Surface Science 672–673 (2018) 19–22

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Native oxide formation on pentagonal copper nanowires: A TEM study

Rashad Hajimammadov, Melinda Mohl, Krisztian Kordas*

Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, P.O. Box 4500, 90570 Oulu, Finland

ARTICLE INFO

Keywords:
Copper nanowires
Penta-twinned crystal
Room temperature oxidation
Growth kinetics
Copper oxides

ABSTRACT

Hydrothermally synthesized copper nanowires were allowed to oxidize in air at room temperature and 30% constant humidity for the period of 22 days. The growth of native oxide layer was followed up by high-resolution transmission electron microscopy and diffraction to reveal and understand the kinetics of the oxidation process. Copper oxides appear in the form of differently oriented crystalline phases around the metallic core as a shell-like layer (Cu_2O) and as nanoscopic islands (CuO) on the top of that. Time dependent oxide thickness data suggests that oxidation follows the field-assisted growth model at the beginning of the process, as practically immediately an oxide layer of ~2.8 nm thickness develops on the surface. However, after this initial rapid growth, the local field attenuates and the classical parabolic diffusion limited growth plays the main role in the oxidation. Because of the single crystal facets on the side surface of penta-twinned Cu nanowires, the oxidation rate in the diffusion limited regime is lower than in polycrystalline films.

1. Introduction

Oxidation of copper altering its advantageous properties has kept researchers busy for several decades as this metal is being one of the most commonly used one by various industrial sectors. Owing to its outstanding electrical and thermal properties that brought forth numerous applications, this metal gained considerable interest. The unavoidable oxidation of its surface opened new horizons for research and development as formation of p-type oxides with narrow band gap enabled application in solar cells [1], catalysis [2,3] and electronics [4,5]. Starting from the beginning of the last century, vast amount of papers on copper and its oxides has been published, revealing the process of native oxide formation on thin films of copper. By the advancement of technology researchers attained control over synthesis procedure allowing to produce copper nanoparticles with well-defined shape and size, thus fostering oxidation studies of such structures under distinct ambient and temperatures.

Though surface characterization of copper thin films remains actual and reports about the facile synthesis of related oxides, e.g. by heating of copper foil, to this day appear in the literature; [6–8] due to intensive development of the field of electronics, optoelectronics, sensors and catalytic materials one-dimensional (1D) materials are in great demand. Therefore, taking into account the size and shape dependent changes in the electrical and optical properties of 1D copper nanostructures, here we disclose the behavioral nature of the native oxidation process on pentagonal copper nanowires. Using a 22-days follow up with transmission electron microscopy, we discuss the oxide growth mechanism considering the generic local electric field-assisted as well as diffusion-limited models and highlight the peculiarities in reference to already reported single and polycrystalline thin films as well as to bulk copper.

2. Materials and methods

For the synthesis of copper nanowires, a conventional hydrothermal method was used [9]. Copper chloride dihydrate $CuCl_2{\cdot}2H_2O$, D-glucose and hexadecylamine (Sigma Aldrich) were used as received without further purification. Copper chloride dihydrate (0.17 mg) was dissolved in deionized water (80 mL) then D-glucose (0.39 mg) and hexadecylamine (1.44 mg) were added slowly under vigorous stirring. After 5 hours of stirring, a light blue turbid dispersion formed and was placed into a Teflon® lined autoclave (Parr Instrument, Model 4525, 1000 mL) and heated to 393 K. After 24 hours of reaction and spontaneous cooling, the obtained brown dispersion was collected, centrifuged at 2500 rpm (990 RCF) for 15 min. The supernatant was discarded and the reddish solid was redispersed in DI water, n-hexane and ethanol to clean the product. The centrifuging, decantation and redispersion cycle was repeated three times in each solvent, and finally, the obtained copper nanowires were kept under ethanol until further analyses to prevent them from oxidation [10].

