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Atomic-Scale Observation of Pressure-Dependent Reduction Dynamics of $W_{18}O_{49}$ Nanowires in an Environmental TEM

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Electronic Supplementary Information

Movies 1-5 and Figs. S1-S7

Movie 1: Real-time TEM video showing the electron beam induced wire to wire transformation (Electron beam density ~ $2x10^6$ Am^{-2}, temperature ~700 ^oC, oxygen pressure ~ 0.095 Pa).
Movie 2: Real-time TEM video showing the electron beam induced reduction of a single nanowire (Electron beam density ~10^7 Am^{-2}, temperature ~700 ^oC, oxygen pressure ~ 0.095 Pa).
Movie 3: Real-time HRTEM video showing the electron beam induced reduction of a single nanowire (Electron beam density ~$5x10^6$ Am^{-2}, temperature ~700 ^oC, oxygen pressure ~ 0.0004 Pa).
Movie 4: Real-time HRTEM video showing the interface migration during the electron beam induced wire to wire transformation (Electron beam density ~$5x10^6$ Am^{-2}, temperature ~700 ^oC, oxygen pressure ~ 0.0004 Pa).
Movie 5: Real-time TEM video showing the interface migration during the electron beam induced wire to wire transformation (Electron beam density ~$2x10^6$ Am^{-2}, temperature ~700 ^oC, oxygen pressure ~ 0.0004 Pa).

1 The effect of electron beam density on the electron beam induced reduction of nanowire

We found that in an appropriate electron density range (10^6~ $5x10^6$ Am^{-2}), all $W_{18}O_{49}$ nanowires will transform into single crystal WO_2 nanowire from bottom to top (see Fig. 1 in main text) induced by electron beam irradiation. When keeping the temperature (700 ^oC) and oxygen pressure (0.095 Pa) unchanged, the value of electron beam density was found to dramatically affect the reduction route. Fig. S1 shows the dependence of migration rate of the $W_{18}O_{49}$-WO_2 interface on the electron beam density. We can see that higher electron beam density results in faster interface migration. However, if we increase the electron beam density to more than 10^7 Am^{-2}, $W_{18}O_{49}$ nanowires will decomposes into several nanoparticles very quickly with crystal

nuclei nucleating immediately in the nanowire by the time we started electron beam radiation (Movie 5), as shown in Fig. S2. When decreasing the electron beam density to less than $5x10^5$ A m^{-2}, the transformation will proceed very slow or will not occur after a long time (10 min).

