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Electrical conductivity and segregation effects of doped $SrTiO_3$ thin films

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Abstract

The potential of perovskite type thin films for applications in electronic devices or oxygen sensors strongly relies on a detailed understanding of electrical properties. While the conduction mechanisms of single crystal $SrTiO_3$, frequently referred to as a model system, have been widely investigated and are usually described in terms of point defect chemistry, the conductivity behavior of thin films has not been studied in detail. In this paper we report on investigations on doped $SrTiO_3$ thin films under varying oxygen partial pressures and at temperatures between 700 and 1000°C. The electrical measurements show remarkable results, where a sharp drop and a plateau region are the dominant characteristics in $\log(\sigma)$–$\log(pO_2)$ plots. Recent investigations of the structural behavior of $SrTiO_3$ single crystal surfaces under certain atmospheric conditions suggested accompanying examinations by SEM and AFM, primarily addressing the morphological phenomena of the films.

Keywords: $BaTiO_3$ and titanates; Defects; Electrical conductivity; Electrical properties; Morphology

1. Introduction

Electroceramic thin films are rapidly gaining influence for applications in the field of electronic devices (e.g. FeRAMs) and selective gas sensors. One of the key challenges addressed by recent research is the understanding and the tailoring of material properties with respect to the nm-scale dimensions of the final structures. One of the most promising materials in this area is $(Ba_{1-x}Sr_x)TiO_3$ for its outstanding electrical properties.[1,2] To analyze certain properties, often the paraelectric pendant $SrTiO_3$ is used as a model system, exhibiting a lot of similarities in structure and electrical behavior.[3]

Regarding the electrical conductivity, the conduction behavior of $SrTiO_3$ is usually described by the bulk point defect chemistry.[4,5] This model combines essential parameters like temperature (T), oxygen atmosphere (pO_2) and the concentration of extrinsic dopants with the intrinsic generation of charge carriers and the condition of charge neutrality through laws of mass action, once a thermal equilibrium has been reached. But this model, which is based on statistical assumptions, neglects influences by the surface and does not include contributions by extended defect structures. However, there is still not much known about the conduction behavior of titanate based thin films.[6] Regarding other electrical properties, thin films often behave quite differently.[7]

Now it is a matter of discussion in how far the model of bulk defect chemistry allows the appropriate description of the thin film conduction behavior. This will be studied by high temperature conductivity measurements. A second approach focuses on morphological phenomena and takes into consideration that the thin films can be regarded as surfaces of bulk material.

The determination of the electrical conductivity through 4-point dc-measurements under controlled atmospheric conditions has been a common method to investigate bulk materials in the past. Our experimental set-up uses a YSZ solid state oxygen pump which allows to adjust any partial pressure in the range from 10^{-20} to 1 bar. By this, the temperature range is limited from about 600 to 1000°C. Undoped and doped $SrTiO_3$ thin films were grown on sapphire substrates by means of CSD to a final thickness of approximately 500 nm. In

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the case of doping, the precursor solutions were mixed to give a stoichiometric composition according to $Sr_{1-3/2x}La_xTiO_3$ or $SrTi_{1-x}Mn_xO_3$, respectively. More details on the experimental aspects can be found in Ref. 8.

A $SrTiO_3$ bulk single crystal was examined to check for the capabilities of the set-up. The results (Fig. 1) are in excellent agreement with the data found in literature[9] and serve as a reference for comparison with the thin film data. By linear fitting of the electronic dominated regions with slopes of ($\pm 1/4$), a band-gap energy of $E_G = 3.23$ eV ($T = 0$ K) with a temperature dependence of $\beta_G = 5.43 \times 10^{-4}$ eV/K was calculated.

The other way to look at thin films was implied by morphological considerations, where a possible relationship between measuring conditions and their influence on the measured data is studied by SEM and AFM. The surface layer of perovskite type structures and their chemical stability has been investigated thoroughly by Szot in recent years.[10-12] He has shown distinctive segregation phenomena in the near surface region due to thermal treatment in oxidizing or reducing atmospheres, especially regarding BTO and STO. The explanation proposed is a restructuring by Ruddlesden Popper phases and Magnéli type structures.

