

## **Electron Radiolysis Effect for in-situ Electron Microscopy: Super-Dissolution and Direct Writing Transformation of Metal Oxides**

Lu, Y.<sup>1</sup>, Zhang, Z.H.<sup>1</sup>, Chen, F.R.<sup>2</sup> and Sui, M.<sup>1</sup>

<sup>1</sup> Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, China, <sup>2</sup> City University of Hong Kong, Hong Kong

In-situ electron microscopy now day has been a popular technique that scientists frequently use to on-site investigate the physical or chemical response under external stimuli, e.g., the mechanical force or electric field etc. However, the in-situ observation must be carried out under electron beam irradiation which shall play a role as an extra stimuli. This extra contribution was usually ignored during interpretation of the final results. Here we demonstrate that the electron radiation can alter the dissolution behavior and phase transformation temperature of metal oxides via in-situ electron microscopy. In general, dissolution of metal oxides is a slow and inefficient chemical reaction even in strong acid. Under observation in a liquid environmental TEM, the dissolution rate constant significantly increases by 16–19 orders of magnitude, equivalent to a reduction of 0.97–1.11 eV in activation energy, as compared with the normal dissolution in acid. It is evidenced from the high-resolution TEM imaging, electron energy loss spectra, and first-principle calculations where the dissolution route of metal oxides is dynamically changed by local interoperability between altered water chemistry and surface oxygen deficiencies via electron radiolysis. As a model functional material, vanadium dioxide (VO<sub>2</sub>) usually has a sharp metal–insulator transition (MIT) at temperature around 68 °C. Here, we demonstrate a focused electron beam can directly lower the transition temperature of a nano-area down to room temperature without pre-patterning the VO<sub>2</sub>. This novel process is called radiolysis-assisted MIT (R-MIT). This direct electron writing technique can open up an opportunity to precisely engineer nano-domains of diversified electronic properties in functional material-based devices. As a summary, electron beam effect shall be considered as an external source that may alternate the in-situ experiments. In the case of beam sensitive system, such as for a system involving "water", we shall specially use a low dose mode to minimize electron beam contribution.

This work is supported by the National Key Research and Development Program of China (Grant No. 2016YFB0700700), the National Natural Science Foundation of China (Grant Nos. 51621003 and 11374028) and the Scientific Research Key Program of Beijing Municipal Commission of Education (KZ201310005002).