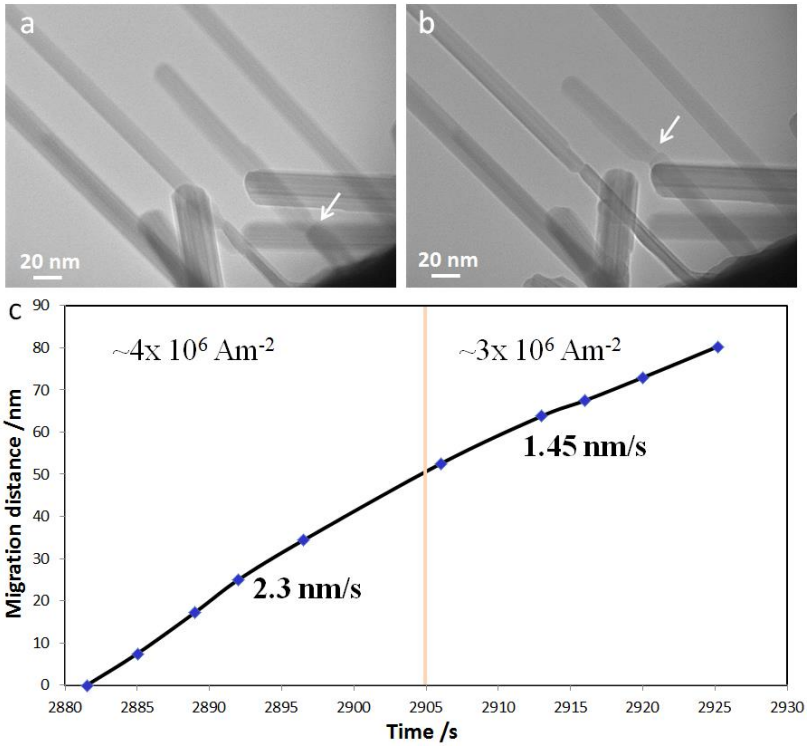

Fig. S1 Interface migration kinetics curve of the same $W_{18}O_{49}$ nanowire under electron beam irradiation with different current density at 700 ^oC in 0.095 Pa oxygen atmosphere: left $4x10^6$ Am^{-2} and right $3x10^6$ Am^{-2}.

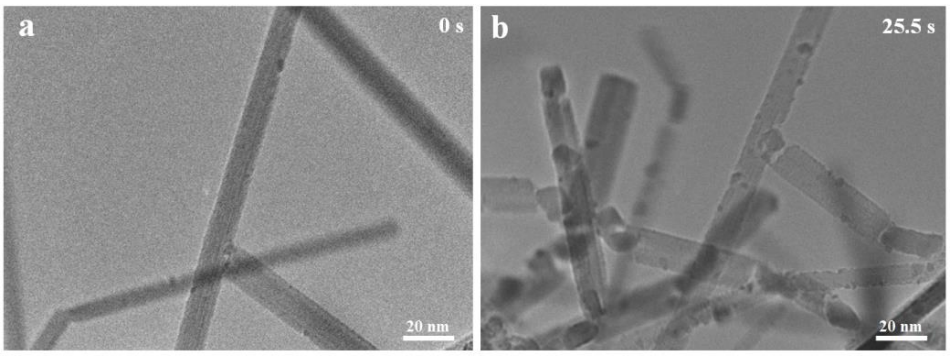

Fig. S2 Reduction of nanowire under electron beam irradiation with high current density (10^7 Am^{-2}) at 700 ^oC in 0.095 Pa oxygen atmosphere.

2 The effect of nanowire diameter and oxygen pressure on the electron beam induced reduction

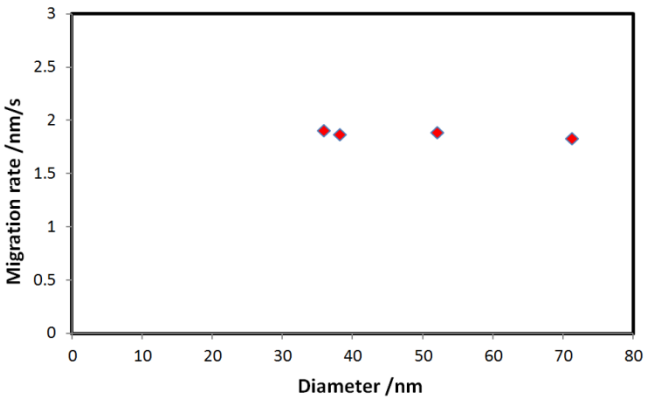

Fig. S3 Migration rates of the $W_{18}O_{49}$-WO_2 interface of nanowires with various diameters (35-71nm) under the same reduction conditions. Electron beam density~$2x10^6$ Am^{-2}, temperature~700 ^oC and oxygen pressure~0.095 Pa. The interface migration rates in the transformation of nanowires with various diamaters are close with each other.

