Reactive growth of ultra-thin ceria islands on Rh(111): Structure and morphology

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The conversion of biomass feedstock into an effective energy carrier such as methanol or hydrogen gas has received increasing attention in the search for new sources of energy, Hydrogen gas can be obtained from alcohols with high efficiency and selectivity using catalytic processes such as the steam reforming reaction. A promising catalyst components for this reaction is the Rh/ceria system as Rh breaks the C-C bond and ceria dissociates H_2O. To further improve the understanding of this model catalyst system, we studied the reactive growth of its inverse model counterpart using in-situ low-energy electron microscopy (LEEM) and spectroscopic photoemission microscopy (PEEM). Samples were prepared in-situ by reactive Ce deposition. The impact of the deposition temperature was studied in the range of 700°C to 900°C at a fixed oxygen background pressure of $5x10^{-7}$ Torr.

At a deposition temperature of 700°C we observe a high nucleation density of 100 nm-sized islands. Between 750°C and 850°C triangularly shaped islands nucleate preferentially at step edges and, with temperature, the nucleation density decreases and the average island size increases. At 900°C during growth the islands lose their triangular form. Instead, growth along the substrate step edges becomes favorable, leading to a maze-like architecture. Atomic force microscopy reveals the formation of ceria islands with a thickness of 1 or 2 trilayers (O-Ce-O) of ceria. Moreover, the second layer of the islands is also triangularly shaped, with lateral dimensions of 50 nm and similar step heights. At all temperatures investigated, we find three-dimensional island growth.

Besides the p(1.4x1.4), we also detect a (5x5) reconstruction which has not been reported before. Moreover, we find an azimuthal broadening of the ceria LEED spots indicative for rotational domains and most pronounced for intermediate deposition temperatures around 850°C. Dark-field LEEM shows that individual ceria islands are single domain. A local I(V)-LEEM analysis of the islands reveals nearly fully oxidized ceria and the presence of a reduced CO_x wetting layer.

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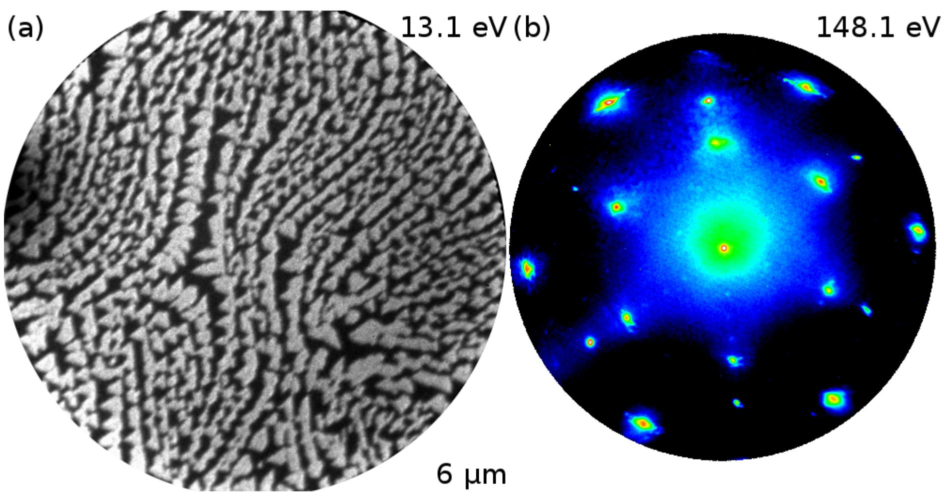

Fig. 1: (a) LEEM image of highly oxidized ceria grown at 850°C and $5x10^{-7}$ Torr oxygen partial pressure. (b) µLEED pattern showing the p(1.4x1.4) reconstruction and a weak (5x5) reconstruction.