

A comparison between chemical and sputtering methods for preparing thin-film silver electrodes for in situ ATR-SEIRAS studies

José Manuel Delgado, José Manuel Orts, Antonio Rodes*,¹

Departamento de Química Física e Instituto Universitario de Electroquímica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

Received 13 November 2006; received in revised form 22 December 2006; accepted 25 December 2006

Available online 21 January 2007

Abstract

Stable silver thin films were prepared either by chemical deposition or by argon sputtering on germanium and silicon substrates, respectively, and used as electrodes for in situ infrared spectroscopy experiments with a Kretschmann internal reflection configuration. The spectra obtained for acetate anions adsorbed from neutral solutions showed a noticeable intensity enhancement (SEIRA effect). This enhanced absorption has been related to the surface structure of the films that have been characterized by ex situ STM and in situ electrochemical measurements (lead underpotential deposition, UPD). STM images of the chemically deposited silver films show mean grain sizes ranging from ca. 20 to 90 nm for deposition times between 2 and 20 min, and the absence of flat domains. On the other hand, STM images of the films deposited by argon sputtering show mean grain sizes around 30 nm for a film growth rate of 0.05 nm s^{-1} and 70 nm for a film growth rate of 0.005 nm s^{-1} . In this latter case, atomically flat domains up to 50 nm wide have been observed. This observation is consistent with a more defined voltammetric profile for lead UPD, that indicates a higher degree of surface order. Moreover, the roughness factor obtained from the charge density involved in lead UPD in the case of the sputtered silver film is lower than that measured for the chemically deposited silver film. All these structural data can be connected with the observations on the effect of deposition conditions of the silver film on the SEIRA effect for adsorbed acetate. Maximum enhancement is observed for chemically deposited films and sputtered films at high deposition rate for which the grain size is around 40–60 nm. The increase of the grain size for the sputtered silver films deposited at decreasing deposition rates can be related to the observed decrease in the SEIRA effect. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Silver electrodes; Thin films; Chemical deposition; Sputtering; ATR-SEIRAS

1. Introduction

Infrared spectroscopy is now a well-established technique for the in situ characterization of the metal/solution inter-phase under controlled potential conditions [1–6]. External and internal (Kretschmann's) reflection configurations have been employed for the study of electrode processes (adsorption/desorption and/or reaction) at single crystal and thin-film electrodes, respectively. The use of thin metal film electrodes with a Kretschmann configuration provides a selective enhancement of the infrared absorption for adsorbates (the so-called surface-enhanced infrared absorption or SEIRA effect [4,7]) that allows increased sensitivity, better conditions for the study of water–metal and water–adsorbate interactions as well as the

possibility of kinetic experiments in the submillisecond range [4,6,8].

Several methods have been described for the preparation of the thin metal films used in the experiments performed with the Kretschmann configuration. In this way, the use of vapour deposited gold [8–11] and silver thin films [12] has been widely described. The sputtering of gold [13], platinum [14] and platinum–ruthenium alloy [15] thin-film electrodes has also been reported. ATR-SEIRAS experiments have also been performed with thin films of platinum [16–19], gold [20,21], palladium [22] and copper [23] deposited chemically on silicon substrates. The study of electrodeposited silver on silicon substrates has been reported by Maroun et al. [24]. Thin gold films have been modified by electrolytic deposition of platinum [25], palladium [25,26], rhodium [25], ruthenium [25] and nickel [27]. A similar approach has been employed for palladium-modified platinum thin films [28]. Finally, gold nanoparticles self-assembled on silicon windows have also shown an important SEIRA effect [29].

* Corresponding author. Tel.: +34 965903400; fax: +34 965903537.

E-mail address: Antonio.Rodes@ua.es (A. Rodes).

¹ ISE member.

Spectroelectrochemical results obtained with silver films chemically deposited on germanium substrates were published by our group [30,31], using a film deposition method related to well-known procedures used to generate silver metal films and colloids for SERS [32–34] and SEIRAS [35] experiments. The spectra for sulphate [30] and acetate [31] anions adsorbed on these silver thin-film electrodes from either neutral or slightly acidic solutions showed a high intensity of the adsorbate bands that allowed the monitoring of the time-dependent behaviour of the adsorption/desorption processes in time-domain step-scan experiments [30].

The chemical deposition of silver with the method described in refs. [30,31] can be achieved on germanium but not on silicon substrates. This behaviour can be rationalized by assuming that the first step of the deposition process involves the oxidation of the germanium surface by silver cations. Germanium presents also spectroscopic advantages when compared to silicon, namely a lower cutoff for transmission below 800 cm^{-1} [1,36] and, subsequently, absorbance spectra in the range below 1200 cm^{-1} much less noisy than those obtained with silicon, which presents strong infrared absorption in this spectral region [1,36]. On the other hand, the drawback of germanium substrates is the limited stability of this material, which narrows the potential range that can be explored in the spectroelectrochemical experiments.

