Nucleation kinetics and contact angles of silver clusters electrodeposited on indium tin oxide surfaces

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A B S T R A C T

The nucleation rate and the number density of nucleation sites, as well as the contact angle of silver clusters growing under diffusion control, have been determined with single-step potentiostatic experiments, from the electrical current and optical transmittance during electrocrystallization of silver on optically transparent indium tin oxide electrodes. It was found that silver grows at overpotentials as crystallites with an aspect corresponding to an effective contact angle with the indium tin oxide surface of ca. 13°. Comparison with results obtained from ex situ atomic force microscopy analysis suggests that electrodeposited nuclei undergo conformational relaxation at open circuit, leading to significantly higher equilibrium contact angles. The results obtained indicate that while the contact angles measured during growth at overpotentials have no bearing on the values of nucleation rates determined from the electrical and optical responses to potential steps, they lead to lower number densities of sites, in relation to values corresponding to the growth of hemispherical centers. Implications of the results obtained for the clustering of silver atoms leading to the electrocrystallization process are also discussed.

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1. Introduction

The formation of a new phase is an intricate phenomenon where opposing forces intervene. On the one hand the supersaturation drives the phase transformation with release of energy as the newly born phase increases its volume, while on the other hand energy is required for accretion of the surface area of its interface with the mother phase. Thus critical nuclei are clusters of the new phase formed with a maximal work that are in unstable equilibrium with the supersaturated mother phase [1]. Since the area accreted per unit volume change depends on the equilibrium form of the nucleus on the electrode surface, the contact angle has strong effects on the nucleation as well as on the rates of growth, particularly when this occurs under diffusion control. This, however, has not been in general considered in formulations of the diffusion controlled, three-dimensional nucleation and growth processes [2–8].

The significance of the contact angle is put in evidence when trying to reconcile the classical and atomistic description of nucleation processes. In a previous study of the nucleation of silver on vitreous carbon, a phenomenological, Arrhenius-type equation was proposed [9] to explain the variation of the nucleation rates *A* with temperature, associating the reversible work for critical nucleus formation to the activation energy. Analysis of the experimental data in the framework of the classical theory of nucleation resulted that the possible temperature-dependence of the contact angle and the exchange current density affected both the pre-exponential factor and the activation energy, leading to inconsistencies of the results with prior studies. Thus a meaningful interpretation of the nucleation rates within the framework of the simple classical model or the phenomenological Arrhenius equation needs the independent determination of both contact angles and exchange current densities as a function of temperature.

We have also considered the potentiostatic current transient arising from nucleation and three-dimensional diffusion controlled growth of spherical caps contacting the electrode surface at varying contact angles θ [10]. A significant finding was that contact angles either lower or larger than 90° invariably lead number densities of active sites for nucleation N_0 that were lower to those arising from the growth of hemispheres, while the aspect ratio of the diffusion-controlled growing centers did not affect the measurement of the nucleation rates *A*, obtained from analysis of current transients. We also found that the contact angle cannot be resolved univocally from the current transients alone,

thus necessitating measurement of additional quantities. Here we present the results of a study aimed to determining the contact angle of clusters of the new phase on an optically transparent electrode, along with A and N_0, from simultaneous measurement of the electrical current, proportional to the rate of volume change, together with transmittance changes associated to the coverage of the electrode surface with growing crystallites. The results do not necessarily relate only to the initial nucleation processes occurring at the onset of the phase transformation process; as shown below, the aspect ratio of centers may also arise from secondary clustering processes of crystallites growing under diffusion control [11].

2. Experimental

The transient current flow and transmittance across indium–tin oxide (ITO) transparent electrodes were recorded simultaneously during silver deposition from 5×10^{-3} M AgNO$_3$ aqueous solution in 0.1 M KNO$_3$ used as supporting electrolyte, adjusted to pH = 2 with addition of HNO$_3$. The electrochemical cell was a double walled glass cylinder for temperature control, with optical flat quartz windows at both ends for optical measurements, with electrodes and inert gas connections fitted through ground glass joints across the cell's double wall. Working electrodes were glass plates covered with a 1 μm indium tin oxide (ITO) layer (PPG Industries), mounted with a Teflon® holder with Pt electrical contact [12], exposing 2.2 cm^2 of geometrical surface area to the solution. A Pt wire was used as counter electrode. The reference electrode was a silver wire in a separate compartment, connecting to the main cell through a Luggin capillary, thus allowing application of potentials directly as overpotentials with respect to the Ag/Ag$^+$ reaction. Both counter and reference electrodes were located out of the optical path, comprised by the quartz optical flats at both ends of the cell, the solution and the ITO-covered glass plate. All solutions were prepared from analytical grade reagents and Millipore-Q water (17.6 MΩ cm).

A BAS Epsilon potentiostat–galvanostat connected to a personal computer running Epsilon EC ver. 1.30.64 software for experimental control and data acquisition was used for electrochemical experiments. Transmittances were measured at 600 nm with a HP8453 diode array spectrometer. All experiments were carried out at a controlled temperature of 25 °C circulating constant-temperature water through the jacket of the glass cell, using a RM6 LAUDA Brinkmann thermostat, with accuracy of ±0.5 K. Prior to each experiment, the ITO working electrode was maintained at 0.3 V during 180 s, with no faradaic currents flowing at this potential, while the transmittance remained constant at a value very close to 1. Then 10 s pulses to various overpotentials were applied, during which the current flowing across the interface and the decline in transmittance as nuclei formed and grew on the transparent electrode surface were simultaneously measured. After the 10 s pulses, potentiostatic control was released continuing acquisition of transmittance data during several seconds with the system at open circuit.

