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UNDERPOTENTIAL DEPOSITION OF A COPPER MONOLAYER ON A GOLD FILM SENSED BY INTEGRATED OPTICAL SURFACE PLASMON RESONANCE

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Abstract

An integrated optical surface plasmon resonance sensor combined with electrochemical control is used to monitor the underpotential deposition of a copper monolayer onto a gold film from 1 mM Cu²⁺ in 0.1 M perchloric acid.

Introduction

Surface plasmon resonance (SPR) sensing devices have generated considerable interest for biosensing applications [1]. The potential of integrated optical surface plasmon resonance (IOSPR) sensors has previously been demonstrated in immunosensing for simazine analysis [2]. The combination of electrochemical techniques with waveguide sensors through use of conducting overlayers allows electrochemical control and reversal of sensing reactions and may yield complementary information on the nature of electrochemical processes [3]. The underpotential electrochemical deposition (UPD) of monolayers of metal adsorbates on noble metal surfaces occurs below the Nernst potential required for electroplating when the adsorbate atoms are bonded to the noble metal atoms more strongly than to themselves [4]. UPD has been studied by surface techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) and low energy electron diffraction (LEED) [5,6]. Optical techniques such as ellipsometry [7] and electroreflectance [8] have also been employed in UPD studies but these techniques yield low sensitivity and are less suited to miniaturisation. In this paper we describe the combination of an IOSPR sensor with cyclic voltammetry to study the electrochemical underpotential deposition of a monolayer of copper on a gold electrode surface.

IOSPR Sensor

Fig 1 shows the configuration of the IOSPR sensor chip. Polished Pyrex glass wafers 50mm square were coated with a 200 nm thick aluminium film and channels 3µm wide were opened in this film, in the form of Y-junctions as shown in Figure 1, giving rise to a diffusion mask. The coated wafer was then immersed in molten KNO₃ at 389°C for 7.4 hours, to form potassium ion-exchanged waveguides, and the aluminium mask was removed. The surface of the glass was treated to promote gold adhesion by refluxing in a solution of (3-mercaptopropyl) trimethoxysilane (MPS) in water and propan-2-ol in the ratio 1:1:46 for 15 minutes. The wafer was patterned with gold pads 35 nm ± 5 nm thick and 3 mm long on one arm of each of the waveguide Y-junctions, as shown in Figure 1. The gold film serves both to guide the surface plasma wave (SPW) and as a working electrode in electrochemical studies. The second waveguide is used to provide a reference output allowing compensation for the effects of input power fluctuations, so that the device transmittivity is defined as:

$$T = P_{\text{Reference}}/P_{\text{Sensing}}$$

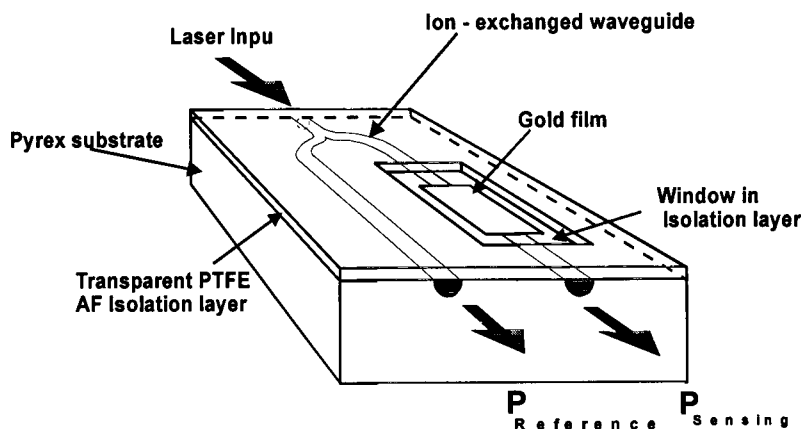


Fig (1) IOSPR Structure

The electrodes were connected by a track to pads at the edges of the substrate. Finally, a 700nm thick layer of Teflon AF 1600 ($n=1.31$) was deposited on the surface of the substrate and patterned to form windows exposing only the gold electrodes on each Y-junction device. This device design matches the velocity of the surface plasma wave at the gold surface and the waveguide mode, for visible wavelengths at analyte indices near water, resulting in resonant coupling observed as a sharp reduction in the transmittivity [2].

