



Nanocrystalline Alkaline Earth Titanates and Their Conductivity Characteristics Under Changing Oxygen Ambients

CHRISTIAN OHLY, SUSANNE HOFFMANN-EIFERT & RAINER WASER

Institute for Solid State Research, Electroceramic Materials, Research Centre Jülich, 52425 Jülich, Germany

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Abstract. This work presents the first systematic study of conductivity characteristics of alkaline earth titanates in the form of polycrystalline and heteroepitaxial thin films as well as nanocrystalline ceramics as a function of temperature (between 600°C and 1000°C) and continuously adjustable oxygen partial pressures ranging from 10^{-20} bar to 1 bar. Compared to the well-known $\log \sigma$ - $\log pO_2$ profiles of single crystals, the conductivity behavior of CSD-prepared, polycrystalline $SrTiO_3$ thin films with a feature size of about 50 nm differs radically. The most prominent characteristics are a sharp drop under reducing conditions followed by a broad plateau region. Tailored investigations on heteroepitaxial as well as polycrystalline thin films grown by PLD and especially by studies on nanocrystalline $BaTiO_3$ ceramics with a mean grain size of ≤ 100 nm allowed an unambiguous assignment of the described effects to the nanocrystalline morphology of the samples.

Keywords: titanates, electrical conductivity, thin films, nanocrystalline ceramics, grain boundary density

1. Introduction

In the fast growing field of information storage and processing, state-of-the-art integrated devices combine the classical semiconductors with electroceramic materials. Major examples are DRAMs (dynamic random access memories), FETs (field effect transistors) or nonvolatile FeRAMs (ferroelectric random access memories). Further applications can be found in mobile communications or sensors [1]. Among the most promising and widely investigated material systems are the titanate-based solid solution series $Ba_{1-x}Sr_xTiO_3$ as a high- κ dielectric and $PbZr_{1-y}Ti_yO_3$ as a ferroelectric material. As a consequence of the ongoing reduction of feature sizes, the dimensions of the integrated thin films have decreased to several ten nanometers on the lateral scale and down to a few nanometers in thickness. Also, the particle size of ultra-fine titanate powders as primary materials for LTCC (low temperature cofired ceramic) components is entering the region of 10 nm and less, offering the possibility of synthesizing nanocrystalline ceramics of similar proportions [2].

For integrated polycrystalline titanate thin films, which are of main interest here, the correlation between the morphology and the electrical properties is of central importance. However, the physical description of nanocrystalline titanates, which is necessary for a precise tailoring of device characteristics, is still difficult because properties often significantly change with decreasing dimensions. To describe the electrical conductivity characteristics of single crystal and bulk ceramic titanates and their relation to parameters like temperature, oxygen atmosphere, dopant incorporation and especially the important influence of blocking grain boundaries, the point defect chemistry has been applied successfully (e.g. [3] and references therein). Additionally, models assigning the inhomogeneity of polycrystalline materials have been formulated [4].

The aim of our investigations is to obtain for the first time a comprehensive insight into the defect chemical behavior of titanate-based thin films and nanocrystalline ceramics with feature sizes of a few ten nanometers, which are smaller than the typical depletion layer width at grain boundaries in coarse grained acceptor doped $SrTiO_3$, which extends to ~ 100 nm.

2. Experimental

2.1. Sample Preparation

Utilizing various methods, it was possible to prepare the SrTiO₃ thin films with different morphologies and densities of interfaces ranging from polycrystalline to heteroepitaxial as well as to synthesize nanocrystalline BaTiO₃ ceramics by pressure assisted sintering of ultra-fine starting powders.

Heteroepitaxial SrTiO₃ thin films were grown on MgO substrates by pulsed laser deposition (PLD) [5]. Within the analytical limits of X-ray diffraction (XRD), Rutherford backscattering (RBS) and scanning electron microscopy (SEM), no internal interfaces could be detected (see Fig. 1). By carefully controlling the deposition parameters, primarily by lowering the substrate temperature during growth, it was possible to prepare thin films with tailorable grain sizes ranging from 50 nm up to ~200 nm.

Polycrystalline thin films were also prepared by chemical solution deposition (CSD). Such films typically exhibit a columnar grain structure with a mean column diameter of 30 to 50 nm (Fig. 2) [6]. Due to batch processing, tiny pores between the individual coatings occur, which can be proved by cross sectional TEM analysis. As a result of this, the defect density of such thin films is the highest of all investigated systems.

