* **99**, 19 (1979).
15. W. J. Lorenz, I. Moumtzis and E. Schmidt, *J. electroanal. Chem.* **33**, 121 (1971).
16. T. Takamura, Y. Sato and K. Takamura, *J. electroanal. Chem.* **41**, 31 (1973).
17. *American Institute of Physics Handbook*, 3rd edn, pp. 6–114 (1972).