Nanoscale manipulation of redox of Ag by electron beam

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Employing electrons for direct control of nanoscale reaction is highly desirable since it provides fabrication of nanostructures with different properties at atomic resolution and with flexibility of dimension and location. In 2016, Kalinin et al summarized past experiments of manipulating atoms with scanning transmission electron microscopy (STEM) and proposed to utilize the imaging tool to create structures atom by atom. 1) Here, applying *in situ* transmission electron microscopy, we show nanoscale oxidation and reduction of Ag can be manipulated by electron beam. We demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix.

Under high vacuum environment (~10^{-7} Torr pressure), oxygen in a TEM can be ionized by high-energy electron beam and causes oxidization of Ag. After enough e-beam illumination, a growth of Ag_2O on the surface is observed when electron beam flux is below ~$5x10^5$ $e^-/Å^2s$. Ag_2O islands epitaxially grow on Ag surface with orientation relationship of $<110>_{Ag}//<110>_{Ag_2O}$ and $\{111\}_{Ag}//\{002\}_{Ag_2O}$ in most cases. In-situ high-resolution transmission electron microscopy (HRTEM) imaging shows that Ag_2O nucleats at atomic steps on Ag surfaces.

With the increase of electron-beam intensity above ~$5x10^5$ $e^-/Å^2s$, the formed Ag_2O islands can be fully reduced back to Ag, such that a fully reversible oxidation and reduction of Ag is achieved by varying electron beam intensity. A brief explanation for this electron-beam dose rate dependence is the competition between the electron-beam ionization induced oxidation of Ag and electron stimulated desorption induced reduction of Ag_2O. Aberration-corrected HRTEM observation reveals that O atoms are preferably inserted and extracted along the {111} close-packed planes of Ag, leading to the nucleation and decomposition of nanoscale Ag_2O islands on the Ag substrate.

Taking another step further, patterned oxidation has also been tested to verify the reliability of the electron-beam irradiation as a nanofabrication technique. By controlling probe size, electron flux, and dwell time, we demonstrated fabrication of an array of 3 nm Ag_2O nanodots in an Ag matrix. These findings do not only facilitate the basic understanding of oxidation/reduction kinetics in Ag-Ag_2O, but also open up a promising approach for precise fabrication of nanostructures with metal or semiconductor properties in devices.

1) Kalinin, Sergei V., Albina Borisevich, and Stephen Jesse. "Fire up the atom forge." *Nature News* 539.7630 (2016): 485.