Nanocrystalline BaTiO₃ ceramics (Fig. 3) with a mean grain size of ≤100 nm were prepared by sinter-forging. To obtain a grain size of the final sample in the order of that of polycrystalline thin films, the raw powders used for this studies were prepared via a

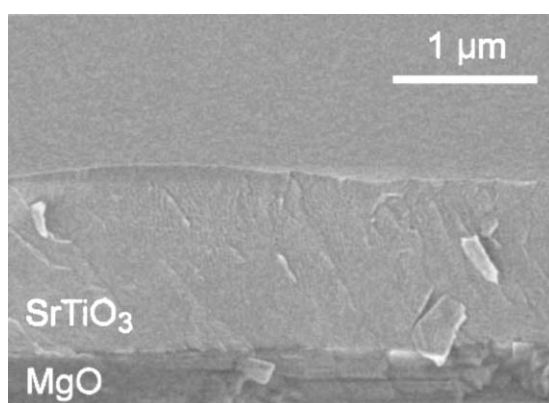


Fig. 1. SEM cross section of a single crystalline SrTiO₃ thin film on MgO by PLD.

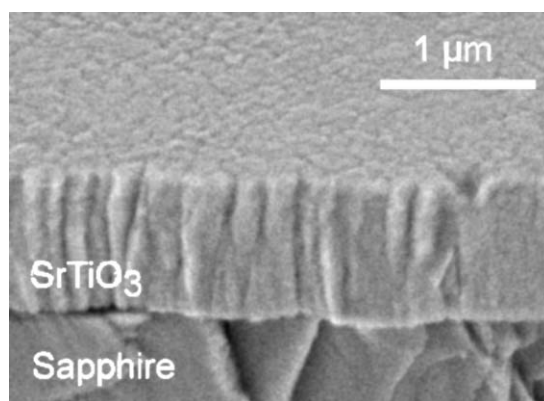


Fig. 2. Cross-sectional SEM picture of an undoped SrTiO₃ thin film made by CSD. The film consists of 55 single depositions. The diameter of the columns can be estimated to be about 50 nm.

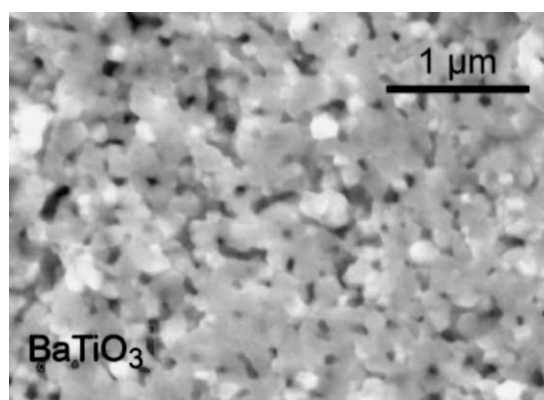


Fig. 3. Nanocrystalline BaTiO₃ ceramic made by sinter forging of microemulsion-synthesized primary powder. The grain size is about 100 nm. This picture was taken at the margin of the sample, showing residual porosity.

special microemulsion synthesis route showing a mean primary particle size of about 8 nm [7]. The sintering temperatures was 1000°C and the pressure amounted to 2000 bar.

2.2. Measurement Procedures

In order to obtain comprehensive information about the electrical conductivity behavior, a wide and continuous range of temperatures and oxygen partial pressures has to be studied. The measurement setup, making use of an electrolytic oxygen pump, is described and illustrated in [6]. The advantage of this technique lies in

the continuously controllable oxygen partial pressures between 10^{-20} bar and 1 bar. Temperatures can be chosen from 600°C to 1000°C. Due to a specially designed sample holder, the setup allows to measure resistances of up to several gigaohms by a common 4-probe dc technique.

3. Results

The reliability of the setup was first confirmed by measuring a SrTiO₃ single crystal. The results, which serve as an internal standard for comparison, are in excellent agreement with literature data [3]. The effects of the measurements regarding morphological stability were extensively studied for nanocrystalline SrTiO₃ thin films [8]. It has been shown that temperatures of up to 1000°C and at the same time extreme atmospheric conditions and prolonged times (~ 24 h) are necessary for a significant activation of recrystallization. A similar behavior is found for the nanocrystalline BaTiO₃ ceramic, where no noticeable change of grain shape was detected after the measurements shown here ($\leq 800^\circ\text{C}$).