The formation of oxide layers on copper surface was studied by the means of transmission electron microscopy (TEM). A small aliquot of nanowire dispersion was sonicated in ultrasonic bath for 15 minutes, then drop casted on Ni grids and placed into the TEM column (Jeol FS 2200) after drying. Copper nanowires were analyzed within the time

---

* Corresponding author.
E-mail address: krisztian.kordas@oulu.fi (K. Kordas).

https://doi.org/10.1016/j.susc.2018.03.005
Received 15 December 2017; Received in revised form 22 February 2018; Accepted 6 March 2018

frame of 0–22 days by collecting statistical data about the oxide formation. The samples on Ni grids were kept in a box at 30% constant humidity after each session of imaging. Images were analyzed using free software EM Measure by Jeol. Since copper surface oxidizes immediately when exposed to ambient oxygen, we were expecting to see some oxide layers on the 0 day of oxidation, formed during the TEM sample preparation period. Each time several nanowires were randomly chosen and assessed by high-resolution imaging and selected area electron diffraction (SAED) in order to assess the evolution of the surface oxides. It is important to note, that because of the curved surface and inhomogeneity of oxide layers, the oxide/metal boundary and the layer thickness are not possible to determine in every location of the samples, thus we collected data only when the lattice fringes of metallic and oxide phases could be clearly identified. For the crystal structure analysis of penta-twinned nanowires a double tilt holder was used. The selected nanowire was tilted along Y axis about 3° and the wire was aligned horizontally, in order to prevent precession during following rotation along the X axis. The zone axis ⟨115⟩ was found by rotation and subsequently recorded SAED images. Due to the penta-twinned structure, the zone axis ⟨112⟩ appears when the NW is rotated with 18° along the X axis.

3. Results and discussion

Nanowires imaged right after sample preparation (0 day of oxidation) showed already a layer of oxide on their surface. While it is commonly known from numerous reports [10–12] that in the early stages of the oxidation process in atmospheric ambient first cuprous oxide forms (because of its lower Gibbs free energy) [13], high-resolution TEM assessment reveals the appearance of both cuprous and cupric oxides (Fig. 1, Fig. S1 and Fig. S3). In most of the TEM images, we observe lattice fringes with *d*-spacing of ~2.5 Å, which may be assigned to both the $Cu_2O(111)$ and CuO(11−1) planes in the close proximity of the Cu core. The observed locations of coexisting other fringes with *d*-spacing values of approximately 3.02 Å and 2.15 Å of Cu_2O (110) and (200) planes as well as *d*-spacing value of about 2.75 Å of CuO (110) indicate that it is the Cu_2O phase being in direct contact with the metal, and CuO is mostly on the top of Cu_2O. It is interesting to note, that the long range ordering and the orientation of oxide phases on Cu as well as on Cu_2O suggest an epitaxial growth the cuprous oxide on copper and cupric oxide on the top of that.

Islands observed in Fig. 1 are copper oxides (e.g. Cu_2O in Fig. 1b, CuO in Fig. 1d, Fig. 1k and Fig. S1 and the mixture of both oxide phases in Fig. 1j). Defect sites (grain boundaries, vacancy islands and the edges of pits) are assumed to be the nucleating sites for island formation [14]. We may assume that once a polycrystalline Cu_2O layer is present on the surface of Cu, some locations favor the nucleation of further oxidation towards CuO thus giving rise to the formation of islands on the top of the Cu_2O layer. In addition, further oxidation of Cu_2O to CuO may also take place with the help of surface adsorbed water via the formation and subsequent dehydration of metastable $Cu(OH)_2$ [17–21] as we showed earlier in an X-ray photoelectron spectroscopy study [10]. It is worth mentioning that carbon contamination exists on the surface of the nanowires in the forms of a very thin amorphous layer (Fig. 1a, e, h and l) and small island-like features (Fig. S2).

