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Contact mode potentiometric measurements with an atomic force microscope on high resistive perovskite thin films

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Abstract

We have investigated the potential distribution on barium titanate thin films with an atomic force microscope in contact mode to find answers to the important question of local electric conductivity. A detailed knowledge about the electrical transport mechanisms is very important to receive a sound operation for highly integrated circuits such as non-volatile memory cells. With this paper we present an advanced method to perform these potential scans in galvanic contact. Key element of the set-up is an optimized electrometer amplifier which has an electronically reduced input capacitance avoiding the work function influence on the surface potential scan. To demonstrate the capability of our set-up we present example measurements performed on thermally reduced $BaTiO_3$ thin films.

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Keywords: Electrical properties; Atomic force microscope; Defects; Surfaces

1. Introduction

Perovskite type oxides like $BaTiO_3$ or $SrTiO_3$ have attracted increasing attention due to their outstanding electrical properties. While the macroscopic behaviour of single crystals and bulk ceramics are already extensively investigated thin films gain more and more interest.[1] These thin films show distinct differences in their material properties.[2–4] Especially, the macroscopic leakage currents are mainly attributed to electrical transport mechanisms in the nanometer regime.

During former measurements we found paths of low conductivity on a columnar grown $BaTiO_3$ film in a top down electrode configuration.[5] To further investigate these paths we changed the top-down to a planar electrode arrangement. Therefore, we placed two planar electrodes on the films top side to apply a field across the gap in between the electrodes. To find paths of current transport we observed the surface potential distribution with the so called scanning voltage microscopy (SVM).[6] Surface potential scans are used to obtain surface charges, contact potentials, and paths of current transport such as regions of low conductivity.[7]

Since many years the Kelvin force microscopy (KFM) for the atomic force microscope (AFM)[8] and also the scanning tunneling potentiometry for the scanning tunneling microscope (STM)[9] are widely used to perform these surface potential measurements. The KFM uses the non-contact mode of an AFM and applies an ac signal to the cantilever tip to utilize the capacitive coupling in between surface and tip. An additional bias voltage on the tip is used to zero the resulting current and serve as a reference which provides the local potential of the surface.

A parasitic effect of the Kelvin probe method is that the measured potential is influenced by the work function of the surface layer. Therefore, we investigated the surface by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) of thermally reduced $BaTiO_3$. These pre-measurements show a distribution of BaO and Ti_nO_{2n-1}

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phases on the surface.[5] Because of this inhomogeneous distribution of different atoms in the surface layer we developed a method for direct potential scanning with galvanic contact to the sample surface. So the work functions of the different phases have no negative influence on the measurements. For this we used an AFM in contact mode as a kind of nano-probe and a modified electrometer amplifier with an electronically reduced input capacitance. Due to the high resistance of the $BaTiO_3$ it is essential to use an electrometer with an extreme small input capacitance and a high input resistance. Only in this case it is possible to perform topography and surface potential scans simultaneous with a speed for which we can neglect the drift phenomena during the scan process. The amplifier has an input capacitance down to the range of 50–20 fF and an input resistance in the range of $10^{15}\ \Omega$.

2. Experimental

2.1. Sample preparation

Our measurements are performed on $BaTiO_3$ thin films of 30 nm thickness deposited on sapphire. The films are generated by a chemical solution deposition process (CSD).[10,11] They have no bottom electrodes but two planar top electrodes to apply an electric field across the gap in between the two electrodes. We build samples with different gap sizes from 1 μm to 10 μm. The electrode length is much longer as the gap size to catch a homogeneous field distribution across the whole gap. To find a conductivity less than 1 TΩ in between the electrodes we reduced the sample thermally. This thermal reduction was performed in a reaction chamber in which the samples were heated up to 750 °C for 30 min. The chamber was first evacuated down to the regime of 10^{-5} Pa and finally filled up with clean H_2 (99.999%) to a pressure of 1000 mbar. Afterwards we shock cooled the samples down to room temperature in a few seconds by a water cooling system to freeze the defect concentration of the $BaTiO_3$ as it is described in.[12] With this procedure we reached macroscopic resistances in between the electrodes of less than 1 GΩ.

