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Impact of the Synthesis Kinetics of Entropy-stabilized Oxide Thin Films Probed with 4D-STEM and STEM-EELS

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The entropy stabilized oxides (ESOs) are a new class of materials designed and synthesized based on the principle of reducing the overall Gibb's free energy by maximizing the configurational entropy in the material.[1] This new materials synthesis strategy shows the promising capability of stabilizing the ESOs with different chemical compositions into various families of single-phase crystalline materials, such as rocksalt, perovskite, fluorite and so on.[2–4] For example, the first rocksalt ESO was successfully synthesized by intermixing five distinct metal oxides (MgO, CuO, CoO, NiO, and ZnO) and incorporating them into a single lattice with random occupancy at high temperature. The follow-up studies indicated that the rocksalt ESOs has interesting properties including colossal dielectric constant, superionic conductivity and storage for Lithium ions, and so on.[5–7]

Recently, we reported that the structural, optical and magnetic properties in similar rocksalt ESO thin films can be tailored by changing the synthesis kinetics during growth.[8,9] In this study, we investigated the correlation between microstructure and the electronic properties by employing the four-dimensional STEM (4D-STEM) and electron energy loss spectroscopy (EELS). The sample used in this study is the rocksalt entropy-stabilized oxide ($(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$) thin film grown using pulsed laser deposition method on an MgO substrate.[8] To directly study the impact of the synthesis kinetics on the physical properties, the sample consisted of two 40 nm epitaxial layers deposited subsequently, the first at a substrate temperature of 500 °C and the second at 200 °C, as shown in the virtual BF-STEM image in Figure 1(a). All other growth conditions were held constant.

Figure 1(b) shows a diffraction pattern extracted from one scanning position of 4D-STEM dataset. The measurement was performed using a patterned aperture to enhance the measurement precision.[10] A large out-of-plane compressive and tensile strain of approximately 2% across the interface were determined in the top and bottom part of the stacked thin film respectively. Additionally, the STEM-EELS measurement was then performed in the same region as 4D-STEM scan, and averaged pattern from two films are shown in Figure 1(c). The spectra clearly shows that a pre-edge peak at 529.5 eV becomes prominent in the O K-edge absorption spectra collected from the layer deposited at 200 °C. The emergence of this pre-edge peak is a signature of the abrupt transition of Co valence related to the synthesis temperature. We also detected a drastic change in L_3/L_2 intensity ratio and Co L edge ELNES features between the two layers, which further suggests the Co ion oxidation states changes depending on synthesis temperature. This study will benefit future studies of physical property tuning in the ESOs thin films.

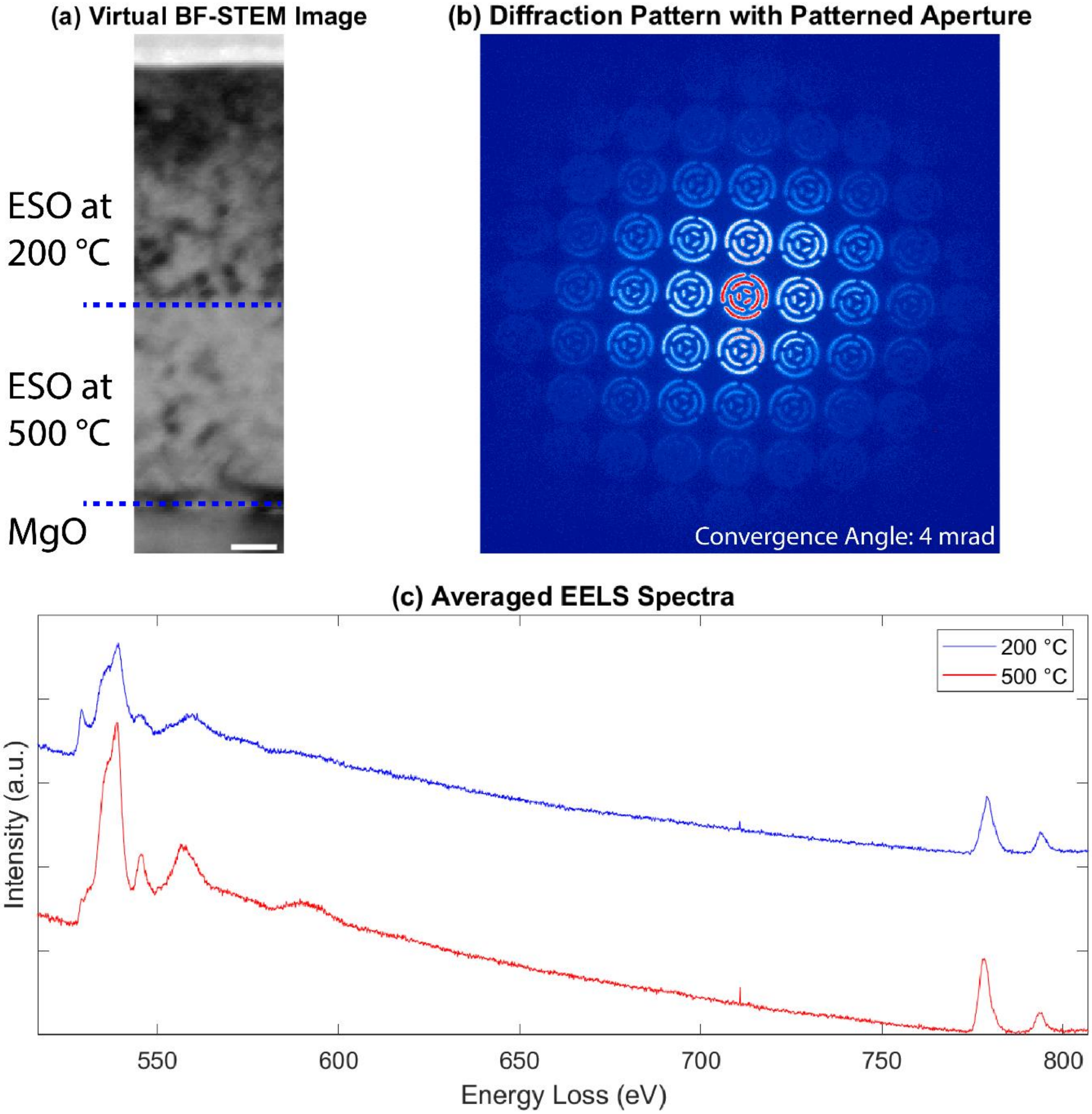

Figure 1. (a) A virtual BF-STEM image extracted from the 4D-STEM data. The scale bar equals 10 nm. (b) a typical diffraction pattern with 4 mrad convergence angle using the patterned aperture extracted from 4D-STEM data. (c) averaged EELS spectra collected from the layers grown at substrate temperatures of 200 °C (blue) and 500 °C (red).

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