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ScienceDirect
Acta Materialia 92 (2015) 299–308
Acta MATERIALIA
www.elsevier.com/locate/actamat

Nanotwinned silver nanowires: Structure and mechanical properties

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Received 25 November 2014; revised 9 February 2015; accepted 24 February 2015
Available online 11 April 2015

Abstract—Ag nanowires have been manufactured with the ultrathin layer electrochemical deposition method. Transmission electron microscopy revealed a multiple twinned nanostructure that has not been reported in comparable structures using a non-template self-assembling preparation method. The $\{1\,1\,1\}$ twin planes are oriented parallel to the $\langle 1\,1\,2\rangle$ wire axis. The influence of the twin boundaries on the elastic and plastic properties of these wires has been investigated. Atomistic calculations revealed no influence of the twin boundaries on the Young's modulus of the wire for this geometry and along the $\langle 1\,1\,2\rangle$ direction. However, the twin boundaries exhibited a strong orientation-dependent influence on the plastic deformation when indented orthogonal ($\langle 1\,1\,1\rangle$ direction) or parallel ($\langle 1\,1\,0\rangle$ direction) to the twin boundaries, reflecting the interaction between the glide systems active in fcc metals and the stress direction. Heating experiments showed a high heat resistance for the twin boundaries till sublimation in an *in situ* TEM heating experiment. Sublimation followed the twin boundaries, indicating the lower binding energy of hcp stacking in comparison to fcc stacking.

Keywords: Nanowire; Nanotwinned; Elastic–plastic properties; *In situ* TEM heating and straining; DFT & EAM calculations

1. Introduction

In recent years nanowires (NW) [1–8] as well as nanotwinned materials [9–12] have attracted significant interest because of their superior mechanical properties. Face-centered cubic (fcc) NWs were shown to exhibit high flexibility [13] and tensile strength [8,14]. Beside their superior mechanical properties, NWs show excellent electrical properties which makes them interesting candidates e.g., for nanoantennas [15]. Further possible applications are in micro-electromechanical systems (MEMS) [16–19]. For bulk materials, it is well known that a decreased grain size results in an increased material's strength (Hall–Petch relation (HP)) [20–23]. Introducing nanotwins into the material can increase the ductility while maintaining a high strength [24,25]. On the other hand, little is known about tuning the microstructure of nanowires. Calculations on twinned Cu NWs showed that the strengthening effects seen in bulk material can be transferred onto NWs [26]. However, the strengthening effect highly depends on the shape of the wire [27]. Zhong et al. have reported the preparation of nanoscale twinned copper NWs and their increased strength [4].

Nanowires with different shapes and internal structures have been reported in the literature depending on the materials used and the applied template-free (self-

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http://dx.doi.org/10.1016/j.actamat.2015.02.041
1359-6462/

organized) fabrication methods: For example, Zinc exhibits a hexagonal growth behavior based on its hcp structure [2]. Copper, as a representative for the fcc lattice structure, has been produced as straight single-[28], and poly-[29] crystalline NWs, periodic structured NWs [30] and nanotwinned NWs [4]. Necklace-like periodicity [1] has also been reported for Ag NWs. In addition, Ag NWs with fivefold twins have been grown resulting in a pentagonal cross-section [31,32]. Twinned NWs with twin planes perpendicular to the wire's axis have been observed for Au and Cu NWs [4,33]. For Ag also twin boundaries along the wire axis have been observed for wires grown using a template fabrication process [34].

Here, we report on very uniform Ag NWs with a nanotwinned crystal structure grown by a non-template fabrication process. The preparation method and a first structural analysis was published recently [35]. In this work we present a detailed structural characterization of the nanotwinned NWs and discuss their elastic properties using experimental and theoretical approaches as well as investigate the orientation dependent plastic deformation of the wires.

2. Results

2.1. Morphology

The pure Ag NWs have been prepared by ultrathin layer electrochemical deposition (ULECD) as described in detail by Zhong et al. (Fig. 1) [4,35,36]. Using ULECD at a relatively high temperature of about −0.6 °C that creates an electrolyte layer of several micrometer (20–40 μm) thickness, we were able to grow self-organized Ag NWs with a diameter ranging from 100 nm to 1000 nm and a length of up to 150 μm (Fig. 2a). The loosely piled Ag NWs grow mainly straight over several micrometers in ⟨1 1 2⟩ direction. In some cases, branching at an angle of 60° is observed. The branch also keeps the ⟨1 1 2⟩ growth direction. The wire axis has been evaluated from an automated crystal orientation mapping transmission electron microscopy (ACOM-TEM) crystal orientation map (See Supporting Information Fig. A1) and the corresponding diffraction patterns. The thickness shrinks slightly along the wire axis, but shows nearly parallel sides with little roughness (Fig. 2b). However, wires with saw teeth like bumps (Fig. 2a, red box) exist in addition to the smooth wires. After switching off the voltage the driven growth comes to a halt. This leads to a slow equilibrium growth resulting in different shapes for the end of the wires. One of these end shapes is displayed in Fig. 2c.

