

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 $\approx 1.2 \times 10^{-5}$ Pa during the entire experiment.

After 4 hours' e-beam irradiation with a dose rate of $\sim 0.1 \text{ A}\cdot\text{cm}^{-2}$, a new structure was observed. The structure was found to be Ag₂O, similar to the results from Zheludkevich *et al.* [1], with the prevalent orientation relationship $\langle 110 \rangle_{\text{Ag}} // \langle 110 \rangle_{\text{Ag}_2\text{O}}$ and $\{111\}_{\text{Ag}} // \{002\}_{\text{Ag}_2\text{O}}$. Fig.1 shows a typical configuration of the Ag-Ag₂O interface. The Ag₂O lattice was distorted, which results from the relatively larger d-spacing of the Ag₂O {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 Ag₂O 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 Ag₂O grain gradually transformed to Ag [Fig.2(b)-(d), $>100 \text{ A}\cdot\text{cm}^{-2}$]. The e-beam was then expanded for 239.5 s, leading to the growth of the Ag₂O grain [Fig.2(e)-(i), $\sim 1 \text{ A}\cdot\text{cm}^{-2}$]. When e-beam was focused again, the newly formed Ag₂O grain reduced again to Ag [Fig.2(j)-(o), $>100 \text{ A}\cdot\text{cm}^{-2}$]. 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 Ag₂O 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.

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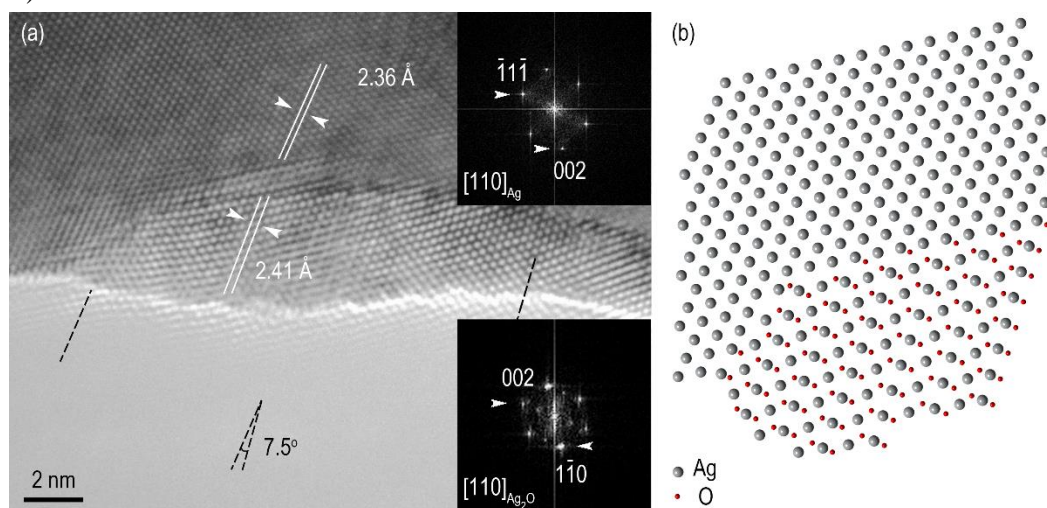


Figure 1. (a) HREM image showing the configuration of a typical Ag-Ag₂O interface. The insets are the FFT of the top Ag substrate and bottom Ag₂O grain. (b) Illustrative graphic showing the possible atom arrangements at the interface.

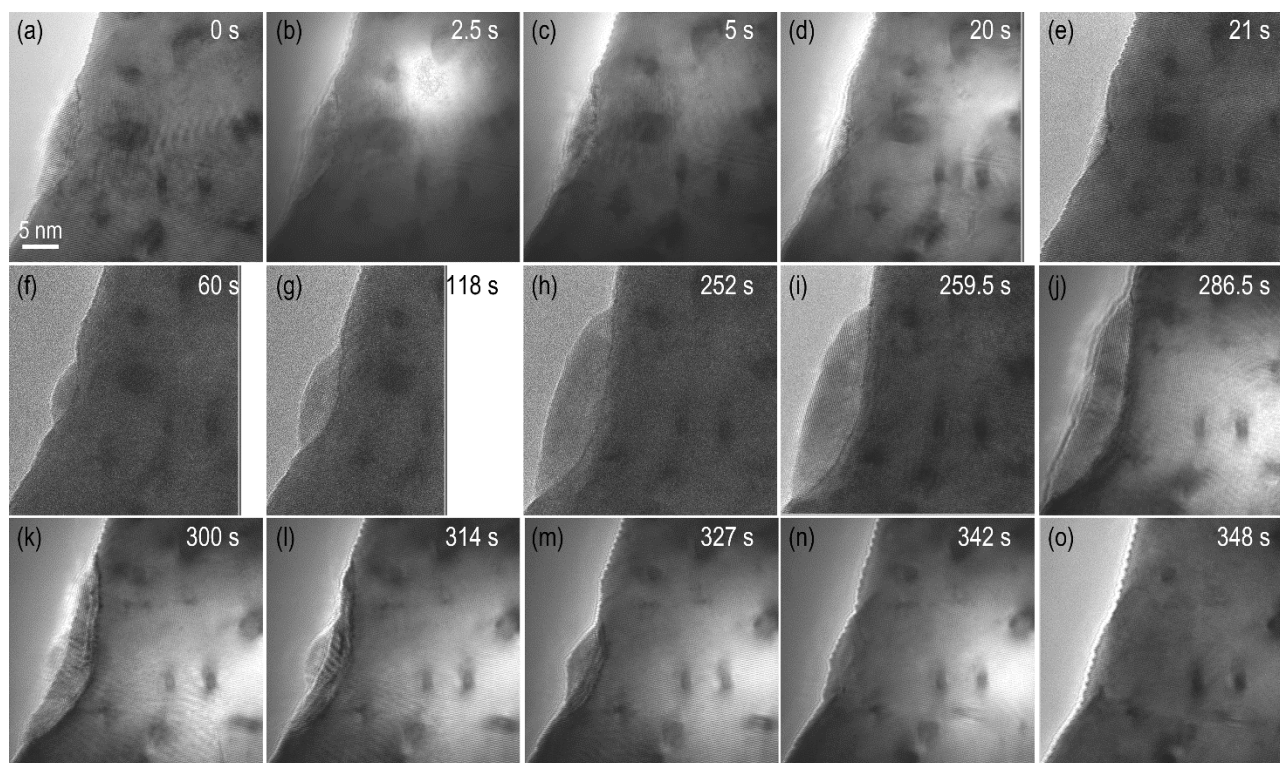


Figure 2. Modulation of the reversible redox of Ag by varying e-beam irradiation.