Underpotential Deposition Measurements

A silica cell was clamped to the waveguide surface and filled with 2 cm³ of 1.0×10^{-3} M Cu²⁺ in 0.1 M perchloric acid ($n = 1.334$). A three-electrode cyclic voltammetry circuit was established by introducing a platinum wire counter electrode and a saturated calomel (SCE) reference electrode into the cell, with the gold film pads acting as the working electrodes. Permanent contact was made to the gold electrodes outside the cell at the edge of the substrate. All three electrodes were connected to a conventional potentiostat, allowing the potential of the working electrode, E, with respect to the reference electrode, to be controlled and the current, I, through the working electrode to be measured. Optical measurements were performed using the apparatus shown in Figure 2. Light from a HeNe laser at 633nm was chopped and passed through a half-wave plate and polariser, to select the TM polarisation supported by the SPW, and through a variable attenuator to adjust input power. The light was end-fire coupled into the device under test and the waveguide outputs were focussed onto two silicon photodetectors. The transmittivity of the gold-coated waveguide, T, was recorded after removal of the effects of ambient light using lock-in amplifiers. The potential applied between the working electrode and the reference electrode was swept back and forth between 0.1 V and 1.6 V at a constant

rate of 5mV/s, starting by increasing from 0.5 V. This range includes the potentials at which underpotential deposition of a monolayer of Cu²⁺ ions (0.1 V – 0.4 V) and oxidation and reduction of the gold film (0.8 V – 1.5 V) occur. The potential, current and optical transmittivity were recorded simultaneously.

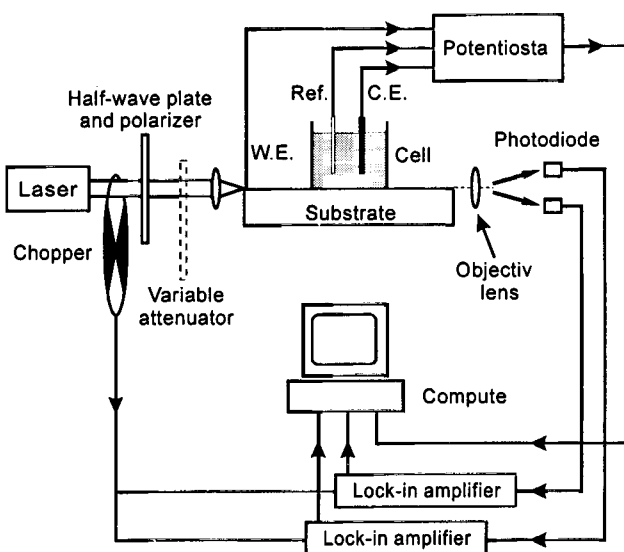


Fig (2) Experimental apparatus

rate of 5mV/s, starting by increasing from 0.5 V. This range includes the potentials at which underpotential deposition of a monolayer of Cu²⁺ ions (0.1 V – 0.4 V) and oxidation and reduction of the gold film (0.8 V – 1.5 V) occur. The potential, current and optical transmittivity were recorded simultaneously.

Results and Discussion

Fig 3 shows the optical transmission, T, and the electrochemical current, I, against the applied potential, E, after several cycles. The first part of the potential scan, from 0.5 V to 1.6 V, causes the anodic oxidation of the gold surface, as shown by the current peak at about 1.1V and the corresponding drop in transmission [9]. The cathodic scan shows the corresponding reduction peak in the current and increase in the optical transmission. The reduction is completed at about 0.7V where the optical transmittivity has returned to

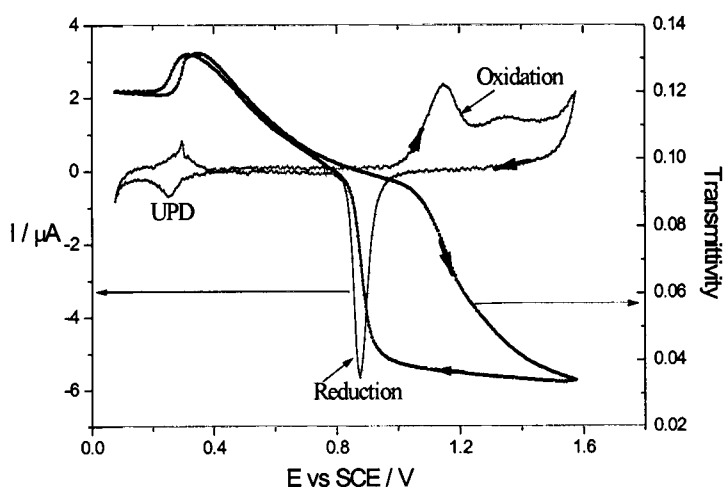


Fig (3) Optical and Electrochemical response to UPD of copper and the oxidation of a gold film.

