

Piezoresponse in the light of surface adsorbates: Relevance of defined surface conditions for perovskite materials

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We report on the influence of a surface layer prevailing on perovskites on the piezoelectricity measured by piezoresponse force microscopy. Surface sensitive measurements show that this layer consists of chemisorbates and physisorbates. The surface layer can be removed to a large extent by heating the sample under ultrahigh vacuum conditions. It is shown that the effect of this treatment on the piezoresponse of the material is significant as the potential difference applied to the sample is no longer reduced by a voltage drop across the adsorbate layer. As a consequence the internal electric field is higher in comparison to the presence of a layer and so the piezoresponse is higher as well. © 2004 American Institute of Physics. [DOI: 10.1063/1.1799241]

Piezoresponse force microscopy (PFM) is a powerful method to analyze local piezoelectric activity and to study the domain structure.¹⁻⁷ This method plays a significant role in the study of the ferroelectric limit, i.e., the dimension below which the order parameters (P_S) cannot be sustained in the material.⁸⁻¹⁰ Several problems arise when the dimensions of ferroelectric thin films are continually decreased: the control of the composition, morphology, and the screening effect is strongly connected to the physical properties of the surface layer.¹¹ The reconstruction or relaxation contribute to screening phenomena. Another important effect for the surface is the adsorbate layer which drastically influences the applied electric field. In this letter our focus lies on the adsorbates on the surface, their influence on PFM measurements, and a method on how they can be removed.

This problem arose when interpreting PFM measurements of chemical solution deposition (CSD) fabricated BaTiO₃ samples. Figure 1 shows the in-plane piezoresponse of a CSD fabricated BaTiO₃ sample depicting domains <10 nm (regions B and C) measured under *ex situ* conditions. In other areas (region A) no piezoelectric activity can be seen. With PFM it is impossible to determine if the chemical composition is different in regions A and B, the surface is covered by something or if size-effects are responsible for the different piezoelectric activity in the two regions.

X-ray photoelectron spectroscopy (XPS) with Al_{K α} -mono excitation has shown that BaTiO₃ thin films prepared by CSD are globally stoichiometric, but different valencies of Ti (+4 and +3) as well as a tail of additional states with 2*p* character can be observed. This indicates an inhomogeneous chemical composition.¹² On the other hand the surface layer of a BaTiO₃ single crystal surface presented a perfect electronic structure. Only Ba core lines have an additional surface compound. In order to have a defined chemical compo-

sition and to single out the other effects we studied the adsorbates on a stoichiometric archetype perovskite, a 5 mm × 5 mm × 1 mm BaTiO₃(100)_{pc} single crystal epipolished on both sides (rms ≈ 2 nm). The structure of the real surface layer of BaTiO₃ single crystal shows two additional components.

An XPS measurement at room temperature of the O 1s core line is shown in Fig. 2. Three different compounds of core lines can be detected: The oxygen in the lattice (component 1) of the BaTiO₃ with an energy of 529.8 eV and two additional core lines with higher binding energies (component 2 with 531.5 eV and component 3 with 533.8 eV). According to Ref. 13 component 2 can be regarded as chemisorbed CO or CO₂ and component 3 can be assumed to be physisorbed OH or H₂O. Measurements at different angles at room temperature have shown that under grazing incidence the intensity of component 3 is reduced indicating that this peak comes from the layer on top of the crystal. A schematic cross section of the stacked layers of the covered substrate is given in the inset in Fig. 3.

In situ XPS measurements show that above ≈350 °C H₂O and OH is completely removed (Fig. 3). At room temperature the C 1s core lines present three different compounds ($E_1=290.1$ eV, $E_2=288.8$ eV, $E_3=286.6$ eV). After

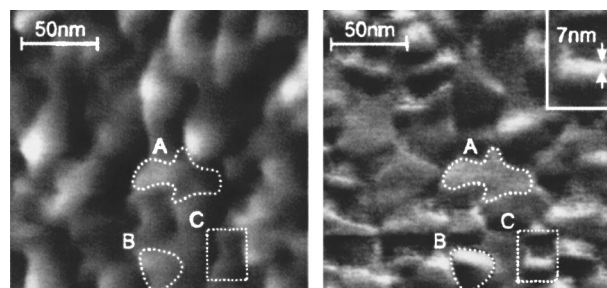


FIG. 1. Topography (left) and in-plane piezoresponse measurement (right) of BaTiO₃ sample prepared by CSD. The inset in the piezoresponse measurement displays an enlargement of area C and shows a domain of 7 nm.

