

Ellipsometric study of hydrous gold oxide layers and gold surfaces resulting from their electroreduction

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Abstract

The ellipsometric responses of hydrous gold oxide layers (HAuOLs) and electroreduced gold surfaces (EDAuEs) resulting from HAuOL electroreduction have been studied in the 400–700 nm spectral range. For HAuOL the values of n and k are in the $1.760 \leq n \leq 1.930$ and $0 \leq k \leq 0.24$ ranges respectively. These results are discussed in terms of possible H₂O–Au oxide molar ratios. For EDAuEs the values of $n(\lambda)$ are $k(\lambda)$ depend on the preparation conditions. These results are interpreted in terms of a composite EDAuE structure consisting of Au domains and solution-filled voids.

1. Introduction

The electrochemical roughening of several f.c.c. metals can be achieved in a reproducible way by using the procedure described in the literature [1, 2] which involves two stages: (i) the formation of a metal oxide layer by applying a periodic potential routine; (ii) the electroreduction of the oxide layer. By adjusting the different electrical parameters it is possible to obtain metal overlayers with appreciable roughness depending on the metal [3, 4].

Ellipsometric data of both hydrous Au oxide layers (HAuOLs), and Au overlayers (EDAuEs) resulting from the electroreduction of HAuOLs under different potential-controlled conditions are reported in this work. The HAuOL can be described as a quasi-homogeneous layer with a stoichiometry comprising definite H₂O–Au oxide molar ratios, whereas the EDAuE behaves as a material made of Au and solution-filled void domains.

2. Experimental details

A gold disc (Johnson Matthey Chem. Co.; Specpure quality; 0.64 cm² apparent area) working electrode, an Au foil auxiliary electrode and a hydrogen reference electrode in the cell solution (0.5 M H₂SO₄) were assembled in a conventional cell for ellipsometric measurements. Potentials are referred to the reversible hydrogen electrode (RHE) scale. The electrolyte solution was prepared from H₂SO₄ Merck p.a. and Milli-Q* water.

The working electrode was first mirror polished with 0.3 and 0.05 μm alumina, then rinsed several times with Milli-Q* water and finally immersed in the cell. The ellipsometer (Rudolph Research type 437002/200 E) was employed in the null mode, with the incident light beam at 69° and the azimuth angle (compensator) set at 135°. The 400–700 nm spectral range was covered using adequate filters.

The experimental procedure was as follows.

(i) The cyclic voltammogram of the working electrode in 0.5 M H₂SO₄ was attained between $E_{s,a} = 1.75$ V and $E_{s,c} = 0$ V at $v = 0.1$ V s⁻¹. This voltammogram was taken as the reference.

(ii) The ellipsometric parameters of the initial Au surface were obtained at 0 V.

(iii) Relatively thick HAuOLs were formed by applying a symmetric square-wave periodic potential at $f = 5$ kHz, between $E_u = 2.7$ V and $E_l = 0.45$ V for $1 \text{ min} \leq \tau \leq 9 \text{ min}$; f , E_u , E_l and τ are the frequency, the upper potential step, the lower potential step and the treatment time respectively [5].

(iv) The ellipsometric parameters of the HAuOL were measured at 1.5 V and at six wavelengths.

(v) The HAuOL was electroreduced at either $v = 0.1$ V s⁻¹ or $v = 0.001$ V s⁻¹, and the value of Q_{HAuOL} , the Au oxide charge, was calculated.

(vi) The EDAuE optical parameters were determined at 0 V and six wavelengths.

(vii) The voltammogram of the EDAuE were obtained as indicated in (i). The surface roughness of EDAuE was evaluated as the O-electrodesorption voltammetric charge ratio corresponding to the EDAuE and that of the initial gold surface of (i) [6].

