Novel quasicrystalline approximants in two-dimensional oxides

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When approaching the two-dimensional limit, oxides are known to exhibit structures and properties that strongly depart from those of their respective bulk counterparts and are promising materials for both fundamental science and technological applications. [1]. One of the extreme examples are the two-dimensional oxide quasicrystals (OQCs) with twelve-fold rotational symmetry which have been discovered in reduced perovskite oxide thin films epitaxially grown on Pt(111) single crystal substrates [2].

Here, we use an all-thin-film approach in which the single crystal is replaced by a 10 nm thick Pt(111) buffer layer grown by molecular beam epitaxy on an Al_2O_3(0001) substrate [3]. An ultra-thin film of $SrTiO_3$ is subsequently deposited by pulsed laser deposition. The film stacking and structure are fully characterized by diffraction and microscopy techniques. We report the discovery of two new complex phases obtained by reduction of this system through high temperature annealing under ultrahigh vacuum conditions. The formation of a giant square approximant with a lattice parameter equal to 44.4 Å is evidenced by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) (see Figure). Additionally, a new 2D hexagonal approximant phase with a lattice parameter of 28 Å has been observed depending on the preparation conditions. Both phases can be described by two different tilings constructed with the same basic square, triangle and rhombus tiles possessing a common edge length of ~ 6.7 Å. Using the tiling built from high-resolution STM images, an atomic model is proposed for each approximant, which accounts for the experimental observations. Simulated STM images indicate that the bright protrusions observed experimentally are protruding Sr atoms. In addition, we found that the adhesion of the oxide layer on the metal substrate is rather strong (-0.30 eV.$Å^{-2}$). This is attributed to charge transfer, from the most electropositive elements (Sr and Ti) to the most electronegative ones (Pt and O), and to hybridization with Pt-states. Density of states calculations indicate differences in the electronic structure of the two approximants, suggesting different chemical and physical properties. This all-thin-film approach may be more versatile to explore the formation of complex two-dimensional oxide phases in other metal-oxide combinations in future works.

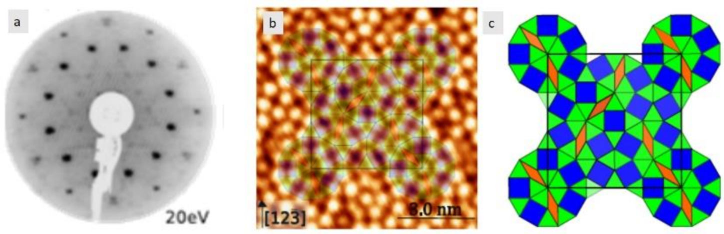

Figure: LEED pattern (left), STM image (middle) and model (right) of the giant square approximant obtained by reducing $SrTiO_3$ thin films deposited on Pt(111) buffer layer on sapphire (0001).

References

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