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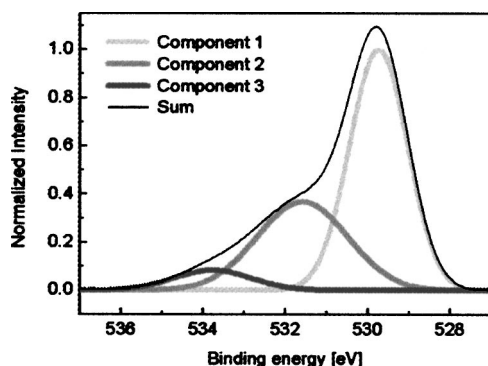


FIG. 2. O 1s core lines with additional components. Component 1 has been used as reference for calculating the binding energies.

thermal desorption at 800 °C the two compounds with the higher energy have been removed, only the core line E_3 is observed, but with a drastically reduced intensity. After the sample has been heated under ultrahigh vacuum (UHV) to 800 °C it was cooled down *in situ*. No change in the core lines could be detected after cooling. A short exposure to ambient surrounding results in a restoration of the physisorbate layer of the surface similar to the condition before heating.

All PFM measurements were done on a modified Jeol 4210 AFM fitted with the commercially available heating element. To facilitate desorption the sample was heated and cooled under high vacuum (3×10^{-5} mbar) conditions. For the piezoresponse measurements of the single crystal a voltage of $U=50V_{pp}$ at 7 kHz was applied to the PtIr₅ coated cantilever (“ContPt” from Nanosensors, $f_0=13$ kHz). The magnitude of the piezoresponse was checked to be a function of the applied generator voltage.

For the presented measurements the aim was not to maximize the resolution as shown in Fig. 1 but to determine an average value of the piezoactivity over a relative large area as a function of the physisorbates. In the single crystal the inherent domains or those which were created by heating the sample over the Curie temperature T_C of 120 °C are relatively large, as can be seen by the inspection with an optical

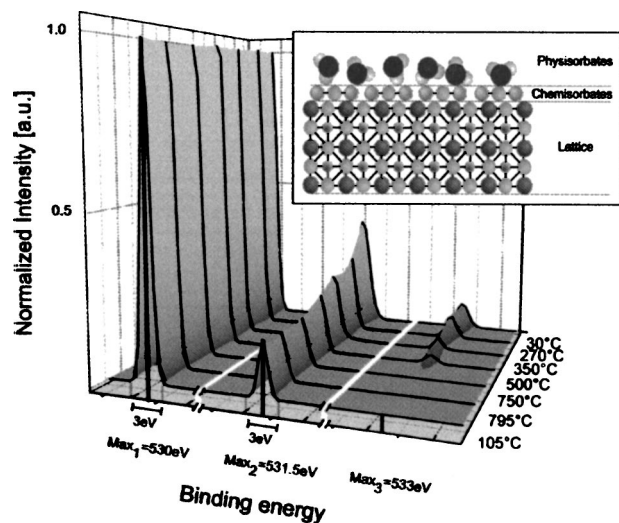


FIG. 3. Deconvoluted XPS *in situ* measurement of the 1s energy state of different oxygen compounds as a function of temperature (heating and subsequent cooling). Inset: Cross section of the sample indicating the adsorbates.

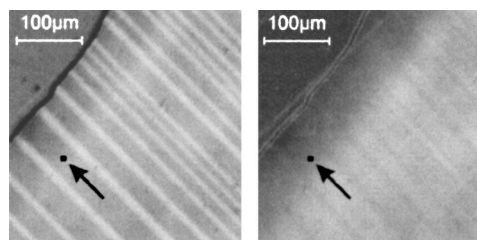


FIG. 4. *a* and *c* domains of the BaTiO₃ crystal as observed by an optical polarization microscope. In the right image the polarization of the light has been turned 90° relative to the left image. The arrows point to a typical place of an *a* domain where the following PFM investigations have been made.

