

Electron-Beam Manipulated Nanoscale Reaction

Huaping Sheng^{1,2}, Jianbo Wang^{2,3,*}, Jianguo Wen^{1,*}

¹ Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL, USA

² School of Physics and Technology, Center for Electron Microscopy, MOE Key Laboratory of Artificial Micro- and Nano-structures, and Institute for Advanced Studies, Wuhan University, Wuhan, China

³ Science and Technology on High Strength Structural Materials Laboratory, Central South University, Changsha, China

* Corresponding author: wang@whu.edu.cn; jwen@anl.gov

Employing electron beam for nanofabrication is highly desirable since it provides both the highest resolution and location flexibility. Sun *et al.* has demonstrated that reversible oxidation and reduction of Ag in a gas cell containing air could be controlled by changing the e-beam current density in TEM [1]. However, the gas cell contains high concentration of oxygen such that the redox reaction is extremely intense. In this work, taking advantage of low oxygen partial pressure in TEM, we show direct visualization of the redox of Ag at atomic resolution and manipulation of redox reaction at nanoscale.

A thin foil of Ag was ion milled to electron transparency for the TEM experiment. No noticeable oxidization is observed on the surface of thin area, after leaving the TEM specimen inside microscope overnight. As shown in Fig. 1, a nucleation of Ag₂O island is observed on the surface of Ag, similar to the observation by Zheludkevich *et al.* [1]. With a relatively weak e-beam ($\sim 10^5 e/\text{\AA}^2\text{s}$), Ag₂O island continues to grow, with crystallographic orientation relationship: $\langle 110 \rangle_{\text{Ag}} // \langle 110 \rangle_{\text{Ag}_2\text{O}}$ and $\{111\}_{\text{Ag}} // \{002\}_{\text{Ag}_2\text{O}}$. When increasing beam intensity to a dose rate of $\sim 10^6 e/\text{\AA}^2\text{s}$, Ag₂O begins to shrink, partially reduced to Ag (Fig. 1c). Reducing beam intensity below a dose rate of $\sim 10^5 e/\text{\AA}^2\text{s}$ triggers the growth of Ag₂O again as shown in Fig. 1d. The reversible redox of Ag is achieved by varying the e-beam dose rate and irradiation time.

It is highly desirable to directly control nanoscale reaction using electron beam due to its potential utility in the fabrication of nanoscale devices. By reducing electron beam size to few nanometers with suitable dose rate, we demonstrated fabrication of an 3x3 array of 3 nm Ag₂O nanodots in an Ag matrix. As shown in Fig. 2a, some of nanodots such as dots #2, #5, #6, #7, #9 are fully converted into Ag₂O. Enlarged #5 nanodots in Fig. 2b clearly shows the lattice difference between Ag₂O and the Ag matrix. Fast Fourier Transformation (FFT) pattern in Fig. 2c also supports the conclusion. However, some nanodots like dots #1 and #4 are not converted into Ag₂O yet and some of them like #3 and #8 are drilled into a hole. Using through focus imaging, we found out there exists a small amount of Ag₂O exists on surface. Due to the large thickness at #1 and #4, these two nanodots are partially fully converted into Ag₂O nanodots. As for nanodots #3 and #8, a small amount of Ag₂O at the edge of the drilled nanodots is observed, indicating that Ag₂O nanodots were formed and then drilled into a hole due to over-time irradiation. Therefore, a dynamic monitor of the reaction status and an automatic stopping beam system is needed for complete manipulation of nanoscale reaction. We plan to carry out high-speed imaging using a high-speed direct electron detector; real-time on-the-fly data processing with a capability for the phase formation; and immediate feedback to the microscope to make smart decisions including choosing beam location, diameter, intensity, dwelling time, etc. [3]

References:

[1] ML Zheludkevich et al., *Oxid. Met.* **61** (2004), p. 39.

[2] L Sun et al., *Langmuir* **27** (2011), p. 14201.

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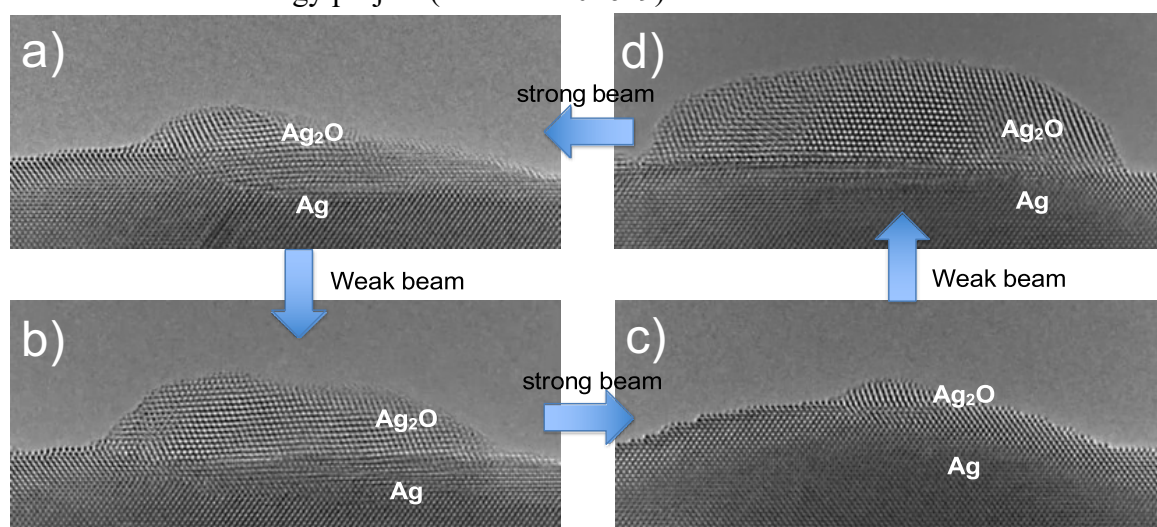


Figure 1. HREM images of redox of Ag by varying e-beam intensity. a) initial growth of Ag₂O island; b) further growth of Ag₂O under weak beam ($\sim 10^5 e/\text{\AA}^2\text{s}$); c) reduction of Ag₂O into Ag under strong beam ($\sim 10^6 e/\text{\AA}^2\text{s}$); d) regrowth of Ag under weak beam.

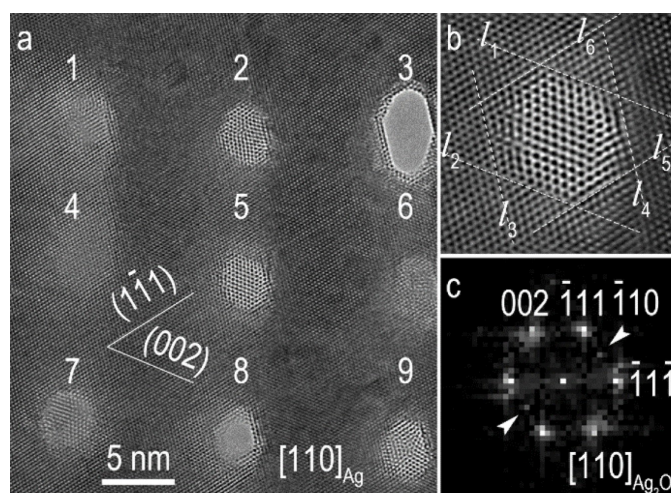


Figure 2. Manipulation e-beam to form Ag₂O nanodots in Ag matrix.