2. The conductivity of $SrTiO_3$ thin films

Fig. 2 shows the electrical conductivity of a nominally undoped $SrTiO_3$ thin film of about 500 nm thickness. In comparison to the bulk behavior (Fig. 1), the results show a substantially different conduction behavior. Looking at the region of highly reducing atmospheres the slope is somewhat smaller than the ($-1/4$) slope known from single crystals. The following occurrence of a sharp drop to a plateau region in mid range pO_2 is fundamentally different to bulk material. (It should be mentioned here that there are certain publications presenting similar results. Waser discussed acceptor doped $SrTiO_3$ in the quenched state.[13] Other papers report on different materials, but do not explain this characteristic.)[14–16]

In addition, the further decrease under oxidizing ambients is opposite to the expectations for bulk materials. In this region the conductivity shows its lowest values, but an intrinsic minimum is not observed.

The influence of doping was investigated on a 2 at.% La-doped (donor-type) and a 0.7 at.% Mn-doped (acceptor-type) thin film (Figs. 3 and 4). Qualitatively, similar results (the sharp drop and a subsequent plateau region in mid-range pO_2) as for the undoped sample are found, so that this behavior is attributed to a special thin film characteristic. These characteristic features were found to be reproducible in repeated measurements.

The influence by doping on conductivity shows the same tendencies as for bulk material. For a better comparison, the values of the plateau region of the undoped sample are plotted into the diagrams as dashed lines. An acceptor type doping by Mn leads to a decreased absolute conductivity. The relative errors in the measurements, which originate from leakage currents in the setup and through the substrate, are thought to be less

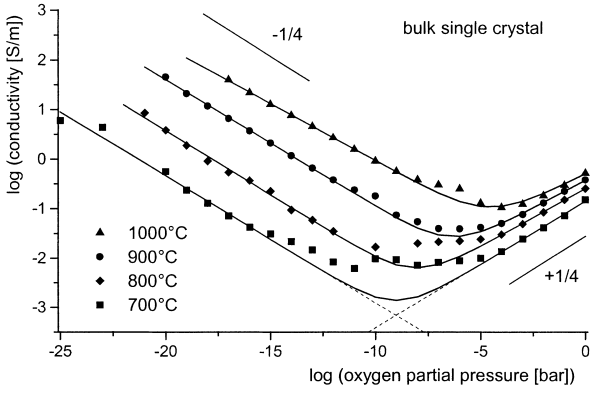

Fig. 1. Conductivity behavior of a nominally undoped $SrTiO_3$ single crystal.

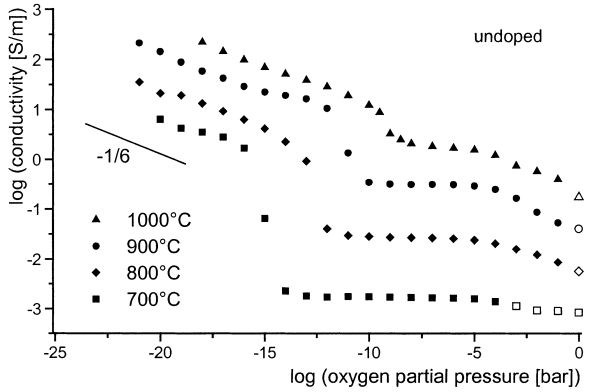

Fig. 2. Conductivity behavior of a nominally undoped $SrTiO_3$ thin film.

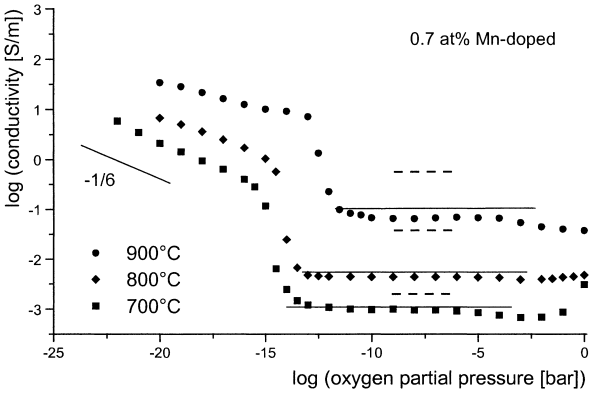

Fig. 3. Conductivity behavior of an acceptor-doped $SrTiO_3$ thin film. The dashed lines indicate the plateau values of the undoped thin film for comparison.