Silver crystallites potentiostatically electrodeposited onto the ITO electrode surfaces were characterized ex-situ after 5 s growth with atomic force microscopy (AFM) applying the tapping method, with a Digital SPM Multimode, Nanoscope IIIA microscope. Silicon nitride cantilevers of 193 mm length, 0.6 mm thickness, and 36 mm width from Digital Instruments Inc. were used for imaging the surfaces.

3. Results

Fig. 1 shows current and transmittance transients obtained during silver electrodeposition onto ITO transparent electrode from 5 mM Ag$^+$ solution at 25 °C resulting from pulses to several overpotentials. No transmittance changes were observed during or after similar potential pulses in the absence of Ag$^+$ in solution. The diffusion coefficient of Ag$^+$ was determined from linear i vs. $t^{-1/2}$ Cottrell plots of the potentiostatic current decay at long times. As described below, analysis of the current transients with the standard model (SM) [13] allows in each case determining the nucleation rate A, while concurrent analysis of transmittance
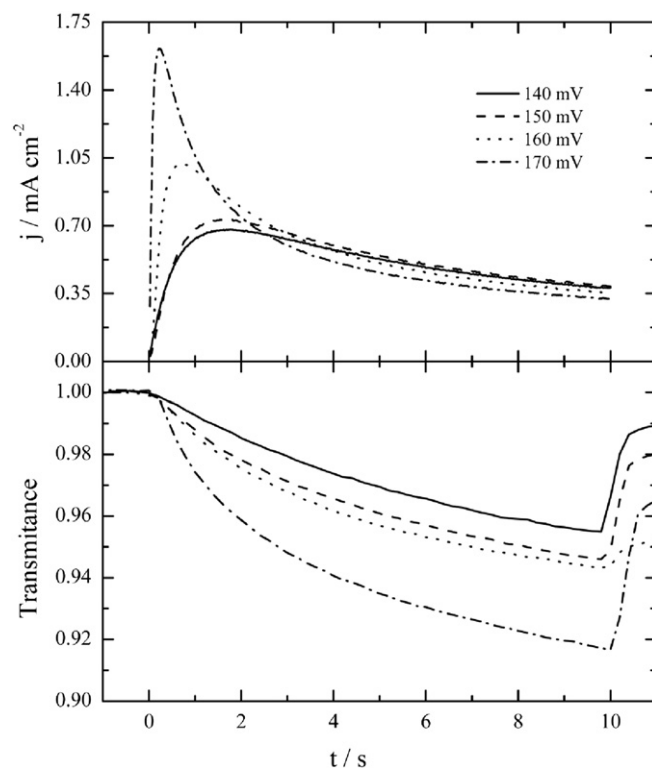

Fig. 1. Current (above) and transmittance (below) transients obtained during silver electrodeposition from 5 mM Ag$^+$ solution at the indicated overpotentials: 140 (—),150 (– –), 160 (· · ·) and 170 (– · –) mV.

data allows also resolving the contact angle θ and the number density of active sites for nucleation N_0, which appear entangled in the chronoamperometric response. In this work, we found the coordinates of current maxima such as those shown in Fig. 1(a) from polynomial fitting of the currents around the maximum, obtaining t_m from the root of its time-derivative and i_m from evaluation of the polynomial at t_m. The results obtained from transients recorded at the various overpotentials at room temperature analyzed with the SM formulae [13] are given in Table 1.

Although some workers report variation of D with the overpotential [14,15], the diffusion coefficient is a transport property in solution and should remain constant at a single temperature; thus we have considered the average value of $1.71 \times 10^{-5} \pm 0.27$ cm^2 s^{-1} as the meaningful experimental value. However, for estimation of A, θ and N_0, the individual values obtained from the Cottrell analysis in each case were used, as no solution was found for A and N_0 with the mean D value at the higher overpotentials, possibly due to distortion of the current transients due to the ohmic drop caused by the resistance of the ITO films used as working electrodes [16,17]. The effects of the resistance became more evident with the larger currents occurring at higher overpotentials.

The transmittance behavior after releasing potential control shown in Fig. 1(b) is noteworthy. From the start of the potentiostatic pulse, the transmittance diminishes continuously as nuclei form at the pace imposed by nucleation kinetics and grow under diffusion control. After

Table 1
Coordinates of current maxima (t_m, i_m), diffusion coefficients and kinetic parameters obtained using the SM formula [13] from current transients recorded during silver electrodeposition from 5 mM Ag$^+$ solution at the indicated overpotentials.

η/mV	t_m/s	i_m/10^{-3} A cm^{-2}	D/10^{-5} cm^2 s^{-1}	A/s^{-1}	N_0/10^6 cm^{-2}
140	1.717	0.68	1.909	7.75	0.40
150	1.647	0.73	2.028	5.31	0.44
160	0.698	1.02	1.701	12.98	1.21
170	0.222	1.64	1.403	46.63	4.47