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A simple electrochemical strategy for the characterisation of defects in alumina-coated metal substrates

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ABSTRACT

A simple electrochemical procedure is proposed to obtain defect information in alumina-coated platinum substrates prepared by r.f. magnetron sputtering. The method makes use of cyclic voltammetry, chronoamperometry and scanning electrochemical microscopy (SECM), the alumina-coated samples being the working electrodes. Cyclic voltammograms, performed in solutions containing $Ru(NH_3)_6^{3+}$ and Cu^{2+} ions, indicated that the systems investigated, due to the presence of defects in alumina layers, behaved as arrays of recessed microelectrodes with no overlap of individual diffusion layers. These features, along with data obtained from steady-state voltammetry, nucleation of metallic copper in the defect sites and SECM images of copper-decorated defects, provided information on defect density and spatial distribution, as well as on average defect sizes.

1. Introduction

Alumina films deposited on metal substrates (M/Al_2O_3) have been extensively studied and used for a number of technological applications [1–7]. They can be prepared by different thin-film chemical and physical techniques [1–7]. Among them, r.f. magnetron sputtering (RFMS) is very attractive, as it allows the preparation of densely packed films with a good control of the material composition and thickness [7]. However, since no deposition technique is perfect, a feature in high demand for the evaluation of quality of the films is defects information, such as their densities, sizes and locations. This is relevant especially in those circumstances where M/Al_2O_3 systems come into contact with water solutions, as defects can act as channels through which the underlying metal substrate can be wet; this may lead to various and often undesired chemical phenomena [5,6].

Surface structural measurements can be done by various scanning probe techniques, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). However, these techniques are unable to reveal directly electrochemically active defects, i.e., those that are continuously open across the entire thickness of the insulating coating. Polymer and metal decorations have been employed for filling the defects present in various non-conducting thin films [8,9]. However, spatial distribution and sizes of the defects in the coatings have been obtained only after surface examination by SEM or AFM.

In this paper we propose a simple strategy, which makes use only of the electrochemical techniques cyclic voltammetry, chronoamperometry and scanning electrochemical microscopy (SECM) [10], to obtain defect information in alumina films grown on platinum substrates (Pt/Al_2O_3) by RFMS.

2. Experimental section

2.1. Chemicals

All chemicals employed were of reagent grade and purchased from Sigma–Aldrich. They were used as received. All aqueous solutions were prepared using Milli-Q water. Target materials for film preparation by sputtering were 2″ diameter Cr (99.9%), Pt (99.99%) and sintered Al_2O_3 (99.99%) disks. Sputtering was performed in pure Ar (99.9995%) at the pressure of 0.5 Pa.

2.2. Pt/Al_2O_3 samples preparation and characterisation

The Pt/Al_2O_3 samples were prepared in a custom-built r.f. magnetron sputtering system (13.56 MHz) [11]. Platinum and alumina layers were deposited in sequence onto silicon wafers. A good adhesion of the Pt layer to the substrates was ensured by a thin Cr layer sputtered at first onto the bare substrates. The thickness of Cr and Pt layers was kept constant at 8 (±1) nm and 380 (±20) nm, respectively, while the alumina layers were 250

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(±10) nm and 520 (±20) nm. X-ray diffraction measurements, performed by a PW 3710 X-ray diffractometer in Bragg–Brentano geometry using the Cu Kα radiation (40 kV, 30 mA, λ = 1.54056 Å), indicated that the alumina layers were amorphous. SEM micrographs of the surface and cross-section of the samples were obtained by a JEOL JMS 5600LV microscope. From the cross-sections the thickness of the various films were determined.

2.3. Electrochemical measurements and electrodes

A CH760B workstation (CH Instruments) and a home built SECM apparatus (which was described previously [12]) were employed for all electrochemical experiments. All measurements were carried out in a classical three-electrode cell arrangement, located in a Faraday cage. A platinum microdisk of 25 μm diameter was employed as both SECM tip and microelectrode for comparative voltammetric measurements. The platinum microdisk, sealed into a glass capillary and tapered to a conical shape, was polished and fully characterised as described elsewhere [12]. The reference electrode was an Ag/AgCl (saturated KCl) and the counter electrode was a Pt wire. The Pt/Al_2O_3 samples, used as working electrodes, were immobilised at the bottom of the cell by an O-ring (inner diameter ~4 mm), which defined the alumina surface in contact with the solution. Electrical connection of the samples was made by fixing a copper wire at one edge of the uncoated Pt film.

