

In situ AFM observation of the electrochemical reduction of a single silver sulphide crystal and the recrystallization of the resulting silver crystal

Ulrich Hasse, Fritz Scholz *

Institut für Chemie and Biochemie, Universität Greifswald, Soldmannstrasse 23, D-17489 Greifswald, Germany

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Abstract

Single silver sulphide (Ag_2S) crystals immobilized on gold electrodes and possessing edge lengths of about 400 nm, were electrochemically reduced to silver. In situ recorded AFM images clearly show how the reaction starts at the three-phase junction gold– Ag_2S –solution. The initial reduction product is a hump of silver atoms that is rather soft and that is clearly affected by the tip motion. Within minutes, this amorphous hump of silver atoms recrystallizes and attains the well-developed shape of a silver single crystal.

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1. Introduction

Atomic force microscopy is an elegant technique to interrogate electrochemical solid-state reactions, and it was ex situ applied for the first time by Bond and Marken [1] to analyze such electrochemical solid-to-solid conversions [2]. The present work is a continuation of our attempts to study the electrochemical conversion of nanosized crystals by in situ atomic force microscopy. Previously, we have studied the reduction of PbO [3], the reduction of silver and mercury halides [4,5], and the electrochemical reductive dissolution of goethite [6]. The oxidation of silver nanocrystals immobilized on gold electrodes to silver halide crystals follows a nucleation-growth kinetics, in some cases even exhibiting a double nucleation [7]. In the present study, we can, for

the first time, report images that clearly show the recrystallization process of silver that was formed in the course of reduction of silver sulphide crystals.

2. Experimental

2.1. Equipment and chemicals

The experiments were performed with the AFM/STM of Digital Instruments (Hardware: NanoScope Version 1.0, Software: NanoScope E Version 4.23r3) with the external potentiostat Picostat™. Details are as described in [3]. The gold electrodes were purchased from Schröer GmbH, Lienen, Germany. A platinum sheet served as counter electrode and a $\text{Ag}|\text{AgCl}$ electrode (3 M KCl) was used as reference electrode ($E = 0.208$ V vs. SHE). The reference electrode was connected with the cell with the help of a polyethylene tube (inner diameter 0.5 mm) filled with 3 M KCl, Agar–Agar.

* Corresponding author. Tel.: +49 3834 86 4450; fax: +49 3834 86 4451.

E-mail address: fscholz@uni-greifswald.de (F. Scholz).

2.2. Preparation of silver sulphide nanocrystals and their immobilization on the electrode surface

The precipitation of Ag_2S was achieved as follows: at room temperature, H_2S was bubbled through a silver nitrate solution of 0.1 mol L^{-1} in such way that a small concentration of silver ions was left in the solution, i.e., the precipitation was still incomplete. The precipitate was washed with bidistilled water at least five times. Then the precipitate was suspended in bidistilled water (150 ml) and kept at 80°C for 4 weeks without stirring. This step is necessary to achieve a recrystallization by Ostwald ripening resulting in well-shaped crystals. Eventually, these crystals were carefully suspended and a

droplet ($75 \mu\text{l}$) of the suspension was allowed to slowly dry on a gold electrode at room temperature. This drying usually takes 3–4 h. It was observed that well-shaped silver sulphide crystals stick rather firmly to the surface whereas less regularly shaped crystals tend to sit loosely on the surface. The modified electrode was assembled in the in situ AFM cell as described previously [3].

