

The Growth of Catalyst-free NiO Nanowires

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NiO is a stable p-type semiconductor with wide band gap (3.74 eV). Nanostructured NiO has drawn much attention as a low-cost material for several applications including electrochromic devices, electrode materials in battery systems, and electrochemical supercapacitors. It is also one of the most promising materials for resistive-switching memory devices. There have been reports of different methods to prepare NiO nanocrystals, including evaporation, sputtering, sol-gel techniques and electrochemical deposition using anodic alumina membranes (AAM). To the best of our knowledge, there have been no reports on thermal oxidation-driven NiO nanowire growth. Thermal oxidation is a proven, low-cost, easy-to-control approach for growing oxide nanowires such as CuO [1], α -Fe₂O₃ [2, 3] and ZnO [4]. Here we present the *in situ* study of NiO nanowire growth in an environmental transmission electron microscope (ETEM) and elucidate the atomic structure, morphology, and growth mechanism of NiO nanowires from the oxidation of Ni.

A pure Ni foil was loaded in a TEM furnace heating holder followed by plasma cleaning for the *in situ* environmental TEM experiments. Pure oxygen (99.9999 %) was introduced into the microscope column to oxidize the Ni foil. After achieving a stable O₂ partial pressure of 0.6 Pa, the specimen was heated to 500 °C and held at this temperature for oxidation. Meanwhile, the oxidation driven NiO nanowire formation was monitored, *in situ*, by various TEM techniques including imaging, diffraction, and electron energy-loss spectroscopy (EELS) using the aberration-corrected ETEM operated at 300 kV.

Our *in situ* TEM observations show that NiO nanowires start to grow after 30 min of O₂ flow at 500 °C. Electron diffraction analysis show that the nanowires grow on a NiO layer, instead of directly on the Ni metal substrate. Fig. 1a is a TEM image of a NiO nanowire and Fig. 1b is a nanodiffraction pattern obtained from the nanowire, which can be indexed well with the crystal structure of NiO oriented along $\langle 011 \rangle$ zone axis. Fig. 1c is an HRTEM image of the NiO nanowire, which shows clearly that the nanowire has a bicrystal structure with the $\langle 011 \rangle$ zone axis and $\{111\}$ grain boundary plane. The bicrystal structure was not observed in the nanodiffraction pattern since it was collected from a small region that included only one half of the bicrystal. The diffractograms (insets in Fig. 2c) of both sides of the bicrystal, show that the two crystals have a rotation angle of about 16.5°. The axial growth direction of the NiO nanowire is $\langle 111 \rangle$. The HRTEM image also shows that the nanowire has $\{111\}$ side facets. $\{111\}$ planes are normally the low surface-energy planes for a cubic structure such as NiO. This implies the one dimensional growth along the $\langle 111 \rangle$ direction is driven by the minimization of the surface energy of the nanowire. Fig. 1(d) shows the EELS obtained from the nanowire. Quantitative analysis of the O K and Ni L edges of the EELS gives an atomic ratio of Ni to O of 1:1.

Fig. 2(a-e) show a series of TEM images extracted from an *in situ* TEM video capturing the growth of a single NiO nanowire. The growth kinetics shown in Fig. 2f was obtained by measuring the length evolution of the nanowires from the *in situ* TEM video. The data were fit well with a linear model,

which yielded a growth rate of $\approx 0.7 \text{ nm} \cdot \text{min}^{-1}$.

In summary, we have demonstrated that thermal oxidation of Ni can be employed to form NiO nanowires. It is shown that the NiO nanowires have a bicrystal structure with the axial growth direction of $\langle 111 \rangle$. Our *in situ* TEM observations show a linear growth behavior of the NiO nanowires. Detailed *in situ* TEM analysis of the NiO nanowire growth will be presented to illustrate the atomic process of the nanowire formation and demonstrate the tunability of the nanowire growth by controlling the oxidation of Ni.

References:

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 [4] Yuan, L., et al., *Journal of Crystal Growth*, 2014. **390**: p. 101-108.

