Ultrathin Ceria Islands on Cu(111): Work Function and Reaction with Oxygen and Hydrogen at RT

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Ultrathin oxide films can significantly alter the work function (WF) of metal surfaces, with large consequences in the adsorption of nanoparticles (NP) and molecules on the films: the WF is mostly reduced by the oxide film, which often result to an intrinsic charge transfer between the metal and the adsorbed nano-objects [1]. This charge transfer can then modify the geometrical, electrostatic and electronic properties of the nano-objects [2,3], as well as impacting other properties, such as the catalytic activity of NPs [4].

Cerium oxide (ceria) is a key oxide in catalysis thanks to its reducibility and associated oxygen storage capacity. In model catalysis, it is primarily grown as an ultrathin film on a metal surface, providing interesting chemical and physical properties and giving access to a plethora of ultrahigh vacuum (UHV) techniques. Despite the extensive study of such films in the past, little is known about ceria's impact on the metal WF, particularly with regard to its reducibility.

In this contribution, results on oxidized and reduced ceria islands on Cu(111) are presented. Experiments are conducted in UHV with scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) and low-energy electron diffraction (LEED) as well as Kelvin probe force microscopy (KPFM). KPFM measures the contact potential difference (CPD) and, in turn, provides direct access to the WF.

It is shown that oxidized ceria islands reduce the WF of Cu(111) by a few hundred meV, whereas reduced ceria islands reduce the metal WF by more than 1 eV. Reduced islands revert back to the lower WF when exposed to a few Langmuir of O2, due to oxidation (Figure). A possible model explains that because most of the interfacial Ce ions are already in the 3+ state after the thin film preparation, an electron transfer from ceria's oxygen vacancies to the Cu support takes place during reduction. This charge transfer significantly alters the surface dipole, reducing the WF of the metal. – Apart from the WF, the interaction of the pristine Cu(111) surface and supported ceria islands with O2 and H2 is involved in the discussion.

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