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Modulating the Redox Equilibrium of Silver Using Electron Beams

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Metallic silver has been shown to be inert to molecular oxygen but subject to oxidation very easily when exposed to atomic oxygen [1, 2]. Recently, Sun *et al.* has realized the reversible oxidation and reduction of Ag in an environment cell containing air by changing the electron beam (e-beam) current density in TEM [2]. However, the environmental cell prohibited direct observation of the redox dynamics at atomic scale. In this work, the redox of Ag was modulated in an "open-cell" way and visualized at atomic resolution in TEM.

An Ag specimen prepared from bulk Ag was loaded into a TEM. The reversible redox of Ag was achieved by varying the e-beam dose rate and irradiation time. Before introducing any e-beam irradiation, the specimen was held in the microscope for more than 12 hours. No oxides were observed on the specimen after the hold time, and the vacuum was maintained at $\approx 1.2\times10^{-5}$ Pa during the entire experiment.

After 4 hours' e-beam irradiation with a dose rate of ~0.1 $A\cdot cm^{-2}$, a new structure was observed. The structure was found to be Ag_2O, similar to the results from Zheludkevich *et al*. [1], with the prevalent orientation relationship $<110>_{Ag}$ // $<110>_{Ag_2O}$ and $\{111\}_{Ag}$ // $\{002\}_{Ag_2O}$. Fig.1 shows a typical configuration of the Ag-Ag_2O interface. The Ag_2O lattice was distorted, which results from the relatively larger d-spacing of the Ag_2O {002} plane (2.41 Å) compared to that of the Ag {111} plane (2.36 Å).

Fig.2 shows the modulation of the reversible redox of Ag by varying the e-beam dose. At 0 s, a Ag_2O grain was found at the edge of the Ag specimen [Fig.2(a)]. By focusing the e-beam on a nearby region for 17.5 s, the Ag_2O grain gradually transformed to Ag [Fig.2(b)-(d), >100 $A\cdot cm^{-2}$]. The e-beam was then expanded for 239.5 s, leading to the growth of the Ag_2O grain [Fig.2(e)-(i), ~1 $A\cdot cm^{-2}$]. When e-beam was focused again, the newly formed Ag_2O grain reduced again to Ag [Fig.2(j)-(o), >100 $A\cdot cm^{-2}$]. The aforementioned orientation relationship was maintained throughout this redox modulation process.

Considering all these results, we conclude that e-beam irradiation can be an effective way to elicit the oxidation of Ag and the reversible reduction of Ag_2O in the high vacuum condition common in TEM.

References:

[1] M. L. Zheludkevich *et al*. Oxid. Met. **61** (2004), 39.
[2] L. Sun, *et al*. Langmuir **27** (2011), 14201.
[3] Electron microscopy was performed in the Electron Microscopy Center at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility under Contract No. DE-AC02-

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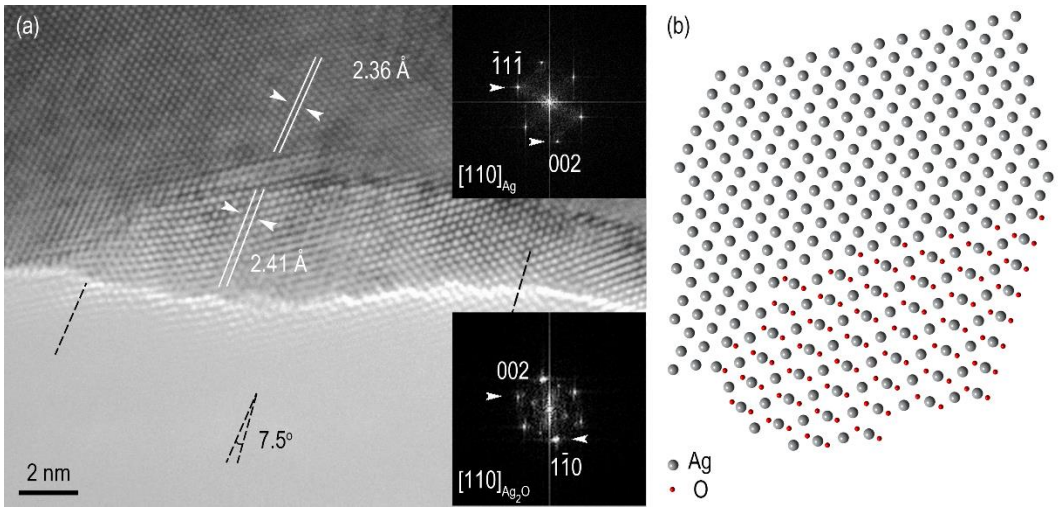