3. Results

3.1. Determination of the optical parameters

Ellipsometric data for HAuOLs at 1.5 V and EDAuEs at 0 V were obtained at 405, 450, 492, 546, 580 and 671 nm. Measurements were made in a range of times in which the influence of the decay process [7] could be neglected. The average of two series of readings at all wavelengths was taken to compensate small shifts due to the time effect. For each wavelength λ and different film thicknesses d_{HAuOL} , the experimental amplitude ratio Ψ and the phase shift Δ were obtained. Theoretical Δ and Ψ values were calculated by means of a subroutine which finds the local minimum of a function of several variables [8]. The refractive index n and the absorption coefficient k were determined assuming a single isotropic and homogeneous film [9].

3.1.1. The hydrous gold oxide layers

Values of Δ and Ψ for HAuOLs at 1.5 V corresponding to different thicknesses d_{HAuOL} as well as those resulting from the fitting procedure are shown in Fig. 1. Depending on λ , values of n of between 1.760 and 1.930, and values of k of between 0.24 to 0, were found. The λ dependence of n and k are shown in Fig. 2 including error bars.

3.1.2. The electroreduced gold overlayers

Ellipsometric data for EDAuEs depend on whether the HAuOL electroreduction was made at $v = 0.1 \text{ V s}^{-1}$ or $v = 0.001 \text{ V s}^{-1}$. This reflects in the value of the film thicknesses d_{EDAuE} . The dependences of n and k on λ are displayed in Fig. 3. Only for $\lambda = 405 \text{ nm}$ does the value of n approach that of bulk Au [10, 11]. For EDAuEs prepared at 0.001 and 0.1 V s^{-1} the difference in n becomes greater as λ increases. On the contrary, the values of k for EDAuEs are lower than for bulk Au.

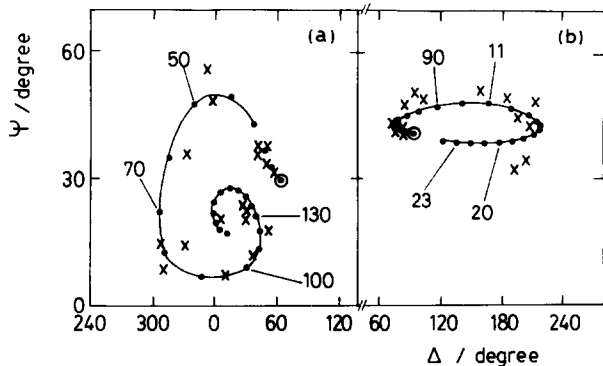


Fig. 1. Plots of Ψ vs. Δ for HAuOL at (a) $\lambda = 405 \text{ nm}$ and (b) $\lambda = 671 \text{ nm}$: \times , experimental data; \bullet , calculated data. The numbers indicate the average d_{HAuOL} values in nanometres.

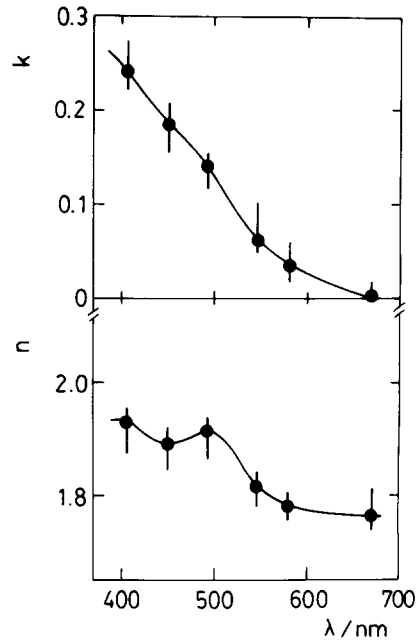


Fig. 2. Plots of k vs. λ and n vs. λ for HAuOL.