3.1. Heteroepitaxial SrTiO₃ Thin Films

The conductivity characteristics for a heteroepitaxial thin film as a function of $p\text{O}_2$ and temperature are depicted in Fig. 4 exemplarily for a 1 μm thick SrTiO₃ film. The behavior is remarkably similar to that of

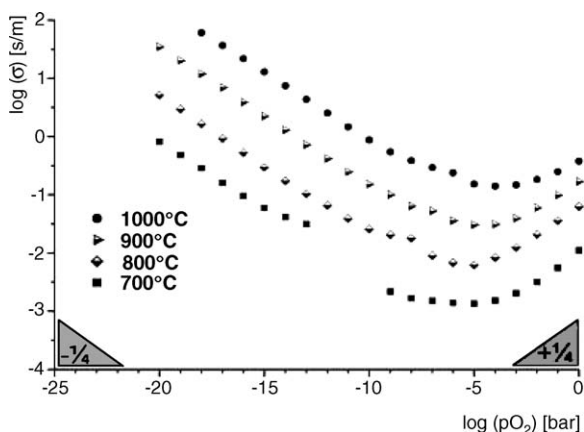


Fig. 4. Conductivity behavior of a heteroepitaxial SrTiO₃ thin film on MgO with a thickness of 1 μm (see Fig. 1). Missing values are due to technical problems.

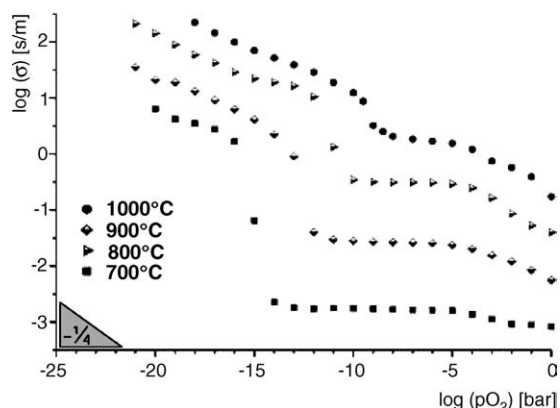


Fig. 5. Conductivity characteristics of a nominally undoped, CSD-prepared SrTiO₃ thin film (see Fig. 2).

bulk materials and corresponds to expectations from the established defect chemical model. The measurement curves at all temperatures reveal an n -type regime under reducing and a p -type behavior under oxidizing conditions and the slopes in these electronic branches fit the anticipated value of $\pm 1/4$ very well. The bandgap energy of this film was calculated as $E_G = (3.35 \pm 0.2)$ eV, which agrees well with the single crystal value (3.30 eV). However, at lower temperatures the intrinsic minimum is shifted towards higher oxygen partial pressures, having direct consequences on the thermal activation of the absolute conductivity values in the reducing and oxidizing regimes. Investigations on thin films with different thicknesses (between 3 μm and 250 nm) show that with decreasing thickness the absolute conductivity values in the n -type region increase, while the values in the p -type regime become smaller.

3.2. Polycrystalline SrTiO₃ Thin Films

Figure 5 shows the conductivity behavior of a nominally undoped SrTiO₃ thin film of 500 nm thickness, which reveals several substantially different characteristics compared to those of the single crystal. Under reducing conditions, the curve resembles the typical n -type behavior due to the loss of oxygen to the atmosphere and generation of electrons. The absolute values of σ in this region are approximately 2 orders of magnitude higher than that of the single crystal. The most remarkable features are certainly the drop in the conductivity profile and the subsequent plateau

region stretching over several decades of pO_2 . The characteristics under oxidizing conditions are also quite different. Unlike the behavior of bulk materials, where p -type conductivity with a slope of $+1/4$ would be expected, the conductivity decreases further. This behavior is more pronounced for higher temperatures. Because of the missing p -type regime, an intrinsic minimum does not occur and the bandgap energy cannot be determined from this measurement. The activation of the plateau values follows an exponential behavior and therefore speaks against the assumption of a classical donor plateau. This can be shown by an Arrhenius-plot, by means of which the activation energy of ~ 2.5 eV was determined.

