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Cathodic deposition of silver on silver bromide at microelectrodes

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Abstract

The cathodic deposition of silver metal on single crystalline silver bromide leads to deposits with different morphologies depending on the cathode geometry and the current density. The deposition at an extended planar electrode results in the growth of silver whiskers. The deposition at a point (micro-)electrode results in dendritic deposits on the surface of the solid electrolyte. The morphological development of the deposits is studied with microelectrodes of different diameters. A characteristic change from dendritic to whisker growth at microelectrodes upon time is always found. As the reason for the change of the growth mode from dendritic to whisker-type, the changing electric field distribution around a growing surface deposit is discussed.

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Keywords: Dendrite; Whisker; Microelectrode; Morphological instability; Electrocrystallization

1. Introduction

Cathodic metal deposition (electrocrystallization) is a fundamental process at electrodes in liquid electrolytes but is still insufficiently investigated in the case of solid electrolytes. Different morphologies of deposits are described in the literature, varying from dendrites on the electrolyte surface [1,2], precipitation in the bulk of the electrolyte crystal [1,3,4] to the formation of single crystalline whiskers [5–7].

Cathodic metal deposition by whisker growth on solid electrolytes has scarcely been investigated. Ohachi and Taniguchi [5] showed that the supersaturation of nonstochiometric silver chalcogenides with silver leads to the spontaneous growth of whiskers on free surfaces of the chalcogenide crystal. Corish and O'Briain [6] where the first to study whisker growth on silver sulfide more quantitatively by relating the growth rate with the silver supersaturation, i. e. the chemical overpotential. A first report on the growth of silver whiskers on silver bromide and the dependence of the number of whiskers per area, their length and diameter on the experimental parameters current (I) and time (t) has been presented by Rohnke et al. [7]. Only few papers deal with the reduction kinetics and thermodynamics at electrodes on solid silver ion conducting electrolytes [8,9]. Yet quantitative and mechanistic information on the growth is still scarce, and compared to the present understanding of electrocrystallization in liquid electrolytes, the level of understanding in the solid state is poor.

Silver bromide is a suitable substrate for cathodic deposition, as it exhibits a high silver ion conductivity (Frenkel disorder) and a negligible electronic conductivity at moderate temperatures around $\theta = 300$ °C. It is available as single crystals and is also stable under ambient conditions. Growth experiments can be performed in a simple cell of the type Ag(anode)|AgBr|Microelectrode(cathode). At the anode the silver metal is oxidized and dissolved, and the silver ions transport the electric charge across the cell. At the cathode, which in our case is usually silver metal too, silver ions from the solid electrolyte are reduced and form the cathodic metal deposit.

2. Experimental setup

2.1. Materials and preparation

Silver bromide single crystals were purchased from Korth Kristall GmbH, cut into small cubes (typically $6 \times 6 \times 3$ mm^3), polished with a fine grained emery paper (particle size 15 μm)

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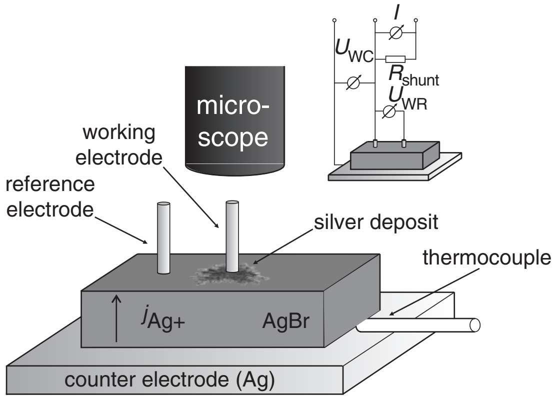

Fig. 1. Experimental setup (schematically) for the electrochemical deposition of silver on silver bromide; (inset) circuit diagram.

and subsequently etched with a $Na_2S_2O_3$ solution. Silver anodes were cut from silver foil with a thickness of 0.5 mm (Chempur, 99.9%) and prepared by grinding and polishing down to 0.25 μm with SiC suspension. The silver microelectrodes with diameters of 100 and 25 μm were prepared by cutting of silver wires with a pair of scissors.