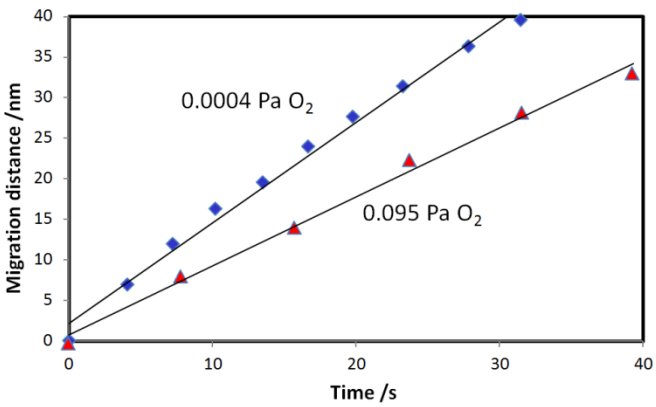

Fig. S4 Migration kinetics of the $W_{18}O_{49}$-WO_2 interface of nanowire under different oxygen pressure. Electron beam density~$2x10^6$ Am^{-2}, temperature~700 ^oC. The diameters of the nanowire in 0.0004 Pa O_2 and 0.095 Pa O_2 are 35 nm and 15 nm respectively.

3 The effect of temperature on the electron beam induced reduction of nanowire.

The effect of temperature on the electron beam induced reduction of $W_{18}O_{49}$ nanowires is investigated. Several temperature values including 700 ^oC, 400 ^oC, 200 ^oC and 150 ^oC are employed while the electron beam density and oxygen pressure of the TEM column are kept at $2x10^6$ A m^{-2} and 0.0004 Pa respectively. The results are shown in Fig. S4. At 400 ^oC, the electron beam irradiation induces several nuclei on the surface of the nanowire, which is different from the case at 700 ^oC that the nanowire transforms epitaxially into another single crystal nanowire, as shown in Fig. S5. We then further reduce the temperature and find that the transformation is similar to the case in 400 ^oC except with smaller rate.

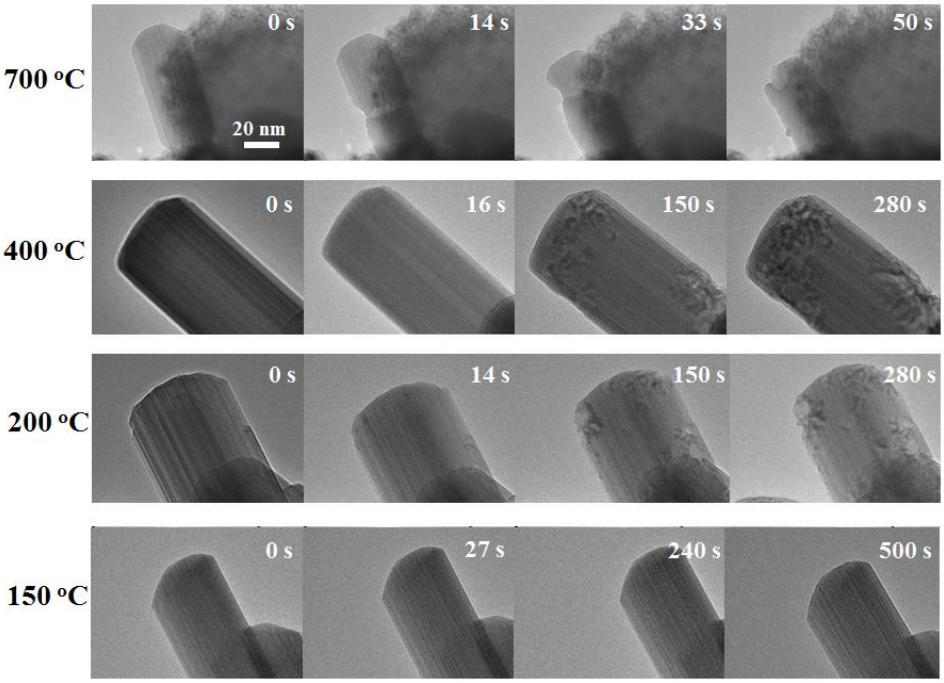

Fig. S5 Reduction of $W_{18}O_{49}$ nanowire under electron beam irradiation at temperature range of 150 ^{o}C to 700 ^{o}C. The electron beam density ($2x10^{6}$ Am^{-2}) and oxygen pressure (0.0004 Pa) are kept unchanged during the whole experiments.

