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Observation of a two-dimensional electron gas at $CaTiO_3$ film surfaces

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ABSTRACT

The two-dimensional electron gas at the surface of titanates gathered attention due to its potential to replace conventional silicon based semiconductors in the future. In this study, we investigated films of the parent perovskite $CaTiO_3$, grown by pulsed laser deposition, by means of angular-resolved photoelectron spectroscopy. The films show a $c(4 \times 2)$ surface reconstruction after the growth that is reduced to a $p(2 \times 2)$ reconstruction under UV-light. At the $CaTiO_3$ film surface, a two-dimensional electron gas (2DEG) is found with an occupied band width of 400 meV. With our findings $CaTiO_3$ is added to the group of oxides with a 2DEG at their surface. Our study widens the phase space to investigate strontium and barium doped $CaTiO_3$ and the interplay of ferroelectric properties with the 2DEG at oxide surfaces. This could open up new paths to tailor two-dimensional transport properties of these systems towards possible applications.

1. Introduction

The discovery of a two-dimensional electronic state at the interface of $LaAlO_3$ and $SrTiO_3$ [1] triggered research on other oxide interfaces where similar states were found [2–5]. These two-dimensional states at interfaces of complex oxides give rise to different phenomena such as superconductivity [6,7], metal-insulator transitions [8,9] or magnetism [10]. More recently, a two-dimensional electron gas (2DEG) was also found on clean $SrTiO_3$ and $KTaO_3$ (001) surfaces [11–15]. These states at the vacuum interface can, in contrast to the burried interface states, be more easily probed by angular-resolved photoelectron spectroscopy (ARPES) in the UV-range, revealing their band structure in reciprocal space. It was shown by spin-resolved ARPES, that the 2DEG at the surface of $SrTiO_3$ exhibits a Rashba-like spin splitting of approximately 100 meV, likely enhanced due to the presence of (anti)ferroelectricity and magnetic order at the sample surface [16]. The strong electron-phonon coupling of the TiO_2 surface [17,18], which depends on carrier density, is most likely responsible for a drastic rise of the superconducting transition temperature of a monolayer FeSe deposited on top [19,20]. The variety of observed properties makes these oxide-based two-dimensional states an ideal platform to explore new functionalities and possible ways towards device application in the future.

$CaTiO_3$ is the very first discovered perovskite of the transition metal oxide (TMO) family and is thus closely related to the members recent studies focus on. Like $SrTiO_3$, $KTaO_3$ and TiO_2 (all compounds shown to host a 2DEG at their surface) $CaTiO_3$ is classified as an incipient ferroelectric or quantum paraelectric material, meaning that it is very close to a ferroelectric phase [21]. Intermixtures of $SrTiO_3$, $BaTiO_3$ and $CaTiO_3$ form a rich phase diagram, especially regarding the ferroelectric properties, exhibiting para-, ferro- and antiferro-electric phases [22–24]. Pure, crystalline $CaTiO_3$ undergoes two phase transitions at elevated temperatures; from orthorhombic to tetragonal at 1512 K and from tetragonal to cubic at 1635 K [25]. According to band structure calculations for the orthorhombic and cubic crystal lattice the band gap is 2.43 eV or 2.0 eV, respectively [26,27]. In today's electronics, $CaTiO_3$ is widely used as a ceramic and as rare-earth doped phosphor with excellent luminescence properties.

In this work, films of 20 unit cells $CaTiO_3$ grown by pulsed laser deposition (PLD) on Nb:$SrTiO_3$ substrates were studied by

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UV-ARPES and X-ray photoelectron spectroscopy (XPS). Our low-energy electron diffraction (LEED) measurements show that the surface of the $CaTiO_3$ films reconstruct while XPS indicates a TiO_2 terminated surface. In addition, observed surface plasmon loss features in the region of the Ti 2*p* core levels suggest the presence of metallic states at the surface of the films. Using ARPES, we found that these metallic states show a purely two-dimensional dispersion with a band width of ≈400 meV. Folded bands are visible as an effect of the surface reconstruction. In contrast to $SrTiO_3$ where the mixture of two- and three-dimensional states is observed [15], this 2DEG is the only metallic state present at the surface. Therefore the $CaTiO_3$ surface states yield easy access to directly manipulate the two-dimensional transport properties of this system by surface structure or gating. Furthermore, with the ferroelectricity introduced in $Sr_xCa_{1-x}TiO_3$ this is a promising material to investigate the influence of ferroelectricity and the connected electric fields on the 2DEG at the surface of perovskites.

2. Materials and experimental method

The $CaTiO_3$ films of 20 unit cell thickness used for this study where grown by PLD on commercial TiO_2 terminated $SrTiO_3$ (001) substrates with a niobium doping of 0.5 wt% (Twente Solid State Technology BV). The growth was performed at a substrate temperature of 680 °C in partial oxygen pressure of 5×10^{-5} mbar. The growth process and film thickness was monitored by reflection high-energy electron diffraction. The prepared films were *in-situ* transferred to the experimental station at the Surface and Interface Spectroscopy beam line of the Swiss Light Source at the Paul Scherrer Institut under ultra high vacuum (UHV) conditions and measured without further treatment. The sample was held at a temperature of 20 K in pressures better than 8×10^{-11} mbar during the measurements. Photoemission spectra (XPS and ARPES) were taken using a Scienta R4000 hemispherical electron analyzer and circular polarized synchrotron light. LEED patterns were obtained at 20 K before the ARPES measurements. The atomic force microscopy (AFM) topography was measured at the NanoXAS beam line of the Swiss Light Source at the Paul Scherrer Institut with the sample at room temperature in UHV environment.