2.2. Cell arrangement

Experiments were performed in a cell arrangement as depicted in Fig. 1. The transference cell Ag|AgBr|Ag was placed on top of a small heating stage mounted on a commercially available Probe Station (PM8 from SUSS MicroTec) used in the semiconductor industry. The cathode is constructed as a microelectrode on the upper side of the silver bromide single crystal. The microelectrode was held in place by a micromanipulator (PH150 from SUSS MicroTec). The reference electrode was also placed on the single crystal surface with a second micromanipulator. The temperature was measured with a thermocouple close to the sample. During silver deposition the temperature was kept constant at about $\theta = 300$ °C. Positioning of the microelectrodes and cathodic deposition of silver on the surface was observed in situ with an optical microscope with its optical axis being perpendicular to the single crystal surface (see Fig. 1). The silver deposits were characterized ex situ with a High Resolution Scanning Electron Microscope (HRSEM, Leo Gemini 982) and by energy-dispersive X-ray (EDX) analysis.

2.3. Experiments

The morphology of the silver deposits was primarily examined as a function of the applied current and the cathode size. The current was varied between 100 nA and 100 μA with a potentiostat (T-1000 from Jaissle) by using a specified ohmic shunt resistance, see inset in Fig. 1. The data acquisition was carried out with a multimeter and a PC (2700 multimeter with 7700 multiplexer from Keithley Instruments). The voltages between the working electrode and the reference electrode (U_{WR}) and between the counter electrode and the working electrode (U_{WC}) were recorded during each experiment as a function of time, together with the temperature.

3. Experimental results

The plasticity of the silver bromide solid electrolyte caused experimental problems in the quantitative reproducibility, but the general features are well reproducible. The cell arrangement under the microscope (in combination with the heating from the bottom side of the cell) always resulted in a large temperature difference between the bottom and the top side of the cell in the range of 20 to 30 K, depending on the thickness of the electrolyte. Thus, a thermovoltage of about $U_{WC} = 20$ mV was measured, which corresponds well with the Seebeck coefficient ε(AgBr, $T = 556$ K) = 882 μV/K of silver bromide as reported by Patrick and Lawson [10]. Under short-circuit conditions, this thermovoltage already led to a current across the cell, resulting in the deposition of silver metal (in the form of dendrites) at the cold upper side. Between the working electrode and the reference electrode, which are both placed on the upper side of the ion conductor, a thermovoltage in the

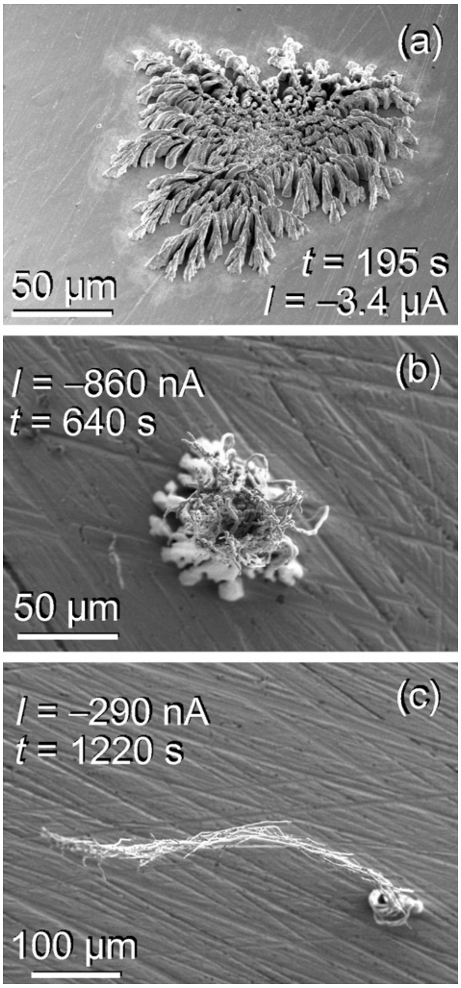

Fig. 2. HRSEM pictures: (a) dendrite: $I = -3.4$ μA, $\theta = 308$ °C, $t = 195$ s, Ø working electrode = 25 μm, (b) transition dendrite–whisker: $I = -860$ nA, $\theta = 305$ °C, $t = 640$ s, Ø working electrode = 25 μm, (c) whisker: $I = -290$ nA, $\theta = 305$ °C, $t = 1220$ s, Ø working electrode = 25 μm.

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