The special properties of oxide ultrathin films on metals

Gianfranco Pacchioni
Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca,
via Cozzi, 53 - 20125 Milano, Italy
gianfranco.pacchioni@unimib.it

Ultrathin oxide films on metallic or semiconducting supports are of enormous importance in a variety of fields like corrosion protection of metals, magnetic tunnel junctions, dielectric barriers in metal-oxide field effect transistors, etc. Recently, it has been found that oxide ultrathin films on metal single crystals can exhibit unusual and unprecedented properties which have no counterparts in the corresponding bulk surfaces [1-10]. For instance, metal atoms or particles deposited on these films can exchange charge with the metal support by direct electron tunneling through the thin dielectric layer. In this talk we will analyze the physical reasons which can lead to charge exchange. In particular, we will focus on the changes in work function of the system which occur when an oxide film is deposited on a metal support and we will consider possible ways to tune the work function so as to induce charge transfers also in those cases where this does not occur spontaneously. We will present cases where adsorbed species become negatively charged (e.g. Au on MgO/Ag), positively charged (e.g. Au on FeO/Pt) or remain neutral (e.g. Au on SiO_2/Mo) because of the different position of the Fermi level in the oxide/metal support, and we will discuss methods to modify these interfaces. In particular, we will show that this can be obtained by co-deposition of alkali atoms, and examples of this effect will be reported for Li-doped SiO_2/Mo(112) films. Finally, we will show that the occurrence of a charge transfer across the interface can also be used to enhance the magnetic moments of supported Fe clusters.

1) G. Pacchioni, L. Giordano, M. Baistrocchi, "Charging of metal atoms on ultra-thin MgO/Mo(100) films", ***Physical Review Letters***, 94, 226104-4 (2005).
2) D. Ricci, A. Bongiorno, G. Pacchioni, U. Landman, "Bonding trends and dimensionality crossover of gold nanoclusters on metal-supported MgO thin films", ***Physical Review Letters***, 97, 036106-4 (2006).
3) M. Sterrer, T. Risse, U. Martinez Pozzoni, L. Giordano, M. Heyde, H.-P. Rust, G. Pacchioni, H.-J. Freund, "Control of the charge state of metal atoms on thin MgO films", ***Physical Review Letters***, 98, 096107-4 (2007).
4) V. Simic-Milosevic, M. Heyde, N. Nilius, T. König, H.-P. Rust, M. Sterrer, T. Risse, H.-J. Freund, L. Giordano, G. Pacchioni, "Au dimers on thin MgO(001) films: flat and charged or upright and neutral?", ***J. American Chemical Society***, 130, 7814-7815 (2008).
5) L. Giordano, G. Pacchioni, J. Goniakowski, N. Nilius, E. D. L. Rienks, H. J. Freund, "Charging of metal adatoms on ultrathin oxide films: Au and Pd on FeO/Pt(111)", ***Physical Review Letters***, 101, 026102-1/4 (2008).
6) S. Ulrich, N. Nilius, H.-J. Freund, U. Martinez, L. Giordano, G. Pacchioni, "Evidence for a size-selective adsorption mechanism on oxide surfaces: Pd and Au atoms on SiO_2/Mo(112)", ***ChemPhysChem***, 9, 1367-1370 (2008).
7) H. J. Freund, G. Pacchioni, "Oxide ultra-thin films on metals: new materials for the design of supported metal catalysts", ***Chemical Society Reviews***, 37, 2224-2242 (2008).
8) S. Prada, U. Martinez, G. Pacchioni, "Work function changes induced by deposition of ultrathin dielectric films on metals: a theoretical analysis", ***Physical Review B***, 78, 235423-1/8 (2008).
9) V. Simic-Milosevic, M. Heyde, X. Lin, T. König, H.-P. Rust, M. Sterrer, T. Risse, N. Nilius, H.-J. Freund, L. Giordano, G. Pacchioni, "Charge-induced formation of linear Au clusters on thin MgO films", ***Physical Review B***, 78, 235429 (2008).
10) S. Ulrich, N. Nilius, H. J. Freund, U. Martinez, L. Giordano, G. Pacchioni, "Modifying the adsorption characteristics of inert silica films by inserting anchoring sites", ***Physical Review Letters***, 102, 016102/1-4 (2009).