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

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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 a new 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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INTRODUCTION

Perovskite type oxides like $BaTiO_3$ or $SrTiO_3$ have attracted increasing attention due to their outstanding electrical porperties. 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 effects 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. Surface potential scans are

used to obtain surface charges, contact potentials, and paths of current transport such as regions of low conductivity [6].

Since many years the kelvin force microscopy (KFM) is widely used to perform these surface potential measurements [7]. This method uses the non-contact mode of an atomic force microscope (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 also as a reference signal 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 secondary ion mass spectrometry (SIMS) of thermally reduced $BaTiO_3$. These pre-measurements show a distribution of BaO and TiO 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 to 20 fF and an input resistance in the range of 10^{-15} Ω.

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EXPERIMENTAL

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) [9,10]. 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 up to 10 µm. The electrode length is much longer as the gap size to catch a consistent 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 minutes. 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 (this means $pO_2 = 10^{-2}$ 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 [11]. With this procedure we reached macroscopic resistances in between the electrodes of less than 1 GΩ.

Measurement set-up

We used a modified Jeol JSPM 4210 in contact mode and a PtIr cantilever with an apex size 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 by 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 scan rate of 1 ms the electrometer should have an input capacitance of less than 200 fF as easily can be calculated with $\tau = R \cdot C$ and $t \approx 5 \cdot \tau$.

Therefore we used an electrometer amplifier 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. Based on investigations of Prume et al. [11] that the cantilever arm has a capacitance of a few fF, we only shielded the base of the cantilever without the arm.

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 [12].

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 Figure 1.

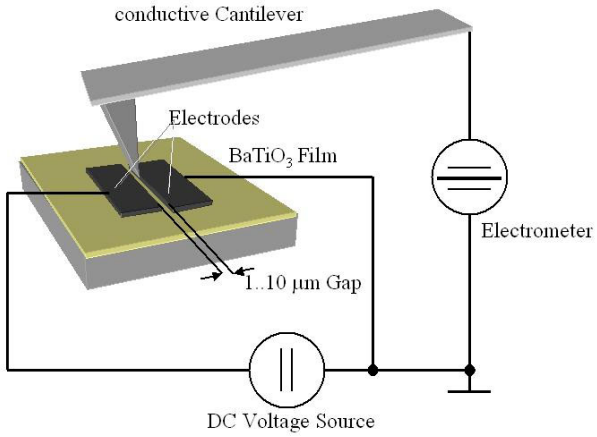

Figure 1: Measurement set-up with AFM-Cantilever as probe tip, the voltage source, and the modified electrometer

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.

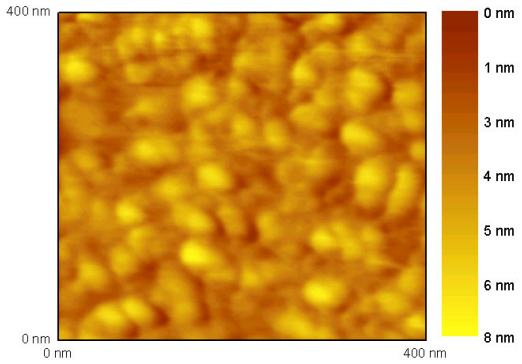

Figure 2: Topography scan of a region within a gap of 4 µm on $BaTiO_3$ thin film of 30 nm thickness

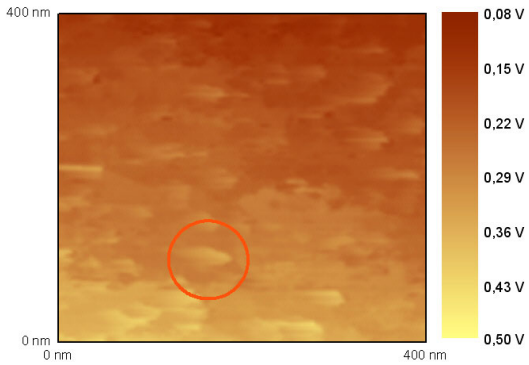

Figure 3: Surface potential scan recorded simultaneously to Figure 2 on $BaTiO_3$ thin film of 30 nm thickness; The red circle marks a grain of high potential in a region of lower potential

In comparison to our top-down current measurements we found a nearly constant potential on single grains as can be seen in Figures 2 and 3. There is a correlation of grains as well as grain boundaries and the potential on it. The resistance of 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.

Furthermore we found some kind of islands of higher potential in a region of lower potential as can be seen in Figure 3 marked with the circle and in Figure 4. 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. [13] for $KNbO_3$.