3. Results and discussion

The Pt/Al_2O_3 samples employed as working electrodes in a 1 mM $Ru(NH_3)_6^{3+}$ + 0.1 M KCl solution provided voltammetric responses, at low scan rates (5–100 mV s^{-1}), as that shown in Fig. 1A. It displays a well-defined sigmoidal wave with very low hysteresis, indicating that pure radial diffusion conditions, typical for microelectrodes [13], are established. This wave compares well with that recorded with a Pt microdisk 12.5 μm radius (inset in Fig. 1A and Table 1). As is evident from Table 1, both half wave potential ($E_{1/2}$) [10] and Tomeš parameter ($E_{1/4} - E_{3/4}$) [14] obtained with the various electrode systems are, within experimental error, in good agreement. The limiting currents recorded at the Pt/Al_2O_3 samples depend somewhat on the alumina layer thickness, and, importantly, they are rather small, in consideration of the rather large surface area exposed to the solution (i.e., ~0.13 cm^2). These results suggest that the Pt/Al_2O_3 systems investigated here behave as arrays of microelectrodes with no overlap of the individual diffusion layers [15]. Clearly, these microelectrodes correspond to small alumina-uncoated platinum regions, which are exposed to the solution through defects or pinholes formed during the alumina deposition. Further information on these aspects was obtained by performing voltammetric and chronoampeometric measurements in a solution containing 0.01 M $CuSO_4$ + 0.1 M Na_2SO_4 and 1 mM H_2SO_4 (Fig. 1B and C). In the voltammogram (Fig. 1B), a current loop, typical for nucleation and growth of a metallic phase onto the surface of a very small electrode [16–18], and the stripping peak of the deposited metal were evident. Also, potential step experiments, performed at high overpotential (i.e., −0.6 V vs. Ag/AgCl), provided current–time profiles (Fig. 1c) that were similar to those observed at single microelectrodes having dimensions of a few microns or less [16,18]. In the latter works, the shape of the transients recorded was explained as due to nucleation and growth of a single nucleus under hemispherical diffusion control. In view of the fact that the overall surface area of the Pt/Al_2O_3 samples investigated was rather large, the features of the transients recorded here were interpreted as due to a diffusion-controlled growth of instantaneously established multiple nuclei with no interaction of diffusion fields. Under these conditions,

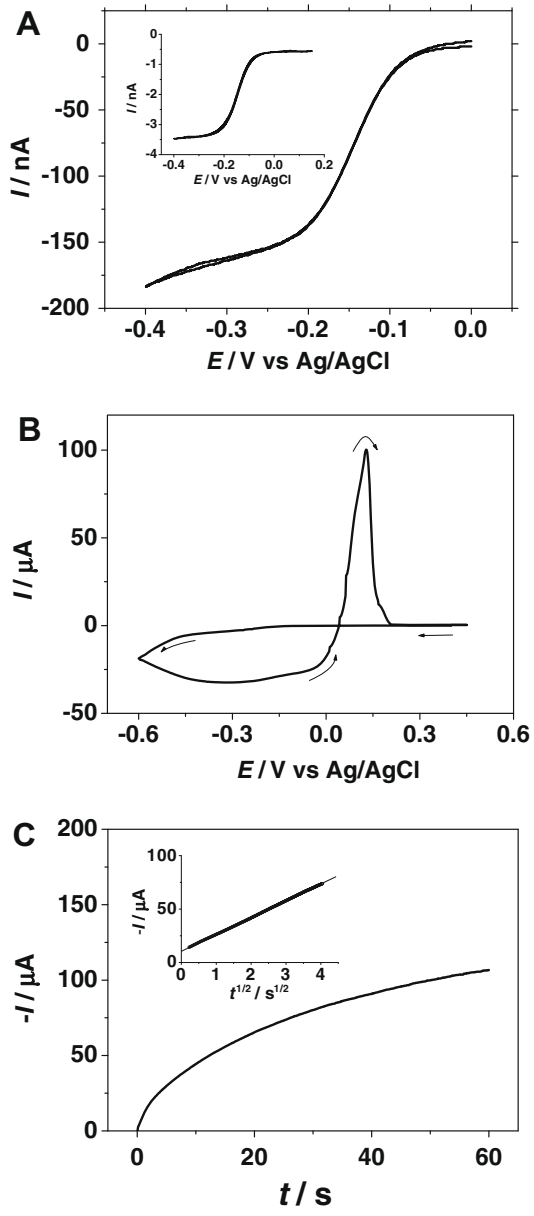

Fig. 1. (A) Cyclic voltammograms recorded at 5 mV s^{-1} in 1 mM $Ru(NH_3)_6^{3+}$ + 0.1 M KCl solution: (main) at a Pt/Al_2O_3 sample, alumina layer 250 nm; inset: at a Pt microdisk 12.5 μm radius. (B) Cyclic voltammogram recorded at 100 mV s^{-1} in 10 mM Cu^{2+} + 0.1 M Na_2SO_4 solution at a Pt/Al_2O_3 sample, alumina layer 250 nm. (C) Chronoampermetry performed at −0.6 V at a Pt/Al_2O_3 sample in 10 mM Cu^{2+} + 0.1 M Na_2SO_4 solution; inset: plot of I vs $t^{1/2}$ of the transient in Fig. 1c.

equation (1), relating current density ($I(t)$) and time (t), applies [19]:

$$I(t) = \frac{nF\pi N(2Dc^b)^{\frac{3}{2}}M^{\frac{1}{2}}t^{\frac{1}{2}}}{\rho^{\frac{1}{2}}} \quad (1)$$

where n is the number of electrons, F is the Faraday constant, D (5.10×10^{-6} cm^2 s^{-1} [20]), c^b, and M are the diffusion coefficient, bulk concentration and molar mass, respectively, of the metal ion species, ρ (8.92 g cm^{-3}) is bulk metal density, and N is the nuclei density. Equation (1) predicts a linear dependence of current density (or current) against the square root of time, and the plot shown in the inset of Fig. 1C actually confirms this. Similar results were obtained by performing measurements in different locations of the samples. From the slopes of the $I(t)$ vs. $t^{1/2}$ plots, the average N