its pre-oxidation value; this process cleans the gold surface before UPD. As the potential decreases from 0.7V to 0.4V, the transmittivity increases due to the alteration of the ionic distribution of the double layer at the metal – electrolyte interface. This ionic redistribution involves the chemisorption of anions i.e. HClO_4^- at the gold surface, and results in a small displacement current. At a potential of 0.24 V a peak in the current is observed, which is due to the deposition of a monolayer of Cu onto the gold film surface. The deposition of this monolayer of approximate thickness 0.3nm [10] gives rise to a 10 % drop in the optical transmittivity. Integration of the peak current over time during deposition gives a charge of $0.41\text{mC}/\text{cm}^2$, which is close the theoretical value of $0.44\text{mC}/\text{cm}^2$ for a monolayer of Cu^{2+} ions transferring two electrons per ion to an ideal Au (111) surface [6]. At lower potentials, the rate of change of transmittivity with potential is reduced, as adsorption of anions is occurring at the monolayer of Cu and no longer at the gold surface (*Why? Could this be an optical effect?*). The direction of the potential scan is reversed at 0.1 V and a peak in current is observed at 0.29V, corresponding to stripping of the Cu monolayer, and the transmittivity increases correspondingly. The hysteresis observed optically confirms that the adsorption and desorption of the copper monolayer occur at different potentials.

Figure 4 shows the current and optical transmission against potential, in the case where there are no copper ions in solution. In the absence of copper ions, there is no current peak corresponding to UPD near 0.24V and the optical transmission continues to increase with decreasing potential due to anionic adsorption. The significant current flowing at potentials between 0.0V and 0.1V is due to the evolution of hydrogen at the electrode (?). As both Figure 3 and 4 show the steady-state situation after several cycles, it is clear that the underpotential deposition process does not affect the oxidation and reduction of the gold film as the optical and electrochemical response

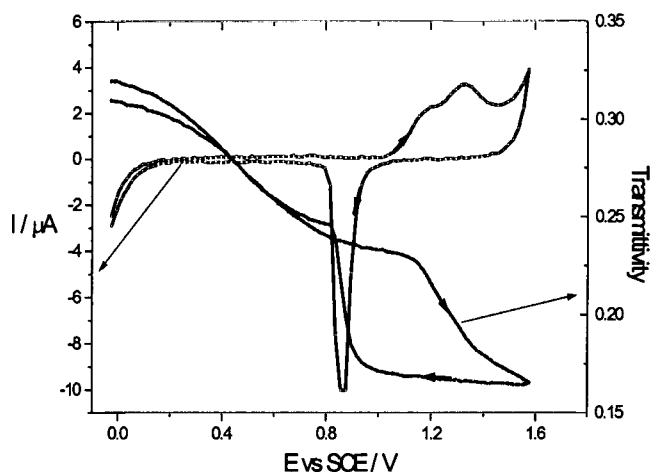


Fig (4) Optical and electrochemical response to oxidation of a gold film

are similar in the presence and absence of the adsorbate. (*I don't think we can get away with this. The reduction peak is much greater in Fig 4 and the oxidation peak is different. Further the transmittivity varies from 0.27 to 0.15 in Fig 4 and over the same potential range from 0.12 to 0.03 in Fig 3. Why?*)

The refractive index of the gold film at a wavelength of 633nm may be taken to be $n_{\text{Au}} = 0.20 - j3.45$ [2], and the thickness and refractive index of the oxidised layer have been estimated by ellipsometry to be $t_{\text{Ox}} = 0.54\text{nm}$ and $n_{\text{Ox}} = 3.3 - j1.3$, respectively, with an accuracy of about 10% on all values [11]. The refractive index of a 0.8nm thick film of copper on gold has been estimated to be $0.70 - j2.25$ at 546.1nm [7], in reasonable agreement with accepted values for thicker films [12]. The latter results may be interpolated to yield an estimate of $n_{\text{Cu}} = 0.27 - j3.40$ for the index of the copper film at 633nm, which is close to that of a gold film. Visscher and Cox [7] observed that the optical changes they observed ellipsometrically upon underpotential deposition of copper on gold were very small and that the optical constants of the copper film were close to those of the gold substrate. In this paper we have shown that the IOSPR sensor yields a large change, of approximately 10%, in transmittivity upon deposition of the copper monolayer, and that the sensitivity of the IOSPR device compares favourably with other optical analytical methods such as reflectance, which exhibited a maximum 1 % change in reflectance [8].

Conclusion

In this paper we have shown that the processes involved in the electrochemical oxidation and reduction of a gold surface and the underpotential deposition of Cu^{2+} on gold can be continuously monitored in-situ with high sensitivity using a compact integrated optical surface plasmon resonance sensor. The waveguide approach is ideally suited for multisensor integration and the results compare favourably with those obtained

using ellipsometry and reflectance measurements. Sensor arrays for interrogation of thin surface films are expected to find wide application in chemical sensing applications, and combined monitoring of electrochemical and optical parameters represents a powerful combination.

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