The orthorhombic unit cell of bulk crystalline $CaTiO_3$ has lattice parameters of $a = 5.367$ Å, $b = 7.644$ Å and $c = 5.444$ Å [28]. An approximate representation of the orthorhombic unit cell can be made by a pseudo-cubic unit cell as marked in Fig. 1(a). The lattice parameters of the pseudo-cubic unit cell $a/\sqrt{2} \approx b/2 \approx c/\sqrt{2} \approx$ 3.822 Å are similar to cubic $SrTiO_3$ with a lattice mismatch of approximately 2%.

In LEED we can identify the primary diffraction spots corresponding to the pseudo-cubic unit cell. Further we observe spots indicating a c(4 × 2) surface reconstruction of the pseudo-cubic lattice with domains rotated 90° with respect to each other (see Fig. 1(b) and (c)). The (1 × 1) TiO_2 terminated surface at the vacuum interface of TMO perovskites might be unstable due to the unshared oxygen atom of the TiO_2 polyhedron sticking out of the surface. Of the surface reconstructions reported for the closely related $SrTiO_3$ system, c(4 × 2) reconstruction has also been observed [29–32].

The AFM topography in Fig. 1(d) shows that the films are of low roughness and follow the substrate steps with a terrace size of approximately 200 nm. However, the AFM measurements do not have the resolution required to observe the surface reconstruction. The observed presence of domain walls is a further indication of the existence of multiple rotated domains corroborating the LEED data.

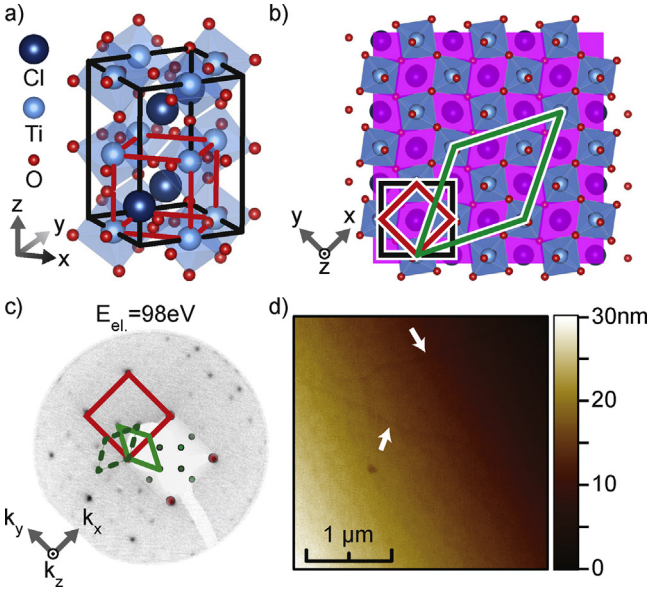

Fig. 1. (a) Orthorhombic unit cell of bulk $CaTiO_3$ (black) with the simplified pseudo-cubic unit cell (red). (b) Crystal surface of TiO_2 terminated bulk $CaTiO_3$ in (001) direction with the orthorhombic (black) and pseudo-cubic (red) surface unit cell and the observed c(4 × 2) reconstruction with respect to the pseudo-cubic lattice (green). (c) LEED image with the marked pseudo-cubic Brillouin zone (red) and c(4 × 2) reconstruction (green) and the 90° rotated domain (green dashed). White square inset shows an overlay with the calculated LEED spots for a c(4 × 2) reconstructed surface. (d) AFM topography of the surface. Arrows indicate the domain walls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

The XPS spectrum of the films in Fig. 2, measured with a photon energy of $h\nu = 600$ eV, shows clear signatures of the expected calcium, titanium and oxygen core levels with no detectable contamination. Comparing the spectra taken with the sample surface normal to the analyzer to the more surface sensitive measurement taken at an angle of 45° between the sample normal and the analyzer axis (see sketch inset in Fig. 2) we can confirm the TiO_2 termination of the grown films. This termination of the film surface is expected due to the TiO_2 termination of the $SrTiO_3$ substrate [33]. When comparing the peak areas (A_i) after background subtraction the ratio A_{Ca2p}/A_{Ti2p} of 0.75 at normal emission is significantly higher than the ratio of 0.65 measured at an emission angle of 45°.

All the titanium peaks show a shoulder towards lower binding energy, indicating the existence of titanium atoms with different valency. The increase of the surface located Ti 3^+ shoulder is a light induced effect commonly observed in this class of materials [15]. The appearance of Ti 3^+ ions is likely linked to a distortion of the TiO_3 octahedron, for example due to the creation of oxygen vacancies in the surface region and/or a structural rearrangement and buckling of the surface layers.

The Ti 2*p* as well as the Ca 2*p* core levels show plasmon loss peaks in their shake-up tail with an energy loss of 13.2 eV for titanium and 9 eV for calcium. Plasmon loss peaks with this loss energy of the Ti 2*p* core levels have been observed in other perovskites. The measured plasmon energy corresponds to surface plasmons present in TiO_2 where the plasmons are trapped at the interface of the metallic surface and the dielectric bulk due to the sudden change in dielectric constant [34–37].

Consequently, we also expect metallic states to be present at the surface of our $CaTiO_3$ films. Indeed, the ARPES measurements in Fig. 3 show an electron-like surface state. The scan over a wide range

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