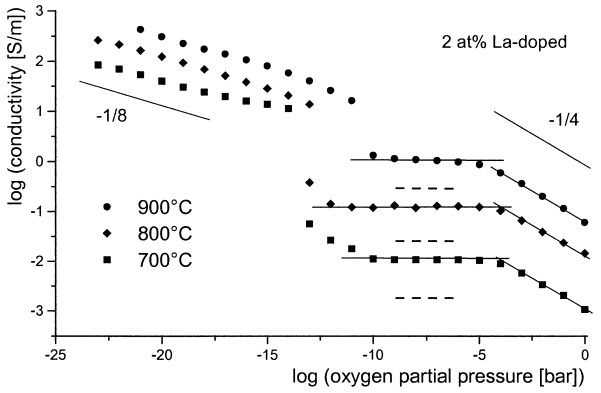

Fig. 4. Conductivity behavior of a donor-doped $SrTiO_3$ thin film. The dashed lines indicate the plateau values of the undoped thin film.

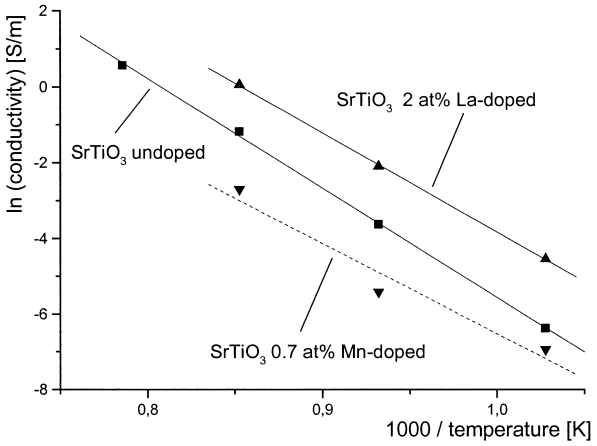

Fig. 5. Arrhenius plot of the conductivity values in the plateau regions of the thin films.

than 10% at low temperatures. Therefore, the absolute values from the measurement taken at 700°C (especially in the plateau region) should only be estimated. The behavior under oxidizing conditions is confusing, because the increasing behavior found at 700°C (what could be attributed to a *p*-type conduction mechanism) leveled out at 800°C and changed to a decreasing curve at 900°C.

Donor type doping by La leads to higher absolute values in conductivity compared to undoped material. Here, the slope under very reducing atmospheres is even smaller and a clear $(-1/4)$ behavior in the $\log(\sigma)$–$\log(pO_2)$ plot can be found towards a pO_2 of 1 bar.

The plateau region, which is common to all of our thin film data, reminds of a "donor-plateau". Such a plateau occurs when the content of donor dopants is compensated by free conduction electrons. If this is the case, the conductivity exhibits only a weak dependence on temperature due to the constant doping concentration. Only the temperature dependence of the mobility, which is a polynomial function, is apparent.

To check if this is the case, the activation energies of the conductivity values in the plateau regions for all three investigated samples were calculated (Fig. 5) by plotting the data in Arrhenius diagrams. The activation energies are 2.1 eV (Mn-doped), 2.3 eV (La-doped) and 2.5 eV for the undoped film. Instead of a polynomial type, a clear exponential kind of dependence is revealed. Therefore, an identification of the plateau region with an electronic compensation found in "classic" donor-plateaus can be excluded.

3. The surface point of view

It was mentioned earlier that the surfaces of single crystal $SrTiO_3$ tend to a certain restructuring. This should be kept in mind when looking at thin films, because the extent of such effects and the thickness of the films investigated in this paper are comparable. In addition, $SrTiO_3$ thin films prepared by CSD are polycrystalline and show a columnar morphology in statu nascendi (Fig. 6). The grain boundaries may also act as possible pathways for a material transport.