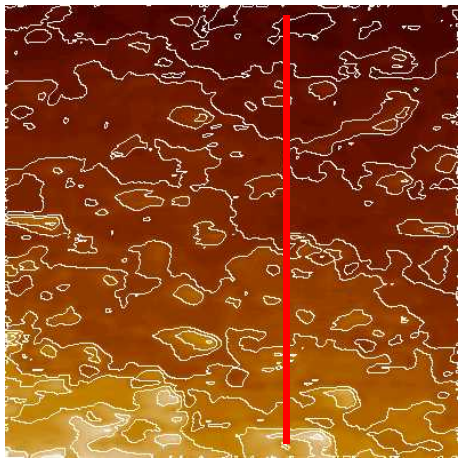

Figure 4: Contours of regions of equal potential from Figure 3; the red line indicates the cut of Figure 5

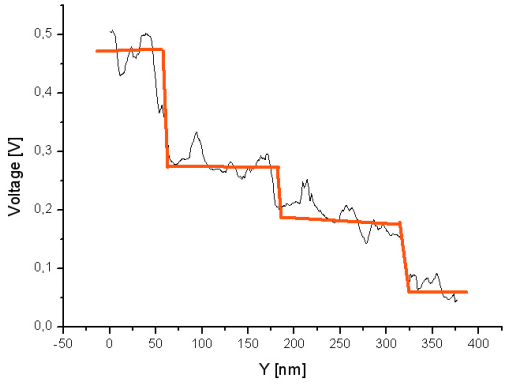

Figure 5: Cut through the potential image of Figure 4 with an indication of plateaus of equal potential

DISCUSSION

With this paper we demonstrate a new 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 (see figure 5). 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.

References

[1] C. Ohly, S. Hoffmann, K. Szot, and R. Waser, "High temperature conductivity behavior of doped $SrTiO_3$ thin films", *Integrated Ferroelectrics*, **33**, 1-4, 363-72 (2001)

[2] W. Hofmann, S. Hoffmann, and R. Waser, "Advanced Chemical Deposition Techniques - from research to Production", *Thin Solid Films*, **305**,66 (1997)

[3] R. Waser and D. M. Smyth, *Ferroelectric Thin Films: Synthesis and Basic Properties*, **47** (1996)

[4] K. M. Schindler, A. Kindlein, C. Hagendorf, H. T. Langhammer, and H. Neddermeyer, "Surface physical studies of barium titanate ceramics", conference paper *21st European Conference on Surface Science* (2002)

[5] B. Reichenberg, K. Szot, T. Schneller, S. Tiedke, and R. Waser, "Inhomogeneous local conductivitiy induced by thermal reduction in $BaTiO_3$ thin films and single crystals", *Conference Paper: European Meeting on Ferroelectrics*, (2003)

[6] Sergei V. Kalinin, and Dawn A. Bonnell, "Surface potential at surface-interface junctions in $SrTiO_3$ bicrystals", *Physical Review B*, **62**, 15, 10419-10430 (2000)

[7] M. Nonnenmacher. M. P. O'Boyle, and H. K. Wickramasinghe, "Kelvin Probe Force Microscopy", *Applied Physics Letters*, **58**, 2921-23 (1991)

[8] S. Hoffmann and R. Waser, "Control of the Morphology of CSD-prepared $(Ba,Sr)TiO_3$ Thin Films", *Journal of the European Ceramic Society*, **19**, 1339-1343, (1999)

[9] R. Waser, T. Schneller, S. Hoffmann-Eifert, and P. Ehrhart, "Advanced Chemical Deposition Techniques - from research to Production", *Integrated Ferroelectrics*, **36**, 3-20, (2001)

[10] C. Ohly, S. Hoffmann, K. Szot, and R. Waser, "Electrical conductivity and segregation effects of doped $SrTiO_3$ thin films", *Journal of the European Ceramic Society*, **21**, 1673-1676 (2001)

[11] K. Prume, A. Roelofs, T. Schmitz, B. Reichenberg, S. Tiedke, and R. Waser, "Compensation of the parasitic capacitance of a SFM cantilever used for measurements on ferroelectric capacitors of submicron size by means of finite element simulations", *Japanese Journal of Applied Physics, Part 1*, **41**, 7198 (2002)

[12] F. Peter, K. Szot, B. Reichenberg, J. Szade, S. Tiedke, and R. Waser, "Piezoresponse in the light of surface contamination - Relevance of defined surface conditions", to be published

[13] K. Szot, W. Speier, S. Cramm, J. Heroins, Ch. Freiburg, R. Waser, M. Pawelczyk, and W. Eberhardt, "Surface layer on $KNbO_3$ and the hysteresis loop anomaly", *J. Phys. Chem. Solids*, **57**, 11, 1765-1775, (1996)