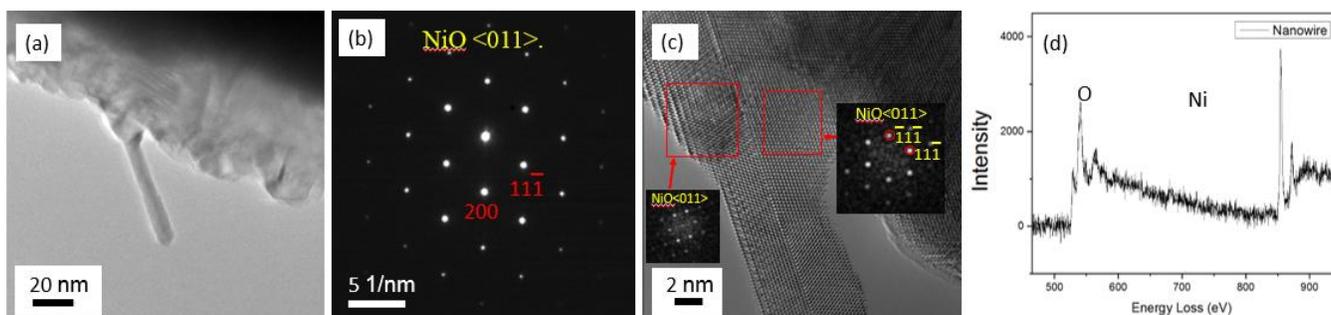


Figure 1. (a) A NiO nanowire grown during *in situ* oxidation in ETEM, (b) Nanodiffraction of the nanowire in (c), with the zone axis of NiO $\langle 011 \rangle$. (c) Atomic structural analysis of a NiO nanowire with the zone axis $\langle 011 \rangle$. The left and right inset are the diffractograms of the marked red squares. (d) EELS spectrum of the nanowire in (b), showing O K and Ni L edge, with the Ni:O ratio of 1:1.

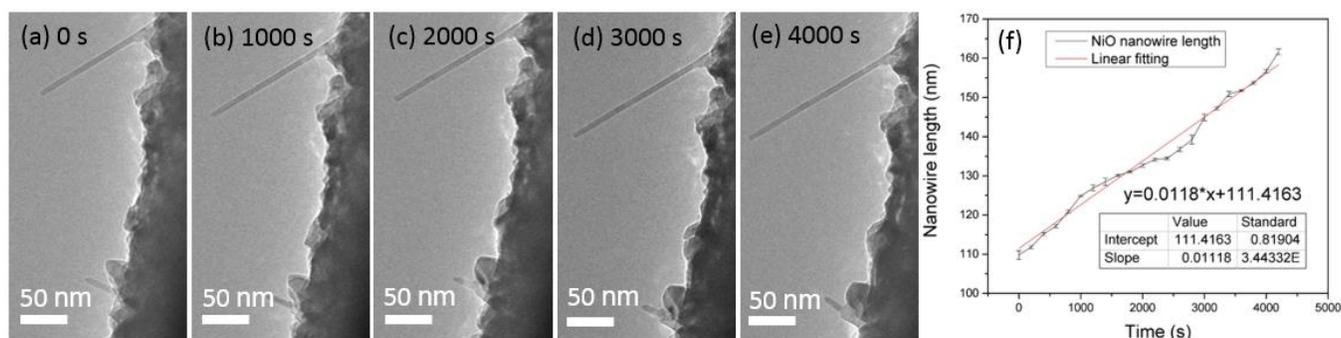


Figure 2. (a-e) TEM video frames showing a NiO nanowire growth in oxygen at 500 °C. The length of the nanowire increased upon continued oxidation. (f) The growth rate chart of the NiO nanowire calculated by measuring the lengths of the nanowire in a series of frames in the video. After applying linear fitting, the growth rate can be determined by the slope of the fitting function, $\approx 0.0118 \text{ nm s}^{-1}$ ($\approx 0.7 \text{ nm} \cdot \text{min}^{-1}$) at 500 °C and oxygen partial pressure of 0.6 Pa.