Ternary nano-oxides with adjustable properties: ultra-thin films of barium titanate

Two dimensional oxide films may display structures and stoichiometries which are significantly different from those of macroscopic crystals. As a consequence, they have new properties, in particular reactivity, and may serve as template for the self-organized growth of nanoparticles. In collaboration with experimentalists from the Physics Department at the University of Oxford, theorists in the INSP “Oxide in Low dimensionality” team have unraveled the mechanism by which two-dimensional films of barium titanate are stabilized, with compositions never found before.

The recent advances in the synthesis of ultra-thin oxide films with no more than one or two atomic layers have revealed an unexpected richness of new ordered phases. Their thorough analysis, systematically coupling experiments and numerical simulations, has evidenced the existence of bi-dimensional oxides displaying structures and stoichiometries never met before. This is true for ultra-thin films of binary oxides, such as TiO$_x$ or MnO$_x$, etc. However, so far, very few if any ternary oxides have benefited from those advances, despite the obvious interest of their flexible compositions which offer additional levers to engineer their properties.

By depositing barium atoms on a Ti$_2$O$_3$ monolayer formed on an Au(111) surface, Martin Castell’s team in Oxford was able to grow a family of ternary oxides BaxTi$_2$O$_3$ with compositions x ranging from 0 to 2/3. The barium atoms adsorb in the center of the hexagons formed by the TiTi$_2$O$_3$ honeycomb structure. Relying on ab initio simulations, the INSP team has shed light on the nature of the interactions between barium atoms responsible for the stability of these nano-oxides.

These interactions are repulsive and long-range. They are inversely proportional to the cube of the Ba-Ba distance, like dipole-dipole interactions. Their origin lies in a large charge transfer which takes place between the barium atoms and the substrate: the former adopt a 2+ oxidation state, and two electrons are transferred and nearly equally shared between the Ti$_2$O$_3$ monolayer and the gold surface. Thus these new BaxTi2O3 compounds can be solely stabilized thanks to the large electron affinity of the metallic substrate, able to accommodate one electron per deposited barium atom.

By introducing the effective barium-barium interactions deduced from their ab initio calculations into a Monte Carlo approach, the INSP team has determined the equilibrium configurations of the BaxTi$_2$O$_3$ compounds. In excellent agreements with STM images obtained in Oxford in the whole composition range (Figure 1), these configurations, and in particular the two ordered phases at x=1/3 and x=2/3, are indeed driven by the strong repulsion between charged Ba atoms.
Figure 1
STM images (top panels) and Monte Carlo snapshots (lower panels) of BaxTi2O3 monolayers. The composition x is specified in each column. The images have 10 x 10 nm2 sizes and are obtained at biases ranging from 0.35 to 1.0 Volts and currents between 0.18 and 0.28 nA. In the x=0.07 STM image, the honeycomb lattice of the Ti2O3 monolayer is visible. In the Monte Carlo snapshots, only barium atoms are represented (yellow color).

The electronic properties of these films are strongly dependent on their stoichiometry. In particular, due to the large electronic transfer to the metallic substrate, a noticeable lowering of the gold work function takes place. Since the latter is proportional to the density of barium atoms, it becomes possible to tune the work function of the whole system at will. Potential applications are numerous, ranging from cathode fabrication to devices in which the Schottky barrier height or interfacial properties are important, in addition to the synthesis of novel inverse (oxide on a metal) catalysts.

Reference
“Stoichiometry engineering of ternary oxide ultrathin films: BaxTi2O3 on Au(111)"
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