2.2. Measurement set-up

We used a modified Jeol JSPM 4210 in contact mode and a PtIr cantilever with an apex radius of 20 nm as our nano-probe. In advanced mode it is possible to measure the topography and the surface potential simultaneous. In this mode the system records 256 × 256 points with a measurement time of nearly $t = 1$ ms per point. This leads to a scan time of a few minutes. With a source resistance R of 1 GΩ and a measurement time of 1 ms per point the electrometer should have an input capacitance of less than 200 fF as easily can be calculated with $\tau = RC$ and $t \approx 5\tau$.

Therefore, we used the electrometer amplifier EMA50F of aixACCT Systems with an electronically reduced input capacitance of below 50 fF. The concept of our amplifier requires a triaxial shielding in between the amplifier and the probe tip, which took into account the investigations of Prume et al.[13]

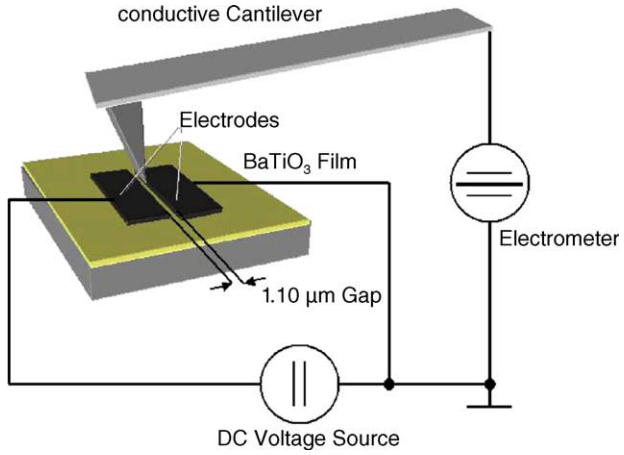

Fig. 1. Measurement set-up with AFM-Cantilever as probe tip, the voltage source and the modified electrometer.

We performed our measurements at high vacuum with pressures of 10^{-4} Pa to prevent the surface from further contamination. But because of the reduction chamber we prepared the samples ex situ. This means that we have to expect a remaining layer of contamination.[14] The two planar electrodes are connected to a battery with an regulated dc output of 5 V. This kind of voltage supply affords us to reduce the noise level to a minimum. The whole measurement set-up is shown in Fig. 1.

3. Measurements

To verify our measurement set-up we performed a simple check. We connected only one electrode with a defined potential of 5.0 V and left the other electrode floating. In case of a source resistance bigger than the input resistance of the electrometer a non constant potential distribution or the saturation voltage of the amplifier should be observed. We found a potential of 5 V across the whole gap and on the floating electrode. Furthermore, we repeated this experiment with a voltage of zero volts to find some local potentials due to polarization charges and found a potential image of nearly zero volts. This confirms us to be able to perform surface potential scans with our set-up.

In comparison to our top-down current measurements we found a nearly constant potential on single grains as can be seen in Figs. 2 and 3. There is a correlation of grains as well as grain boundaries and the potential on it. The grain surfaces seems to be more conductive than the grain boundaries. This kind of surface potential distribution can be interpreted for high resistive grain boundaries and more conductive grains (Fig. 4).

Furthermore, we found some kind of islands of higher potential in a region of lower potential as can be seen in Fig.

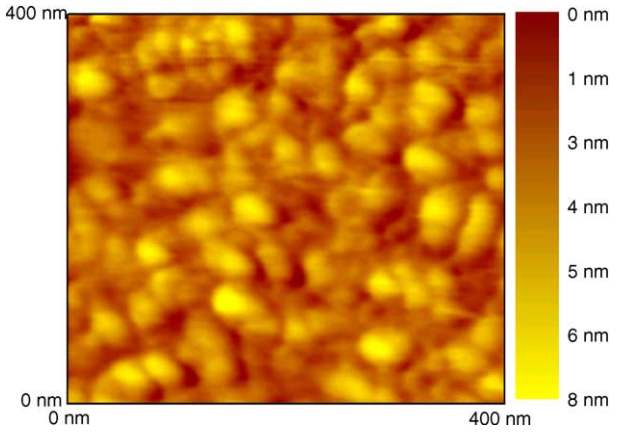

Fig. 2. Topography scan of a region within a gap of 4 μm on $BaTiO_3$ thin film of 30 nm thickness.