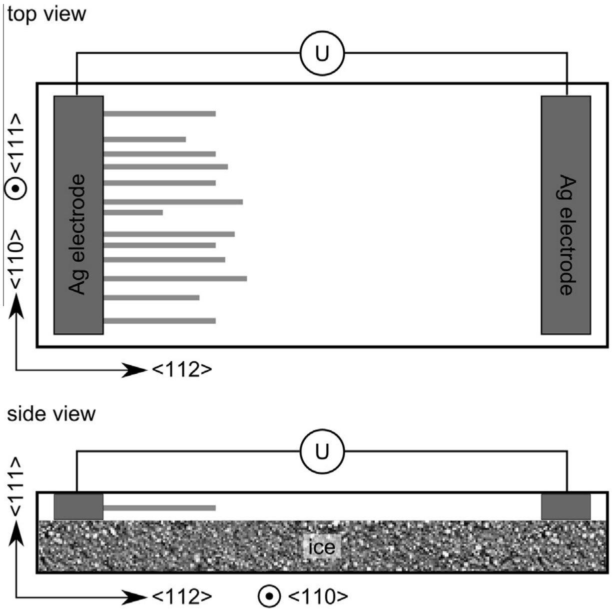

Fig. 1. Schematic illustration of the ULECD. The Ag electrodes sit on a glass substrate (paper plane in the top view image). The coordinate system belongs to the Ag wires and is idealized in respect to the ULECD setup.

A more detailed microstructural analysis of the wires was conducted using bright/dark-field and high-resolution transmission electron microscopy (BF/DF-TEM, HRTEM). It revealed multiple parallel twins, with the twin planes oriented along the wire axis. Fig. 3a and b show DF-TEM images of cross sections parallel and perpendicular to the wire axis. In both cases, the twins are clearly visible with the twin planes {1 1 1} parallel to the substrate. The selected area electron diffraction pattern (SAED) (insets of Fig. 3a–c) clearly shows the two twin orientations on top of each other. Furthermore, from HRTEM we measured the spacing between adjacent twin boundaries to be 2–40 nm (Fig. 3c). No disturbance of the twin boundaries over the length of the prepared cross sections was observed. The cross section of the wire displayed in Fig. 3a shows a flat side parallel to the substrate and a more round shape away from the substrate, leading to a pentagonal-like shape. Beside the pentagonal-like shape, we observed hexagonal-like and rectangular-like shaped wires with different aspect ratios, but always with the twin boundaries parallel to the substrate, indicating the strong influence of the substrate for the growth process. Apart from the flat {1 1 1} facet parallel to the substrate, the surfaces of the NWs do not exhibit other clearly defined facets. Even nearly circular cross sections have been observed. The cross sectional shape can show changes during growth along the length of the wire, e.g., from trapezoid to nearly circular cross sections (Fig. 4). No oxide layer was visible in the investigations, as e.g., Fig. 3a reveals that the twin boundaries reach the edge of the wire. The black layer around the wire is a carbon layer that was intentionally deposited for FIB preparation and TEM investigation.

2.2. Tensile experiments

For *in situ* TEM tensile experiments the combination of Picoindenter and Push-to-Pull (PTP) device (Hysitron) was used. Fig. 4 shows two tensile experiments performed on one wire that was cut into two pieces. The corresponding cross sections from either end of the wires are shown as inset. The strain stress curves reveal a Young's modulus of $E_1 = 66 \pm 8$ GPa and $E_2 = 71 \pm 8$ GPa and a yield strength of $\sigma_1 = 480$ MPa and $\sigma_2 = 700$ MPa. The error of Young's modulus is the systematic error, taking the diameter and the spring constant of the PTP device into account. For a more detailed description of the methodology and the error calculation, the reader is referred to the methodology section.

The strain stress curves of the tensile tests have been acquired in force-controlled mode as it was more stable than the displacement controlled mode. This straining