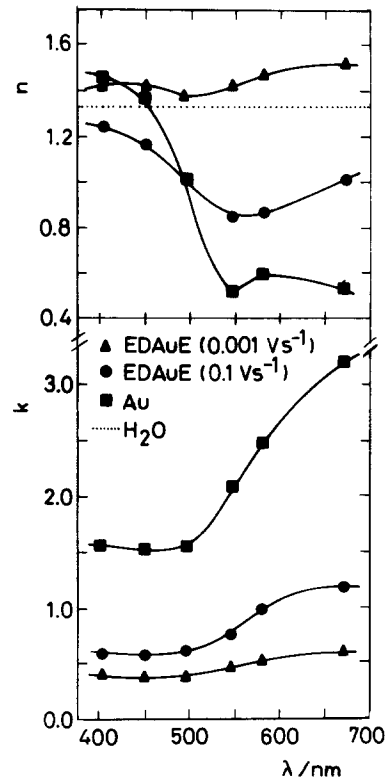


Fig. 3. Plots of n vs. λ and k vs. λ for polycrystalline Au (blank) (\blacksquare), and for EDAuE obtained at $v = 0.1 \text{ V s}^{-1}$ (\bullet) and $v = 0.001 \text{ V s}^{-1}$ (\blacktriangle); \cdots , data when the refractive index of the solution n_{sol} is 1.332.

The d_{EDAuE} vs. d_{HAuOL} plot (Fig. 4) shows that, for the same d_{HAuOL} , the value of d_{EDAuE} resulting at 0.001 V s^{-1} is greater than that resulting at 0.1 V s^{-1} .

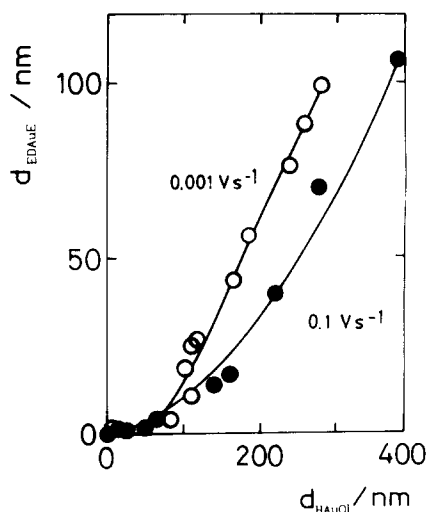
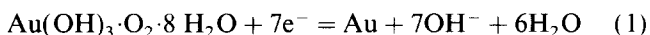


Fig. 4. Plot of d_{EDAuE} vs. d_{HAuOL} for EDAs obtained at $v = 0.001 \text{ V s}^{-1}$ (○) and $v = 0.1 \text{ V s}^{-1}$ (●).

4. Discussion

4.1. The hydrous gold oxide layers

The values of n and k for the HAuOLs are lower than those reported for Au oxide layers grown at 1.5 V [12]. This suggests that the HAuOL contains a larger amount of water than that grown at 1.5 V. Therefore the n and k values for HAuOLs can be compared with those obtained through the effective medium theories [13–19] for an ideal mixture of Au_2O_3 and H_2O . This calculation shows an H_2O content in the HAuOL matrix in the 65–75% range. On the contrary the apparent density ρ and the H_2O content can be estimated from Q_{HAuOL} , the voltammetric electroreduction charge and the molar volume V_{HAuOL} of HAuOL. The latter can be obtained from d_{HAuOL} . To estimate the apparent HAuOL density, it is assumed that the formation of HAuOL at 2.7 V produces $\text{Au}(\text{OH})_3$, H_2O and residual O_2 trapped in the HAuOL. Thus for an average stoichiometry such as $\text{Au}(\text{OH})_3 \cdot \text{O}_2 \cdot 8 \text{H}_2\text{O}$ the electroreduction reaction can be written as follows:



Reaction (1) involves the transfer of seven F per mole of HAuOL. On the basis of these assumptions and the slope of the Q_{HAuOL} vs. V_{HAuOL} plots, the following upper and lower limiting density values were estimated: $\rho_{\text{HAuOL}} = 7.6 \text{ g cm}^{-3}$ and $\rho_{\text{HAuOL}} = 4.6 \text{ g cm}^{-3}$. These values which are much smaller than the $\rho_{\text{Au}_2\text{O}_3}$ value of 11 g cm^{-3} [20] confirm that the H_2O content of HAuOL is in the 65–75% range. This result is consistent with the structure previously proposed for HAuOL [21].

