Harnessing Redox Epitaxy for Tailored Functionalities at Oxide Heterointerfaces

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The tunability of the oxygen content in complex oxides and heterostructures has emerged as a key to designing their physical functionalities. Controlling the interface reactivity by redox reactions provides a powerful means to deliberately set distinct oxide phases and emerging properties – down to the monolayer limit. With regard to metal-oxide growth, the importance of the choice of oxide substrate materials has typically been downplayed with regard to reduction-oxidation reactions. Only lately, the huge potential of this determining factor was received for the design of oxide functionalities via interfacial oxide exchange, such as magnetic oxides. This way, we have accomplished to i) realize the growth metastable oxide phases [1,2], to ii) control reversibly phase transitions of multivalent Fe oxides [3] and iii) tailor 2D electronic and hole states at oxide heterointerfaces [4]. The emerging properties are uncovered by the unique capabilities of photoelectron spectroscopy using hard X-rays to access bulk and interface properties in an element selective way.

Here we will consider two examples. First, by exploiting the active oxygen supply of the substrate material without the need for external oxygen dosing, high-quality, crystalline ultrathin films of the Heisenberg ferromagnet europium monoxide (EuO) can be stabilized on YSZ (001). This so-called redox-assisted growth mode (or, vice versa, the extreme case of a distillation growth) was monitored from end to end by in situ X-ray photoelectron emission spectroscopy and electron diffraction techniques. The evolution of Eu 3d core levels allows us to disentangle the processes of interfacial oxygen diffusion and vacancy formation in stabilizing the very first monolayers of EuO on YSZ (001). An convenient background correction analysis is presented, which allows us to quantify the critical Eu3+/Eu2+ ratio in the ultrathin film regime. We concluded on the key mechanisms of redox-assisted EuO/YSZ (001) thin film synthesis, which merge in a universal three-process growth model (see Fig. 1) that may serve as guideline for redox-assisted synthesis of metastable low-dimensional oxides.

Second, we provide evidence for individually emerging hole- and electron-type 2D band dispersions at Fe-$SrTiO_3$ heterostructures [4]. The emergence of p- or n-type bands is closely linked to the Fe oxidation state which enables the possibility to tune the interface properties to set or even switch between negatively (n) charged electrons or positively (p) charged holes. One of the main processes that controls the interface properties is the oxygen exchange between the film and the substrate.

Using an UHV-MBE system, we grow high-quality ultrathin TM (e.g. Fe, Co) oxide films on $SrTiO_3$ substrates by systematically varying the growth parameters, e.g. (i) growth temperature, (ii) substrate annealing, and (iii) metal film thickness. The present work discusses the effect of different growth parameters on the interfacial properties like oxygen vacancies, the oxidation state of the redox-formed

TM oxide as well as the concentration of defects in $SrTiO_3$, which strongly influences the valence band alignment between electron and hole band bending. In this way, we can effectively control the properties of the 2D interface to ultimately add ferroic functionalities to these confined electronic states.

In summary, exploiting the tunability of the oxygen content in the materials and understanding interface formation are versatile strategies in designing new functional properties through controlled interfacial oxygen exchange.

References

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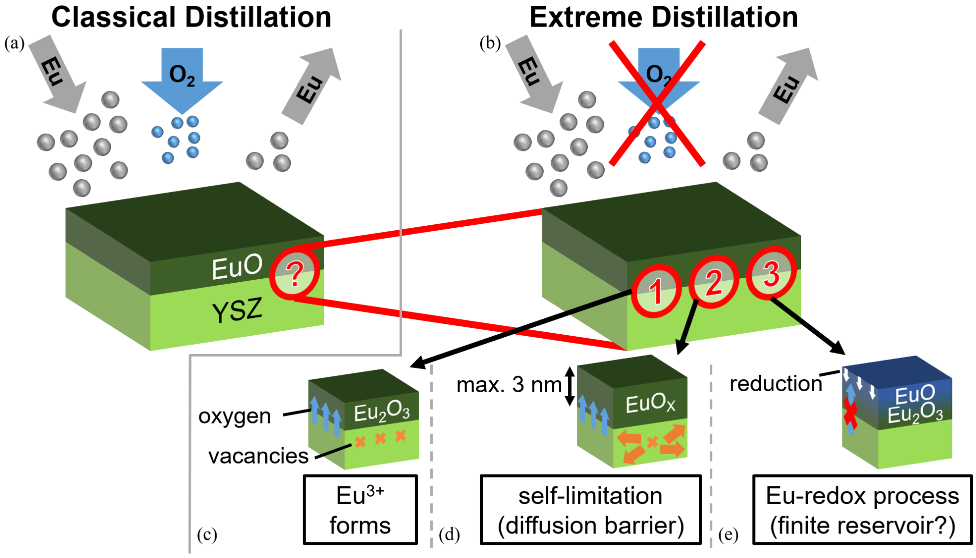

Fig. 1: Sketch of the three-process growth model for EuO/YSZ (001). While mainly hidden under (a) classical distillation conditions the individual processes are best observable under (b) extreme distillation conditions, i.e., the absence of externally supplied oxygen gas. (c) In process 1, a first oxygen-rich layer forms, which (d) acts as diffusion barrier and reduces the oxygen flux from the substrate towards the film surface, resulting in a self-limitation of the growth to a maximum EuO film thickness of about dmax ≈ 3 nm. (e) Finally, an Eu-redox process is part of the growth process whenever the supply of Eu metal is larger than the oxygen supply at the surface (either as O2 gas or by diffusion). Taken from Ref [1].