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DOI: 10.1017/S1431927606068024
Microsc Microanal 12(Supp 2), 2006
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In-situ TEM Synthesis of $WO_{2.9}$ Nanofibers: Characteristics and Growth Mechanism

J.F. Al-Sharab, R.K. Sadangi, V. Shukla, and B.H. Kear

Center for Nanomaterials Research, Rutgers University, Piscataway, NJ 08854, USA

Email: jafarhan@rci.rutgers.edu

Tungsten oxides have been the subject of extensive research over the past decade because of their growing technological importance. The materials have applications in gas and humidity sensors, electronic information displays, color memory devices, photoelectric sensors, superconductors, ferroelectrics and semi-conductors [1-3]. The wide variety of applications is due to the surprising number of crystalline forms displayed by WO_{3-X} phases, which include cubic, orthorhombic, tetragonal, monoclinic and several perovskite structures, depending on processing environment and oxygen partial pressure [4,5]. However, methods capable of synthesizing high quality nanostructured WO_{3-X} materials are still lacking [1]. Some progress has been made in preparing WO_3 nano-rods by heating a tungsten tip [2] and by thermal oxidation [1]. Here, we describe a new method for synthesizing $WO_{2.9}$ nano-fibers and nano-discs that display a high degree of crystalline perfection.

The new method emerged from routine TEM observations of a WO_{3-X} nanopowder, synthesized by a vapor condensation process [6]. It was observed that when the electron-beam intensity was increased sufficiently, a small portion of the nanopowder experienced vaporization, probably by sublimation, and that the vaporized species then condensed to form nano-fibers on the adjacent cooler regions of the carbon substrate. An example is shown in Figure 1, where vapor condensation has resulted in the formation of clusters of nano-fibers along ledges in the carbon substrate. Further analysis showed that the nano-fibers were highly perfect single crystals of tetragonal $WO_{2.9}$. The long axis or growth direction of the nano-fibers was [110] and their flat surfaces predominantly [001], i.e. parallel to the basal plane of the tetragonal structure.

A follow-up experiment to simulate the environment in the TEM resulted in the formation of a mixture of single crystal nano-fibers and nano-discs, Figure 2. In the new experiment, the powder was evaporated in a low-pressure chamber and the vaporized species collected on a water-cooled chill plate. The nano-discs formed on sections of the chill plate nearest to the evaporative source, whereas the nano-fibers formed some distance away from the evaporative source. In addition, some locations on the chill-plate has shown a bundles of elongated nano-fibers which we may refer to as “nano-rods”. A typical nano-disc had an elongated hexagonal morphology, with its long axis parallel to [110]. It appears, therefore, that the two morphologies are related, with the nano-fibers probably formed by preferred growth in a [110] direction from disc-shaped nuclei.

Our observations suggest that growth of the two types of nanostructure depends on the local deposition rate of WO_{3-X} species from the vapor state. A high deposition (or evaporation) rate results in prolific nucleation of nano-discs on the chill plate surface, with their growth severely restricted by the close proximity of neighboring discs. On the other hand, a low deposition rate enables fewer disc-shaped nuclei to grow into nano-fibers. In other words, the morphology is controlled by competition between nanoparticle nucleation and growth on the chilled substrate, which is controlled by the local partial pressure of the $WO_{2.9}$ species in the vapor state. Work is underway to provide additional support for the proposed growth mechanism.

https://doi.org/10.1017/S1431927606068024 Published online by Cambridge University Press

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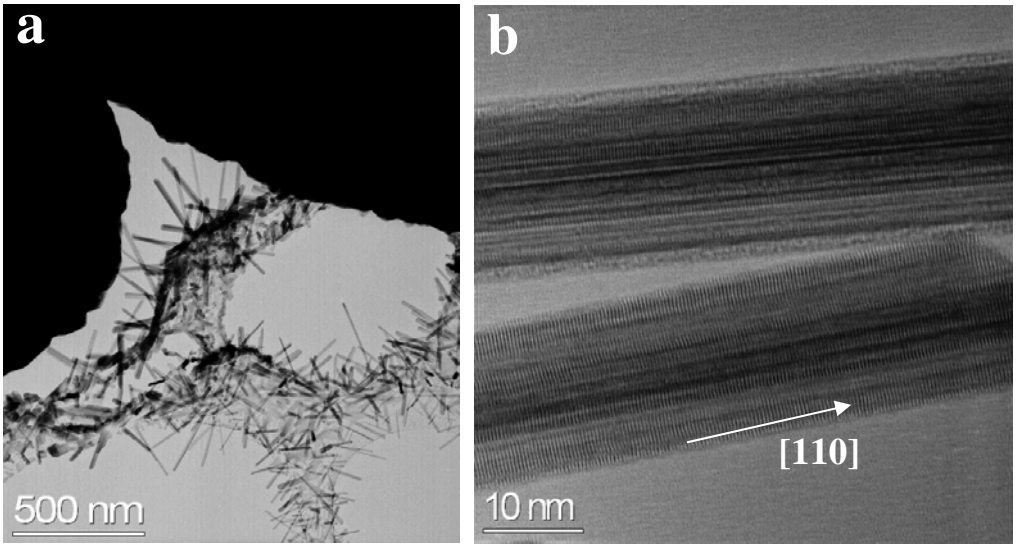

FIG. 1. (a) Bright field TEM and (b) High Resolution TEM images of $WO_{2.9}$ nano-fibers grown in TEM due to the reaction with the electron beam.

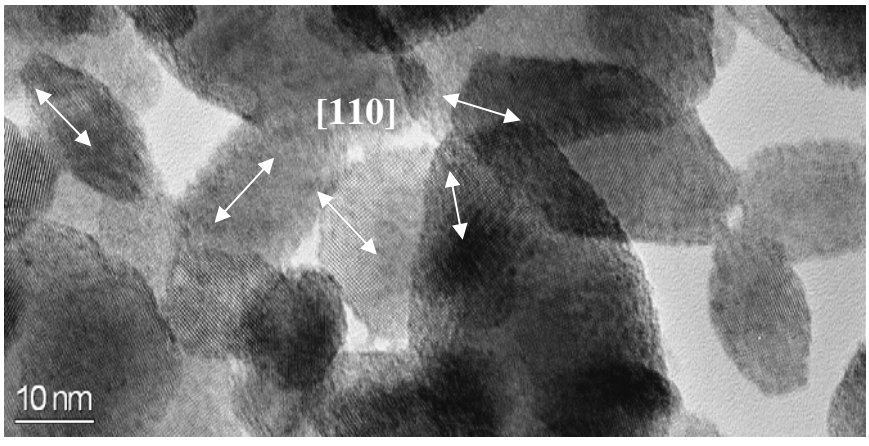

FIG. 2. High Resolution TEM image of the vaporized/sublimated $WO_{2.9}$ nano powder

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