The electron beam irradiation induced reduction of $W_{18}O_{49}$ at 400 ^{o}C is observed at the atomic scale. In Fig. S5a, several nuclei can be seen at the surface of the nanowire due to electron beam irradiation. With continual irradiation , these nuclei grow into nanoparticles, shown in Fig. S3c. Fig. S3d shows HRTEM of the nanoparticle, the lattice fringe 0.224 nm corresponds to the interplannar distance of (111) of α-W(JCPDS#894900). It can be concluded that the $W_{18}O_{49}$ nanowires is reduced to W directly by electron beam irradiation, which is in accordance with the case in chemical reduction process.

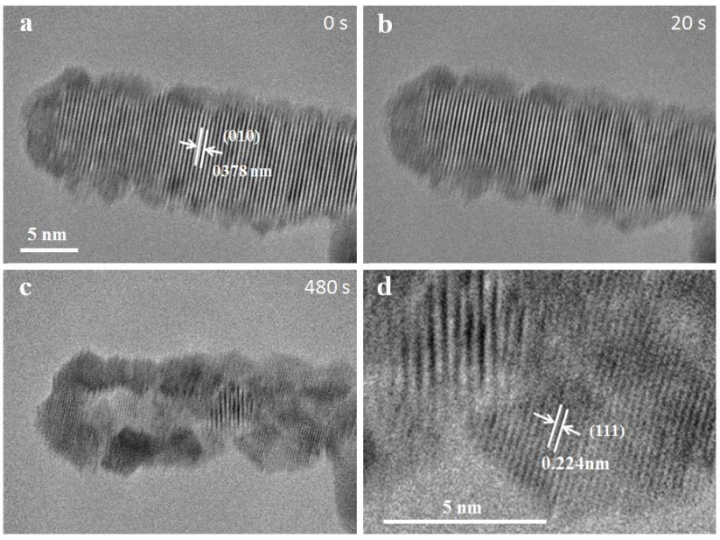

Fig. S6 (a-c) Series of TEM images showing the reduction of $W_{18}O_{49}$ nanowire under electron beam irradiation at 400 ^{o}C. The electron beam density ($2x10^{6}$ Am^{-2}) and oxygen pressure (0.0004 Pa) are kept unchanged during the whole experiments. (d) HRTEM images of the reduction product.

4 The nucleation of β-W nanoparticles in WO_2 during $W_{18}O_{49} \rightarrow WO_2$ reduction

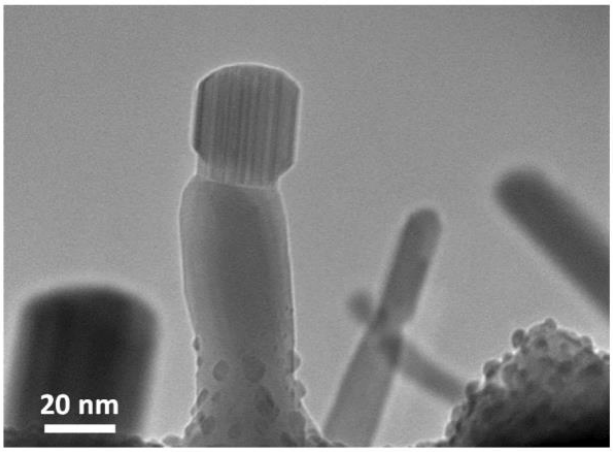

Fig. S7 TEM image captured during the reduction of $W_{18}O_{49}$ nanowire under electron beam irradiation at 700 ^{o}C. Electron beam density was $2x10^{6}$ Am^{-2} and oxygen pressure was 0.0004 Pa.