2.3. The electrochemical reduction of immobilized silver sulphide crystals

The reduction was performed using a 0.1 mol L^{-1} KNO_3 solution in bidistilled water at a potential of -0.35 V vs. $\text{Ag}|\text{AgCl}$ over a time span of 50 min. The

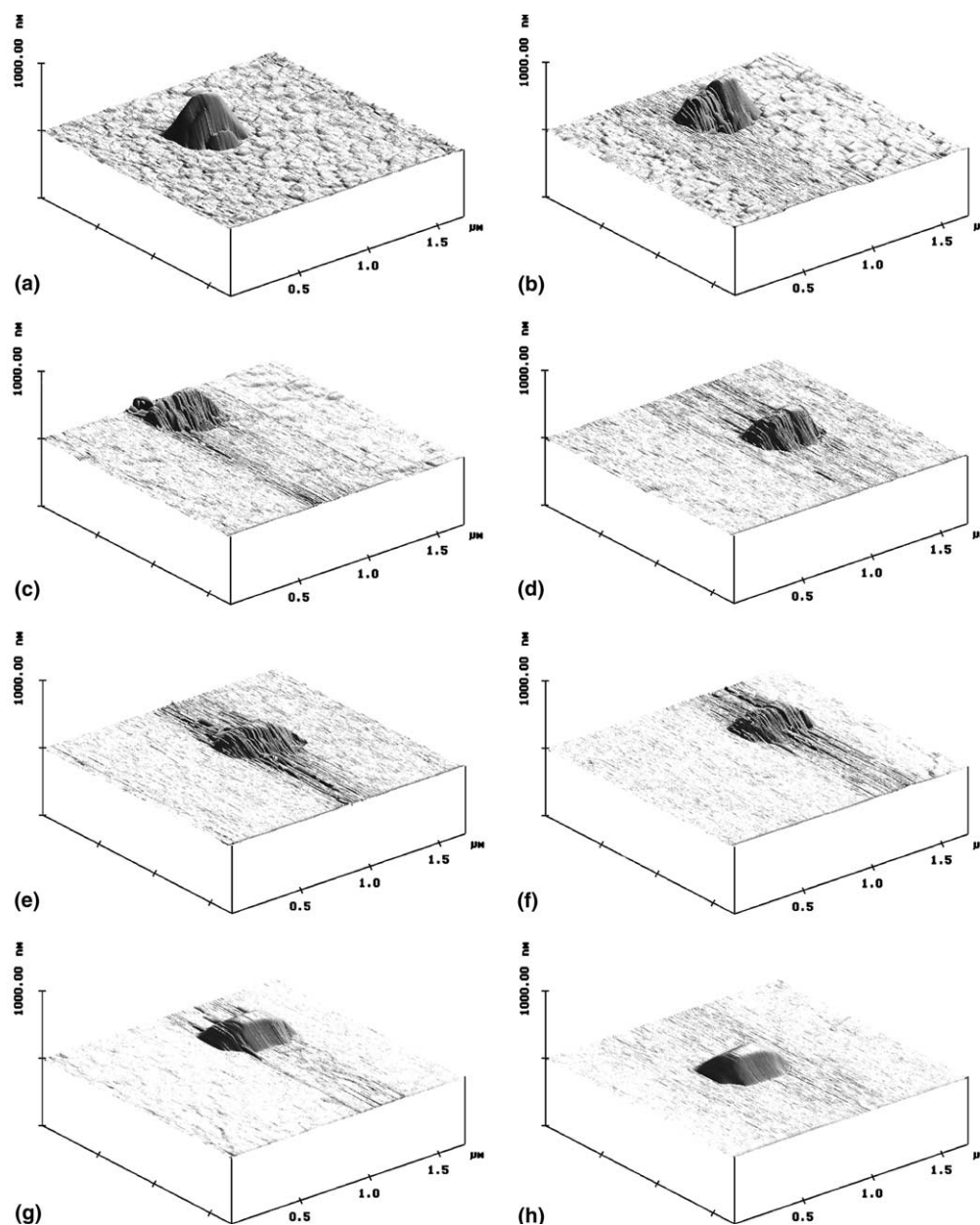


Fig. 1. AFM images of a Ag_2S crystal in situ recorded during the reduction at -0.35 V vs. $\text{Ag}|\text{AgCl}$. The reduction commenced after recording image 1(a). For details see text.

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