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High-Resolution STEM/STEM-EELS Characterization of Entropy-stabilized Oxides Thin Films

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The entropy-stabilized oxides (ESOs) are recently discovered by incorporating five or more elements into a single lattice with random occupancy. The stabilization into the single phase is achieved via increasing the configurational entropy in the system to reduce the overall Gibbs free energy[1]. The ESOs with different compositions can adopt various forms of crystal structures, including the rocksalt[1], fluorite[2], perovskite[3] and so on. This system provides the framework for the researchers to synthesize new phases of single-phase crystalline material, with a great chance for discovering novel properties and applications. For example, there are studies reporting the ESOs to possess colossal dielectric constant[4], room temperature superionic conductivity for Li-ions[5], and reversible Li-ion storage properties[6]. This new class of materials also shows great potential in lead-free electrocaloric, piezoelectric and other devices.

$(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$ entropy-stabilized oxide thin film is grown using the pulsed laser deposition method on the MgO substrate. These films show variation in the lattice parameters, as well as dissimilar optical and magnetic properties at different growth temperatures. to understand the underlying physics behind this behavior, the S/TEM imaging and EELS were conducted on the sample. The thin film is composed of two stacking films, with the first film deposited directly onto the MgO substrate at 500°C, and the second layer of the thin film was grown on top of the first film after it was cooled down to 200 °C. According to our strain measurement using the geometric phase analysis the out-of-plane compressive strain is observed in the 200 °C thin film compared to the thin film grown at 500 °C.

To further investigate the difference in the out-of-plane lattice parameter, we performed the monochromated STEM-EELS measurement on the stacking film. The result of the line scan core-loss EELS spectra for Co, Ni, and Cu across the thin film interface is shown in Fig. 2. Based on the EELS spectra, the $L_{2,3}$ core loss edge of Co ions shows the difference in both shape and energy across the interface between thin films, whereas the edges of Ni and Cu cations are similar across the interface. With this measurement, the majority of the Co ions in the 200 °C thin film are believed to have a different valence state comparing to Co ions in the 500 °C film. Since the multivalent Co ions show significant variations in ionic radii, we can correlate the strain in the film with this observation. In conclusion, our results indicate that the lattice parameter change in the films may be attributed to this sudden change in Co valency at different substrate temperature during growth. This study provides insight into the tuning of the ESOs thin film structures and properties in the future.

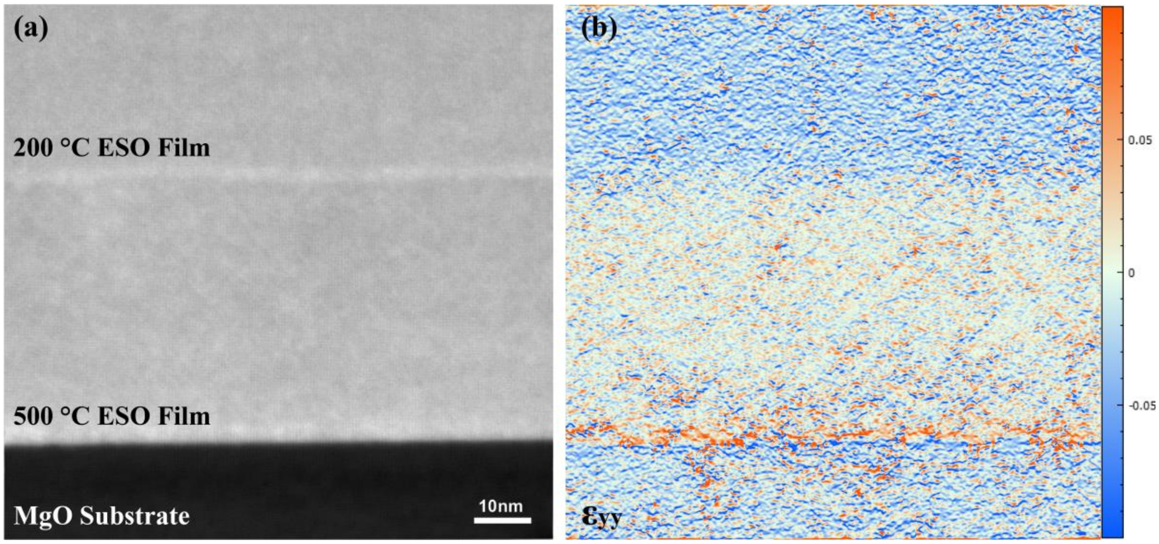

Figure 1. (a) HAADF-STEM image showing the stacking structure of the entropy-stabilized oxide thin film sample. (b) geometric phase analysis showing the out-of-plane εyy strain between film grown at 200°C and 500°C.

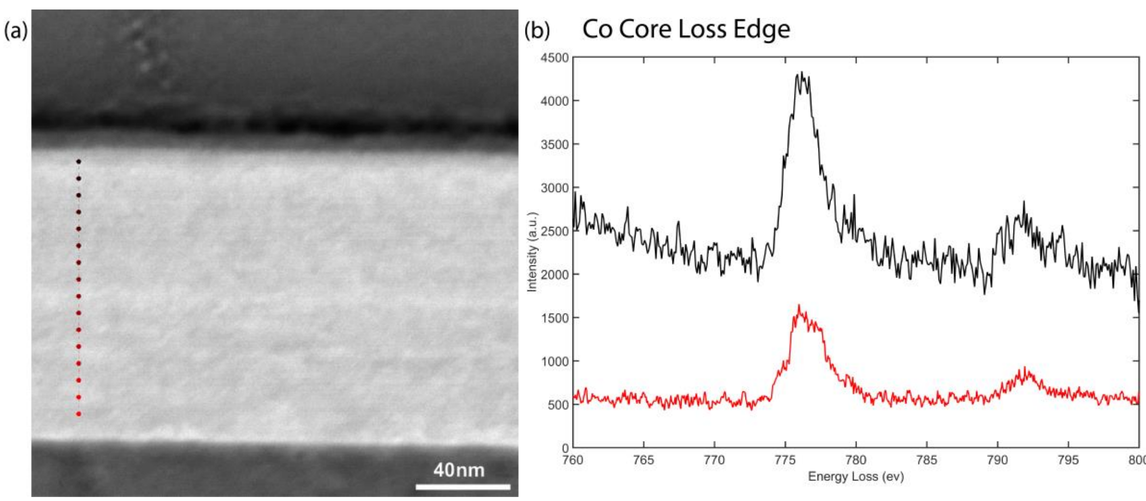

Figure 2. (a) ADF-STEM image showing the STEM-EELS line scan locations. The color of the overlaid spots indicates the location of the spectra. (b) EELS core loss edge spectra of Co.

References

[1] C. M. Rost *et al.*, "Entropy-stabilized oxides," *Nat. Commun.*, 2015.
[2] K. Chen *et al.*, "A five-component entropy-stabilized fluorite oxide," *J. Eur. Ceram. Soc.*, 2018.
[3] S. Jiang *et al.*, "A new class of high-entropy perovskite oxides," *Scr. Mater.*, 2018.
[4] D. Bérardan, S. Franger, D. Dragoe, A. K. Meena, and N. Dragoe, "Colossal dielectric constant in high entropy oxides," *Phys. Status Solidi - Rapid Res. Lett.*, 2016.
[5] D. Bérardan, S. Franger, A. K. Meena, and N. Dragoe, "Room temperature lithium superionic conductivity in high entropy oxides," *J. Mater. Chem. A*, 2016.
[6] A. Sarkar *et al.*, "High entropy oxides for reversible energy storage," *Nat. Commun.*, 2018.