The aim of this work is to study the spectroscopic and voltametric behaviour of silver thin films obtained either by chemical deposition or by argon sputtering. The reversible adsorption of acetate is taken as a model surface process for studying the effect of metal deposition time (chemical deposition) and deposition rate (argon sputtering) on the intensity of the absorption bands for the adsorbed species. Results from parallel *ex situ* STM and *in situ* Pb UPD experiments will be analysed in order to relate the intensity of the SEIRA effect to the morphology of the silver film. Finally, the potential-dependent behaviour of acetate and water co-adsorption on the silver thin-film electrodes will be discussed.

2. Experimental

Chemically deposited silver films were prepared by immersing the Ge substrate in a solution formed by mixing $50\text{ }\mu\text{l}$ of a 0.02 M hydrazine solution with 10 ml of a 0.01 M silver nitrate solution containing ammonium hydroxide (0.46 M) and EDTA (0.14 M) [30,31,37] (all chemicals ‘pro analysi’ quality from Merck). After the desired deposition time, the sample is rinsed with plenty of ultrapure water and dried in argon (N50) stream. Silver thin-film electrodes were also deposited on silicon by argon sputtering in the vacuum chamber of a MED020 coating system (BAL-TEC AG) equipped with a turbomolecular pump. Before deposition, the pressure was reduced below $5 \times 10^{-5}\text{ mbar}$. Then, argon was admitted into the vacuum chamber to reach a pressure around $5 \times 10^{-2}\text{ mbar}$. The thin-film thickness and the deposition rate were controlled with a quartz crystal microbalance. The film growth rate was between ca. 0.05 and 0.005 nm s^{-1} and the thickness ranged from 10 to 50 nm .

In situ infrared spectroscopy and electrochemical experiments were carried out using silver films deposited on a $32\text{ mm} \times 32\text{ mm} \times 32\text{ mm}$ prism made of either Ge (EK SMA, Lithuania) or Si (Kristallhandel Kelpin, Germany) bevelled at 60° . The morphology of the silver films was studied by *ex situ* STM using non-oriented $15\text{ mm} \times 15\text{ mm} \times 1.5\text{ mm}$ Ge and Si plates (EK SMA, Lithuania). Before deposition, these samples were cleaned in an ultrasonic bath with isopropyl alcohol and finally were rinsed with ultrapure water and dried in argon stream. Constant-current STM experiments were carried out in air inside a Pico IC (Molecular Imaging) isolation chamber, with a Nanoscope III (Digital Instruments) system. STM tips were prepared by electrochemical etching (AC current) of a 0.25 mm diameter $\text{Pt}_{90}\text{Ir}_{10}$ wire in a fused mixture of NaOH and NaNO_3 .

The spectroelectrochemical cell has been described elsewhere [2,6]. Electric contact with the silver film that acts as the working electrode is achieved with a thin gold foil placed between the window and the Teflon[®] joint used to avoid leaking between the window and the glass body of the cell. The inner diameter of the joint, that limits the active area of the electrode, was 20 mm . A gold foil was used as counter electrode whereas a saturated mercurous sulphate electrode (SMSE) connected to the spectroelectrochemical cell through a Luggin tube was employed as reference electrode. Experiments were carried out in $x\text{ M}$ $\text{CH}_3\text{COONa} + 0.1\text{ M}$ NaF solutions ($0 \leq x \leq 10^{-2}$) prepared from Merck Suprapur quality reagents and ultrapure ($18.2\text{ M}\Omega\text{ cm}$) water (Elga-Vivendi). UPD experiments were carried out in a 0.1 M $\text{NaClO}_4 + 10\text{ mM}$ $\text{HClO}_4 + 5\text{ mM}$ $\text{Pb}(\text{ClO}_4)_2$ solution prepared also from Merck Suprapur quality reagents. In these experiments, a reversible hydrogen electrode (RHE) was used as the reference electrode. Prior to the spectroelectrochemical experiments, the working solutions were deaerated by bubbling Ar (N50, L’Air Liquide).

Infrared experiments were carried out with a Nicolet Magna 850 spectrometer equipped with a narrow-band nitrogen-cooled MCT detector. A variable-angle Veemax (Pike Technologies) reflectance accessory was used with the angle of incidence fixed at 60° . The spectra, which were collected with p-polarized light and a spectral resolution of 8 cm^{-1} , are represented as $-\log(R/R_0)$. In the *in situ* experiments, R and R_0 stand for the single beam reflectance spectra collected at the sample and reference potentials, respectively. One hundred interferograms were co-added to obtain each single beam spectrum.

3. Results and discussion

3.1. *Ex situ* STM characterization of the silver thin films

The silver thin films deposited chemically and by argon sputtering were characterized *ex situ* by STM. Fig. 1 shows STM images (a and b) obtained for the films deposited chemically on germanium substrates with deposition times of 2 and 20 min , respectively. Images labelled c and d in the same figure correspond to a 20-nm thick silver film deposited on silicon by argon sputtering with different growth film rates (0.05 and 0.005 nm s^{-1} , respectively). In all cases, the films are constituted by grains whose dimensions are in the nanometer scale.

Download English Version:

<https://daneshyari.com/en/article/194554>

Download Persian Version:

<https://daneshyari.com/article/194554>

[Daneshyari.com](https://daneshyari.com)