The overall thickness of the surface oxide does not seem to change significantly with time, in accordance with other works discussing the oxidation of thin films or bulk metal [11–17]. After the rapid formation of the initial oxide layer (within a few tens of minutes) of about 2.8 nm thickness, further oxide build up is observed to be extremely slow. Within the course of more than 3 weeks of follow up, the measured typical oxide thickness was less than 5 nm (3.5 nm on average). Such a nearly self-terminating growth may be explained by two mechanisms. On the one hand, a local electric field (caused by the contact potential difference between metal and adsorbed oxygen) that helps metal ions in drifting from the oxide-metal interface towards the surface is becoming too low to maintain a unidirectional drift of the metal ions (field-assisted model). On the other hand, the rapid formation of a reasonably

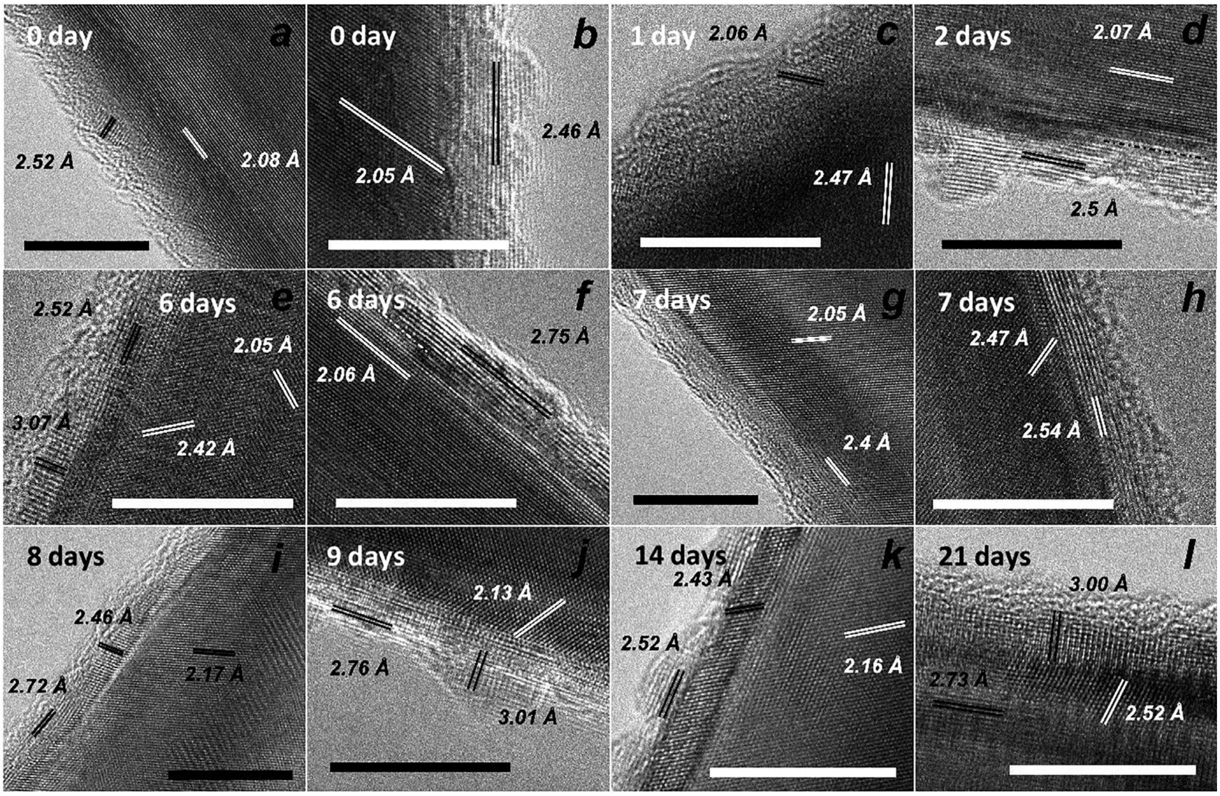

Fig. 1. TEM images of copper nanowires with native oxide layers at 0 day (a and b) and after 1 day (c), 2 days (d), 6 days (e and f), 7 days (g and h), 8 days (i), 9 days (j), 14 days (k) and 22 days (l) of oxidation. Dashed lines (d, f) show the boundary of metal and oxide phases. Scale bars denote 10 nm.