polarization microscope (Fig. 4). In all experiments PFM was first done under ambient conditions, thereafter under high vacuum. To be in line with the XPS measurements the sample was then heated under high vacuum to 350 °C and kept at this temperature for 5 min. After it was cooled down to room temperature the piezoactivity was measured. Thereafter the sample was exposed to ambient conditions for a few minutes before another PFM scan was performed. In this order new domains have not been created between the first two and the last two measurements. Between these two sets of measurements the crystal was heated above T_C so these results of the piezoelectric activity may not be compared directly as the domain structure might have changed. In all four scans (scan size $20 \mu\text{m} \times 20 \mu\text{m}$) the same area of the sample was examined. The whole series was repeated four times at different places. The total piezoelectric activity of the scan has been calculated as the average of the absolute value of each measurement point. From the optical inspection (Fig. 4) it can be seen that most domains are *a* domains which correspond to the in-plane signal of PFM. The average piezoelectric activity of all experiments is shown in Table I.

The influence of the enhanced piezoactivity given in Table I is illustrated in Fig. 5. The images on the left hand side show the topography whereas the images on the right hand side are the in-plane piezoactivity. The same single domain area is shown under vacuum after heating to 350 °C (top row) and after exposure to ambient conditions (bottom row).

Our measurements of BaTiO₃(100)_{pc} single crystals revealed that a chemi- and physisorbate layer is prevalent on the surface of the perovskite leading to an additional potential drop between the tip and the sample. In PFM measurements the layer reduces the effective amplitude of the piezoresponse by 250% in comparison to the adsorbate-free surface. Similar results were observed by a kelvin probe microscopy on silicon structures covered by a hydrophilic oxide layer.¹⁴ To be able to determine qualitative values for d_{ij} only samples which have been freed *in situ* of the physisorbates and chemisorbates can be used. The desorption measurements done by XPS under UHV conditions gave us the opportunity

TABLE I. Average piezoelectric activity under different surface conditions.

Condition	Piezoresponse
Ambient	100%
High vacuum	115%
High vacuum after heating to 350 °C	250%
Ambient after heating cycle	100%

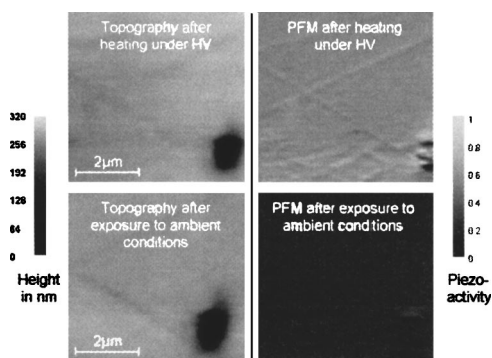


FIG. 5. $6\ \mu\text{m} \times 6\ \mu\text{m}$ scan of topography (left) and piezoresponse (right). The top images are under HV after being heated to $350\ ^\circ\text{C}$ while the bottom images were made after exposition of the “cleaned surface” in air. These measurements were taken in a single domain area as indicated by the small squares in Fig. 4. The topography is comparable whereas the piezoactivity shows drastic differences.

to determine the critical desorption temperature required to free the BaTiO_3 surface of OH groups. This temperature is in the range of $350\ ^\circ\text{C}$. The relative high temperature suggests that the OH groups and the last monolayers of BaTiO_3 have formed a chemical bond by electron transfer. We assume that the BaO-terminated surfaces react in *ex situ* conditions to form BaOH_2 which decomposes under vacuum at higher temperatures (for bulk materials $\approx 370\ ^\circ\text{C}$ ¹⁵): $\text{Ba}(\text{OH})_2 \rightarrow \text{BaO} + \text{H}_2\text{O}$. However the analysis of the C $1s$ line shows that some CH_x are still present after the heat treatment indicating that a complete removal of the adsorbates from the BaTiO_3 surface is impossible. In order to determine local

quantitative values of the piezoelectric constant or in the quest for the ferroelectric limit numerous problems have to be overcome. When doing PFM measurements under UHV conditions after *in situ* heating, the real surface is to a large extent adsorbate-free. The other problems like controlling the composition, morphology and structure of the thin film are further challenges to be addressed.

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