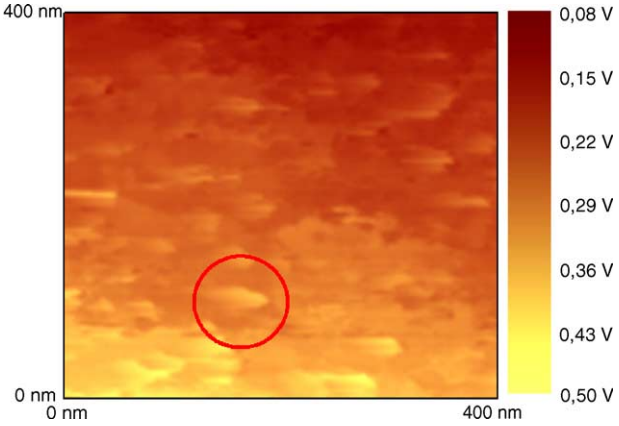

Fig. 3. Surface potential scan simultaneously recorded to Fig. 2 on $BaTiO_3$ thin film of 30 nm thickness. The red circle marks a grain of high potential in a region of lower potential.

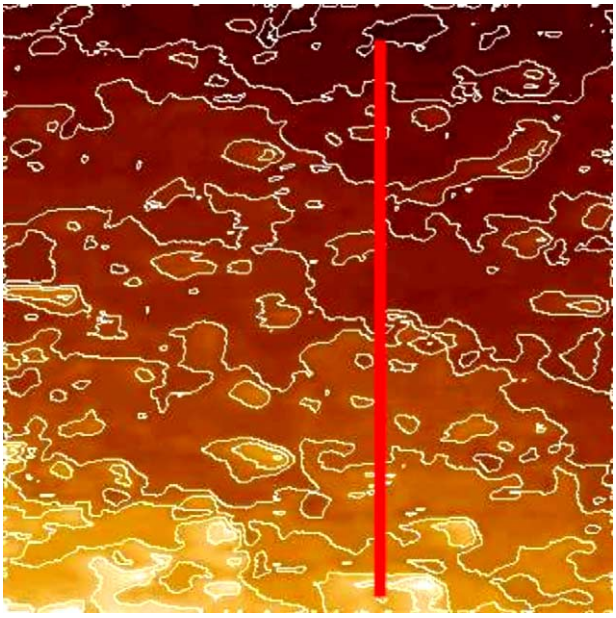

Fig. 4. Contours of regions of equal potential from Fig. 3. The red line indicates the cut of Fig. 5.

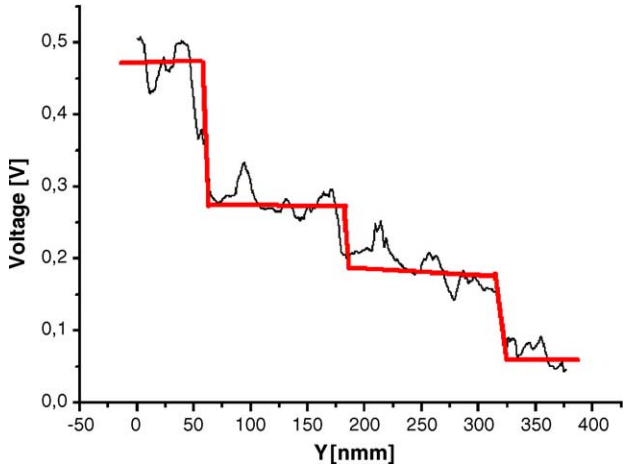

Fig. 5. Cut through the potential image of Fig. 3 with an indication of plateaus of equal potential (red line).

3 marked with the circle and in Fig. 5. These islands can be caused by some sub-surface conducting paths which are insulated to the bordering areas. These paths may be created through segregation effects of BaO and TiO due to the reduction process as it was published by Szot et al.[15] for $KNbO_3$. In between the grains we measured an electric field of approximately 10^5 V cm^{-1} (see Fig. 5).

4. Discussion

With this paper we demonstrate an advanced method to perform surface potential scans. We used a optimized electrometer amplifier with reduced input capacitance in direct galvanic contact with an AFM cantilever as a nano probe. With this set-up comparative and simultaneous measurements of topography and potential distribution of high resistive thin films are possible.

This method of surface potential scan was used to measure the potential distribution of thermally reduced $BaTiO_3$ in between two planar electrodes. Our measurements show a clear correlation of plateaus of equal potential and the topography of grains. As we expected from earlier current and SIMS measurements[5] we found a heterogeneous distribution of surface potential which may be caused by phases of BaO and TiO.

The low input capacitance of the electrometer amplifier in combination with our shielding concept allows us now to investigate high resistive materials with SVM.

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