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In situ Atomic-Scale Visualization of CuO Nanowire Growth

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CuO has received much interest owing to its myriad technologically important applications in solar energy conversion, photocatalysts, lithium ion batteries, and gas sensors. Nanostructured CuO is expected to possess improved or unique properties compared to its bulk form and therefore much effort, the majority using chemical synthesis techniques, has been devoted to the production of CuO nanostructures. Among them, thermal oxidation has recently been employed to generate CuO nanostructures due to its technical simplicity and the ease of applying the method to different metals [1-3]. However, the mechanism of thermal oxidation-driven oxide nanowire formation has widely been debated and is poorly understood [4]. Here we report dynamic, *in situ* TEM observations of the growth of CuO nanowires during the oxidation of Cu, which provide key insight into the atomic processes for the growth of CuO nanowires.

A high-purity Cu foil was loaded in a furnace TEM heating holder. After plasma cleaning, the sample holder was introduced in the environmental TEM (E-TEM), equipped with a post-specimen imaging corrector and operated at 300 kV. Oxygen gas was flowed into the sample area and maintained at a constant partial pressure of 0.5 Pa by a differential pumping system. The specimen was heated up to 400 °C and kept at this temperature for *in situ* observation of the oxidation-driven CuO nanowire growth.

At low magnification, we captured the growth process of a CuO nanowire, as shown in Fig. 1. The CuO nanowire stemmed from the surface oxide layer of CuO, as confirmed by electron diffraction, which is consistent with previous study [1-3]. The growth rate of the nanowires is measured as $\approx 0.33\ nm \cdot s^{-1}$ based on the *in situ* observation. To articulate the growth mechanism, we observed the nanowire growth at atomic resolution.

Fig. 2 is a time sequence of HRTEM images showing the growth of a CuO nanowire at its tip. The HRTEM images show that the nanowire has a bicrystal structure with the bicrystal boundary located at the center of the nanowire. The *in situ* HRTEM observation demonstrates clearly that new atomic layers nucleate at the tip of the nanowire starting from the atomic steps formed by the bicrystal boundary (indicated by the red arrows in Fig. 2) and then grow laterally toward the side of the nanowire.

Fig. 3 shows a sequence of *in situ* HRTEM images illustrating the nucleation and growth along the side surface near the tip of a nanowire. The exposed crystal plane on the side of the nanowire is identified as a $\{111\}$, which is perpendicular to the <011> growth direction. Due to the easy availability of oxygen from the gas flow, the incorporation of oxygen atoms into the nanowire is not a rate-limiting factor for nanowire growth. The nanowire growth rate is determined by Cu diffusion. Our observation of mono-crystal growth at the tip can shed light to explain the mechanism of single-crystal nanowire growth for which the previously reported growth mechanism based on grain boundary does not apply.

References:

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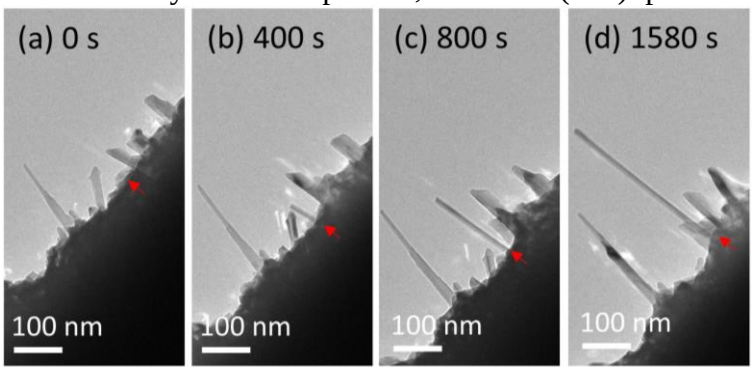

Figure 1. (a-d) *In situ* low magnication video frames showing the growth of a CuO nanowire from the initial stage. The red arrows indicate the site whence the nanowire initiated and grew.

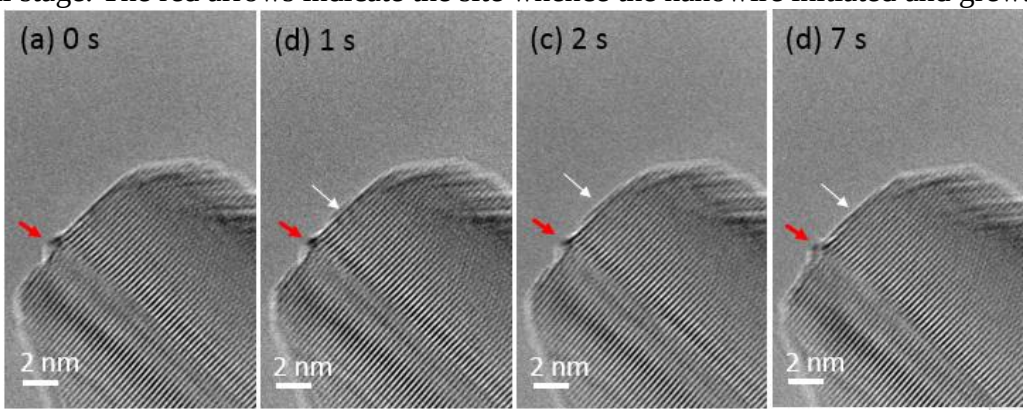

Figure 2. (a-d) *In situ* video frames showing the nucleation at the grain boundary and the growth of a new atomic layer. The red arrows indicate the nucleation site. The white arrows mark the accumulation of a new atomic layer: proving the nanowire growth on the tip area.

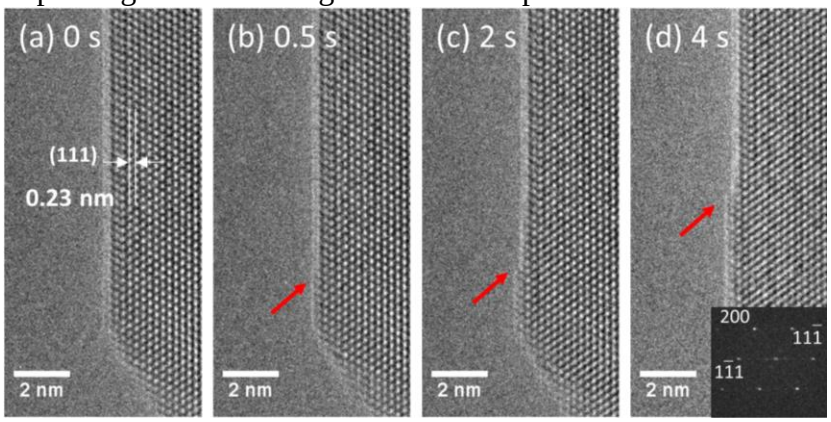

Figure 3. (a-d) *In situ* HRTEM video frames showing the growth of a single atom layer initiated from the corner of the front rim of a nanowire. The inset in (d) is the diffractogram of the HRTEM image, showing the CuO with the front plane of {111} propagation. The red arrows marked the propagation of the atomic layer growth.

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