Figure 1. (a) HREM image showing the configuration of a typical Ag-Ag_2O interface. The insets are the FFT of the top Ag substrate and bottom Ag_2O grain. (b) Illustrative graphic showing the possible atom arrangements at the interface.

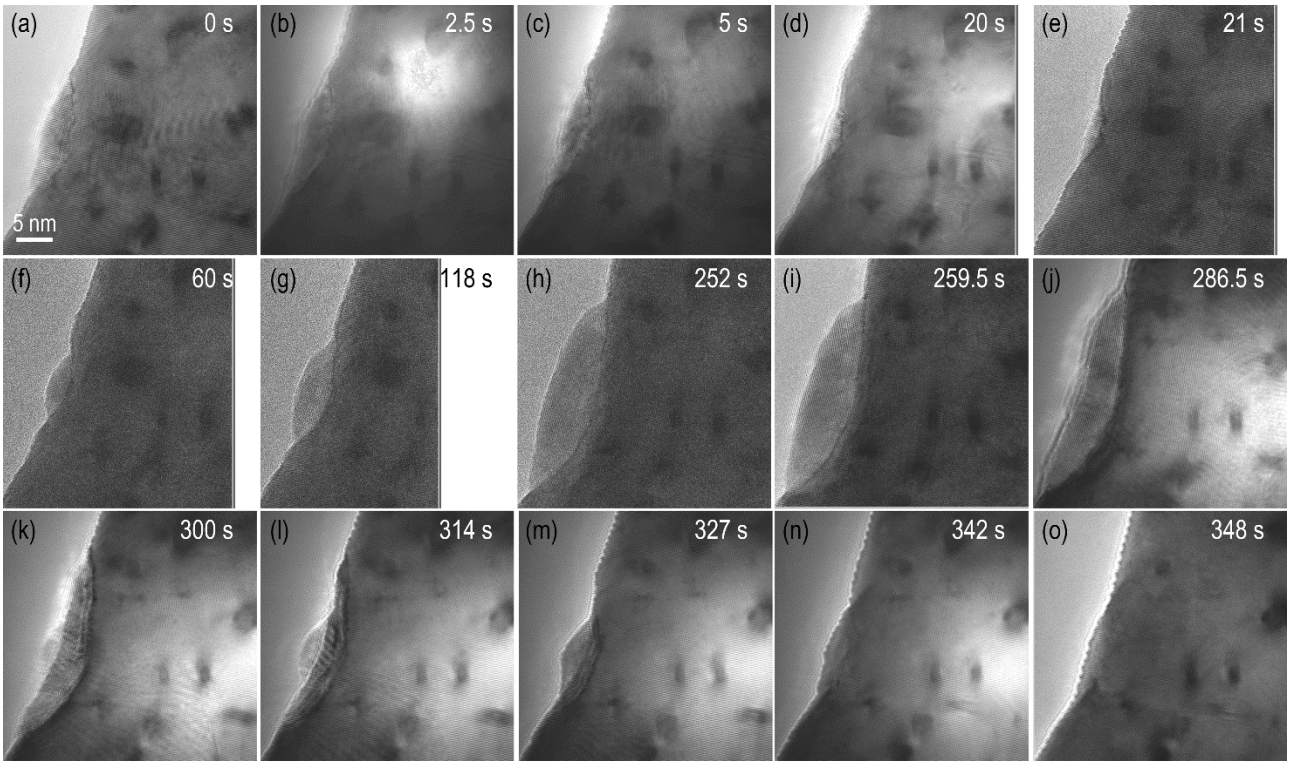

Figure 2. Modulation of the reversible redox of Ag by varying e-beam irradiation.

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