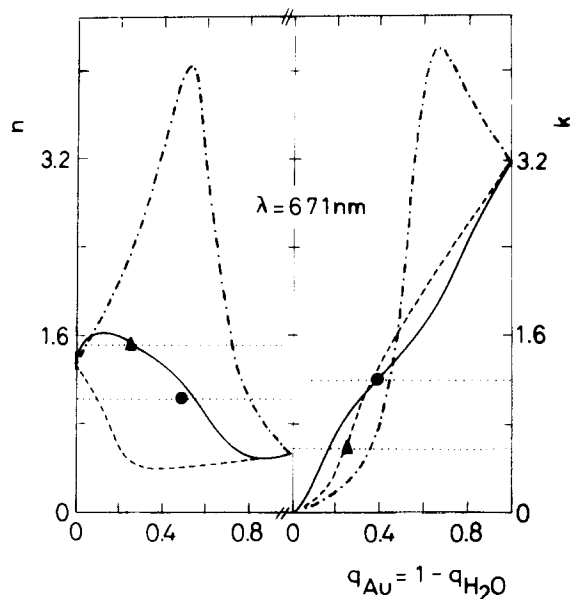


Fig. 5. Plots of n vs. q_{Au} resulting from EMT (---), MGT 1 for H_2O dispersed in H_2O (- - -) and MGT 2 (---) for H_2O dispersed in an Au matrix ($\lambda = 671 \text{ nm}$): ●, experimental values obtained at $v = 0.1 \text{ V s}^{-1}$; ▲, experimental values obtained at $v = 0.001 \text{ V s}^{-1}$.

4.2. The electroreduced gold overlayers

According to the optical parameter the EDAs can be described as a material made of bulk metal domains and solution-filled voids. For a structure of this type the effective-medium theories [13–19] allow us to explain the different properties of EDAs. Correlations for n and k from Fig. 5 were obtained from the Bruggeman effective medium theory (EMT) [18] and the Maxwell Garnett theory (MGT) [16], the latter considering both possibilities, namely Au clusters dispersed in H_2O (MGT1), and H_2O dispersed in the Au matrix (MGT2). For this purpose, different values of the volume fractions q_{Au} of Au and the volume fractions $q_{\text{H}_2\text{O}}$ of solution were considered. At each λ the value of q_{Au} was estimated from the intersection of the experimental n and k values (Fig. 5, dotted lines) at each sweep rate v , and the curves predicted by the different theories.

The d_{HAuOL} vs. d_{EDAuE} plots (Fig. 4) indicate the development of a rough Au structure for $d_{\text{HAuOL}} \geq 60 \text{ nm}$. Also, the roughness development through HAuOL electroreduction increases as v is decreased. The optical indices of EDAs obtained at $v = 0.1 \text{ V s}^{-1}$ and $v = 0.001 \text{ V s}^{-1}$ indicate that the water content changes from 65 to 75%. The EDAs obtained at 0.1 V s^{-1} becomes rougher although more dense than that prepared at 0.001 V s^{-1} . These results are consistent with the brush-like structure of EDAs recently derived from scanning tunnelling microscope imaging [21, 22].

5. Conclusions

(1) Considering HAuOL as an isotropic film, λ -dependent optical constants which are in the $1.760 \leq n \leq 1.930$ and $0 \leq k \leq 0.24$ ranges are obtained.

(2) The HAuOL can be described as a material made of the oxide and water with a H₂O-to-Au oxide volume ratio ranging between 65 and 75%.

(3) The optical indices of ED AuE depend on both λ and the HAuOL electroreduction rate. Higher Au contents and lower ED AuE thicknesses are obtained as v is changed from 0.1 to 0.001 V s⁻¹.

(4) The ED AuE consist of a brush-like structure in which the density of bristles increases as v is increased.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones Científicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC). MEV and JOZ are members of the research career of CIC.

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