This initial state of the nominally undoped $SrTiO_3$ thin film is characterized by low porosity and a very smooth surface. The mean roughness was determined from the AFM measurements to be in the range of the substrate's surface roughness.

After all measurement cycles (of Fig. 2), the situation looks considerably different (Fig. 7). The SEM picture reveals a noticeable increasing porosity along grain boundaries and, via AFM, a visibly higher roughness (approximately 10 times) caused by mass transport can be seen.

Because this can indicate the formation of second phases with a different conduction behavior and/or shifted values, it is necessary to find out, when these segregation effects become critical to the measurements. The aim is to assign the morphological changes with particular measurement parameters like the electrical field or a certain oxygen partial pressure. This was studied through an annealing series, where samples of the undoped $SrTiO_3$ thin film were annealed at 900°C for several hours under selected oxygen partial pressures between 10^{-20} and 1 bar. But here the changes (observed by AFM and SEM) are by far not that drastic

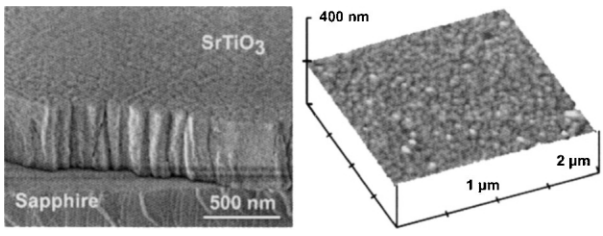

Fig. 6. $SrTiO_3$ thin film as deposited: SEM micrograph of the cross-section (left) and topographical analysis of the surface by AFM (right).

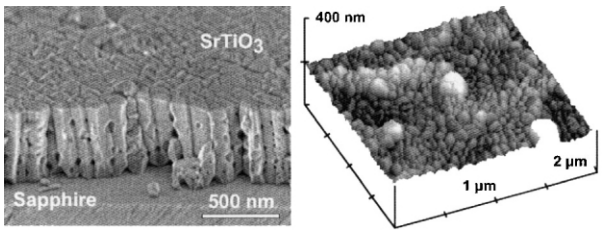

Fig. 7. $SrTiO_3$ thin film after measurements: SEM micrograph of the cross-section (left) and topographical analysis of the surface by AFM (right).

as seen in Fig. 7, so that we conclude that a significant mass transport requires higher temperatures and prolonged times.

4. Conclusion

The results on the electrical conductivity behavior of thin films show distinct differences to that of $SrTiO_3$ single crystals or bulk ceramics. These cannot be explained by the defect chemical model developed for single crystals. Though the behavior of σ in dependence of the ambient pO_2 is still not clarified, it shows a very characteristic behavior. Also, the influence by doping is clearly detectable and follows the trends known from bulk materials. This suggests that there is also a strong correlation between the conduction mechanisms and a defect structure depending on the ambient oxygen partial pressure. In addition it has been shown that the plateau regions are no donor-plateaus.

The observed morphological changes, which are activated by the measurement conditions, imply a rather complex interaction between the morphology, the defect structure and the conduction mechanisms. Up to now, the parameters for the activation of the segregation effects are not sufficiently clarified. But, the drastic changes only occurred after extensive treatment at temperatures up to 1000°C, so that the measurements taken around 700°C (showing the characteristic drop and plateau region) are considered reliable.

5. Looking ahead

To get a deeper understanding of the different effects in play, a clear separation of intrinsic conduction mechanisms and extrinsically induced segregation effects must be accomplished first.

Therefore, the morphological phenomena have to be elucidated with respect to its chemical nature and the influence on the conductivity behavior. In parallel, the different regimes of the conductivity curves will be investigated in more detail. In this context, an identification of the charge carrier types and the real defect structure (point defects, extended defects or a combination) will be addressed. This also means broader studies on doping and familiar material systems (BST, BTZ, etc.). In addition, the influence of scaling (film thickness and grain size) and the morphology (dependent on the particular process) will be studied.

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