In order to elucidate the interplay between these effects on the conductivity curve and the morphological habit, the grain size was varied in a series of nominally undoped $SrTiO_3$ thin films processed by PLD. A successive increase of the grain size, from coarse grained to finally single crystalline, showed a more or less restoring of bulk behavior. The general trend is that with increasing interface density, especially for a nanocrystalline morphology, the n -type conductivity increases while the p -type values decrease. Furthermore, below a grain size (or film thickness) of approximately 250 nm, the conductivity profile changes and the above mentioned characteristics appear.

3.3. Nanocrystalline $BaTiO_3$ Ceramics

From the described experiments, the interface density is primarily thought to be responsible for the effects on conductivity characteristics like the drop and the plateau region. In order to substantiate this picture, nanocrystalline ceramics (with comparable grain size as the polycrystalline thin films) were investigated to see whether they also show the same characteristic effects on the conductivity profile. The results of the nanocrystalline ceramic $BaTiO_3$ sample are depicted in Fig. 6. These are quite remarkable, because they are generally the same as which were found for polycrystalline titanate thin films (Fig. 5).

To separate grain boundary and bulk contributions, an impedance analysis at 700°C as a function of pO_2 was performed (which will be discussed in detail in an upcoming paper [9]). While the bulk part is in fact that of a single crystal, the grain boundary contribution is responsible for the plateau region and the drop. In the p -type and the minimum region, grain bound-

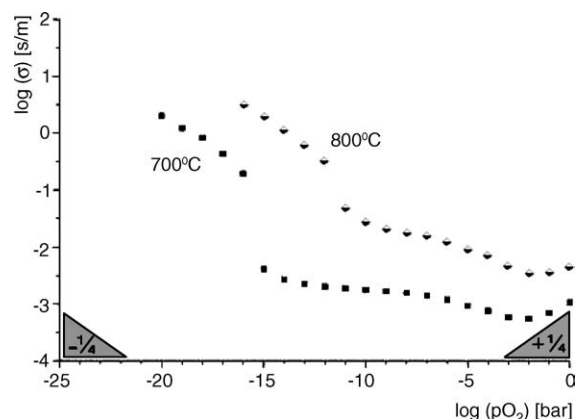


Fig. 6. Conduction behavior of a nanocrystalline $BaTiO_3$ ceramic (see Fig. 3).

ary and bulk profiles are parallel and the bulk dominates the total conductivity. However, with beginning n -type conductivity, the grain boundary resistivity stays constant over several orders of magnitude of the pO_2 . While the bulk resistivity decreases, the total conductivity profile is now dominated by the grain boundary part and builds up the plateau. At a certain partial pressure, the grain boundaries become highly conducting and the total conductivity jumps to the branch ruled by the bulk, following a slope of $-1/4$ towards reducing atmospheres.

4. Conclusions

By a systematic variation of grain size, this work illuminates the extraordinary interplay between the high-temperature conductivity characteristics and the morphology of alkaline earth titanates, when dimensions are reduced to the nanometer scale. It has been shown that an extremely high grain boundary density is responsible for drastically different conductivity profiles exhibited by nanocrystalline titanates.

Similar conductivity characteristics have been reported by Menesklou et al. [10] for a highly porous and donor doped $SrTiO_3$ ceramic and by Knauth and Tuller for nanocrystalline TiO_2 ceramics [11], but no satisfactory nor applicable explanation was proposed. Other profound investigations address the conductivity characteristics of nanocrystalline CeO_2 , which exhibits a similar defect chemistry [12, 13]. The consenting result is an enhanced conductivity of electrons, which is explained by space charge effects [13]. This

might also explain the increased absolute conductivity of nanocrystalline titanate systems discussed in this paper.

To conclude, up to now there is no comprehensive model for such heterogeneous titanate systems that also explains such new effects like the drop and the plateau region. The results much more indicate a special defect chemistry of the grain boundary region, which becomes significant for a certain interface or especially grain boundary density. A future model description has to deal with preferred current paths, spatially inhomogeneous charge carrier concentrations, as well as variable mobilities of the individual species in the different regimes of a nano-sized titanate sample.

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