Heteroepitaxial Growth of Sm_2O_3 Nanoislands on Cu(111)

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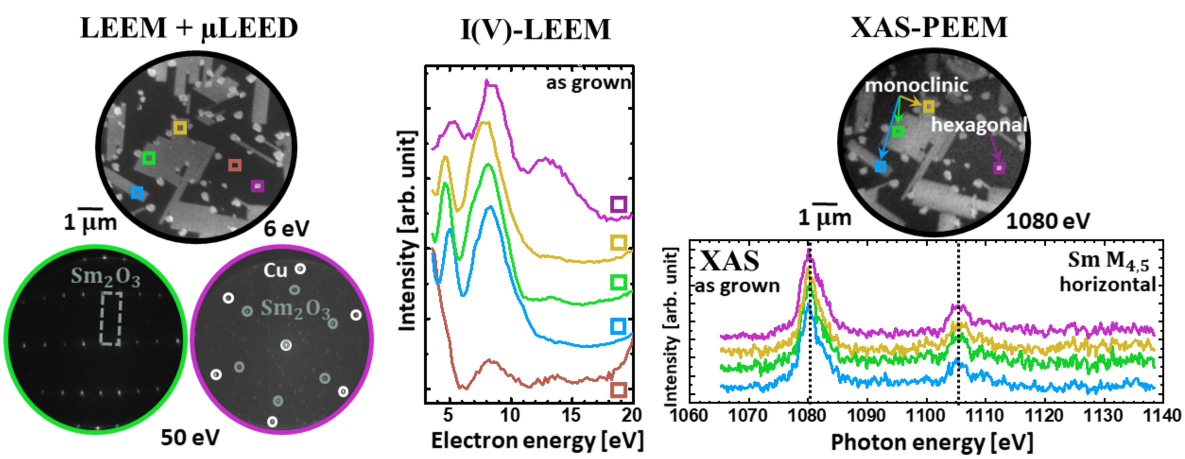
Samarium, which forms sesquioxides (Sm_2O_3), can significantly influence the redox behavior of ceria by promoting the formation and stabilization of reduced Ce^{3+} species [1], which have been postulated to be active sites for CO_2 hydrogenation in the CeO_x/Cu(111) inverse catalytic system [2]. However, to understand analytically the role of Sm in this process, the interaction with the support needs to be studied. Yet, only a few studies have focused on studying samaria on well-defined single-crystal surfaces [3], and the lack of combined structural and spectroscopic studies in model systems results in a gap in understanding the relation between the samaria structure and its chemical behavior.

Here, a multi-method approach has been employed to investigate Cu(111)-supported Sm_2O_3 nanoislands with high structural and chemical sensitivity, using low-energy electron microscopy (LEEM) and micro-spot diffraction (µLEED) and I(V)-LEEM in combination with X-ray absorption spectroscopy photoemission electron microscopy (XAS-PEEM).

Our measurements reveal the phase coexistence of small hexagonal A-Sm_2O_3(0001) islands and rectangular-shaped monoclinic B-Sm_2O_3(100) islands with various rotated rectangular domains after the heteroepitaxial growth of Sm_2O_3 on Cu(111). To investigate the influence of structural differences in the grown Sm_2O_3 nanoislands on their chemical behavior, we examine the redox properties. By exposing the system to reducing conditions (H_2), a phase transition at 500 °C is observed at the edges of the initial monoclinic Sm_2O_3 islands into a mixture of hexagonal and cubic Sm_2O_3, while this transition in the initial hexagonal Sm_2O_3 islands occurs gradually with increasing temperature. These findings indicate a highly dynamic system that can be easily adjusted by modifying the deposition conditions, such as growth temperature and oxygen partial pressure. To explore this tunability in more detail, we employ a range of growth conditions, systematically varying the temperature and oxygen partial pressure. Based on these results, a phase diagram is constructed to map out the structural regimes of Sm_2O_3 nanoislands.



References

[1] R. Sánchez-Barquilla et al., in preparation.
[2] J. Graciani et al., Science 345, 546 (2014)
[3] E. Pożarowska et al., Ultramicroscopy 250, 113755 (2023)