ABSTRACT

Surface Stabilization Mechanisms in Metal Oxides

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Metal oxide surfaces play a central role in modern applications, ranging from heterogeneous catalysis to electronic devices, yet little is known about the processes determining their structural stabilization. Several such stabilization mechanisms are explored via a combination of theoretical and experimental methods. The processes of periodic reconstruction, adsorption and segregation are studied through case studies of model material systems.

The evaluation of structural models of periodic $SrTiO_3$(001) reconstructions via bonding analysis and simulated scanning tunneling microscopy images supports the family of "DL" models terminating in two consecutive layers of TiO_2 composition, and discards alternative proposals such as the models based on periodic Sr adatoms.

Experimental and simulated scanning tunneling microscopy images and complementary spectroscopic data are used to determine the structure of linear Ti-rich $SrTiO_3$(001) nanostructures. The structural solution exemplifies the recurrence of locally stable motifs across numerous surfaces. In particular, the arrangement of edge-sharing TiO_5 surface polyhedra is a trait is shared by (001) nanostructures and DL reconstructions. This is a flexible framework which allows for optimal bonding in surface atoms.

Modeling of water adsorption on reconstructed $SrTiO_3$(001) surfaces reveals that water plays two major roles in the stabilization of oxide surfaces: it may mediate the formation of certain ordered structures, or it may be part of the ultimately stable structures themselves. This can be understood in terms of the inevitable presence of chemisorbed water on defective

surfaces. Since the surface mobility of cationic species is relatively low, the kinetics associated to water diffusion and desorption dominate the surface ordering process.

High-temperature annealing of $SrLaAlO_4$ single crystals leads to the segregation of SrO to the surfaces, in the form of islands. This process is in fact a bulk stabilization mechanism, due initially to the increasing number of bulk Sr-O vacancy pairs. This material enables a second accommodation mechanism for further surface segregation and increasing bulk non-stoichiometry, consisting of the formation of low-energy stacking faults. In spite of previous speculation of a similar fault-based compensation process taking place in $SrTiO_3$, this is found to be decidedly unviable in perovskite systems.

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