Journal of the European Ceramic Society 21 (2001) 1749–1752
www.elsevier.com/locate/jeurceramsoc

The distribution of grain boundary resistivities in $SrTiO_3$ polycrystals: a comparison between spatially resolved and macroscopic measurements

S. Rodewald, J. Fleig *, J. Maier

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

Received 4 September 2000; received in revised form 13 December 2000; accepted 20 December 2000

Abstract

Ohmic $Ag/YBa_2Cu_3O_{7-\delta}$-microcontacts on adjacent grains of polycrystalline Fe-doped $SrTiO_3$-samples have been used to investigate locally the properties of grain boundaries by means of impedance spectroscopy. Experiments at 30 different single grain boundaries permit reliable conclusions to be made on the distribution of grain boundary properties. For comparison conventional impedance measurements on a polycrystal were performed and a brick layer model was used to extract effective properties. The reasonable agreement between these effective parameters and the average of the locally obtained parameters demonstrates that, in this case, a brick layer analysis of conventional impedance experiments yields satisfactory estimates of the grain boundary properties.

Keywords: $SrTiO_3$ and titanates; Electrical conductivity; Grain boundaries; Impedance; Microelectrodes

1. Introduction

The overall electrical properties of many electroceramic materials are determined by grain boundaries. For example, in varistors and positive temperature coefficient (PTC) resistors as well as in high permittivity barrier layer capacitors, grain boundaries are the origin of the specific functions of these devices.[1–3] Such blocking grain boundaries are, on the other hand, highly disadvantageous if fast transport inside the electroceramic material is required.[4] Therefore the electrical characterization of grain boundaries in electroceramic materials is of great importance. Impedance spectroscopy is in many cases a powerful tool in determining the electrical properties of grain boundaries in polycrystalline materials.[5] Usually macroscopic electrodes with an area of at least a few square millimeters are used in impedance measurements and, therefore, only mean grain boundary impedance data averaged over a large number of grain boundaries can be obtained. The averaged properties of the grain boundaries can be evaluated from the measured grain boundary impedance of the polycrystal by using the brick layer model which assumes cubic grains of constant grain size and a homogeneous distribution of grain boundary properties.[5] Deviations from this idealized structure, however, for example due to inhomogeneous grain boundary properties or non cubic grain shapes can hinder a sensible data evaluation.[6] Moreover, detailed information of how the properties vary from boundary to boundary can not be obtained from conventional impedance measurements. Thus spatially resolved impedance experiments would often be advantageous in order to understand the transport properties of polycrystals. The use of microelectrodes to obtain spatially resolved conductivity data has been demonstrated, for example on stoichiometry polarized Fe-doped $SrTiO_3$ single and polycrystals.[7,8] In this contribution we use microcontact impedance spectroscopy to investigate the distribution of the electrical properties of grain boundaries in an Fe-doped $SrTiO_3$ polycrystal. Emphasis is placed on the comparison between the locally obtained properties and the effective properties obtained from conventional impedance measurements.

* Corresponding author. Tel.: +49-711-689-1770; fax: +49-711-689-1722.
E-mail address: fleig@chemix.mpi-stuttgart.mpg.de (J. Fleig).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00108-X

2. Experimental

Polycrystalline 0.2 mol% Fe-doped $SrTiO_3$ samples were prepared by a mixed oxide route. The pellets with a density > 97% of the theoretical density were cut into slices, lapped and polished. After polishing, the samples were thermally etched at 1280°C for 2 h in order to make the grain boundaries at the surface visible. The polycrystals exhibited a rather large mean grain size of 56 μm which enabled us to use microelectrodes with a diameter of 20 μm for the electrical characterization of "individual" grain boundaries.

By means of laser ablation a 150 nm $YBa_2Cu_3O_{7-\delta}$-layer was evaporated onto one surface of the Fe-doped $SrTiO_3$-polycrystals. In order to reduce the contact resistance between the electrode layer and the contacting tip, a 50 nm Ag-layer was evaporated on the $YBa_2Cu_3O_{7-\delta}$-layer. An array of identical microelectrodes (microelectrode diameter of 20 μm with a distance of 40 μm between the centers) was prepared by a lithographical process (a photo resist was applied to the Ag/$YBa_2Cu_3O_{7-\delta}$-layer and partly exposed to light by using a mask). After removing the light-exposed parts of the photo-resist ion milling was used to etch the microelectrode array out of the Ag/$YBa_2Cu_3O_{7-\delta}$-layer.

Two Ag/$YBa_2Cu_3O_{7-\delta}$-layer-microelectrodes were contacted by tungsten tips with a tip-radius of 1 μm as shown in Fig. 1. The tips were electrically connected to a frequency response analyzer (Solartron 1260, Schlumberger) via a homemade high impedance converter. If both microelectrodes are on the same grain only one semicircle was observed in a Nyquist plot.[9] Impedance spectra obtained between microelectrodes on adjacent grains, on the other hand, showed a further semicircle at low frequencies (Fig. 2). We can, therefore, conclude that this additional semicircle is caused by grain boundaries rather than by electrode effects. The grain boundary resistances (R_{gb}), capacitances (C_{gb}) and peak frequencies (ω_{gb}) were determined by fitting the spectra to an equivalent circuit model consisting of a parallel *RC*-element in series with a *RQ*-element (see Fig. 2, *Q* means a constant phase element). In some spectra, additional non-ideal features were seen, such as a further small semicircle overlapping with the grain boundary arc or a loop appearing in the low frequency part of the bulk semicircle; they play no role in the following discussion. The origin of these non-idealities has been discussed in more detail elsewhere.[10,13]

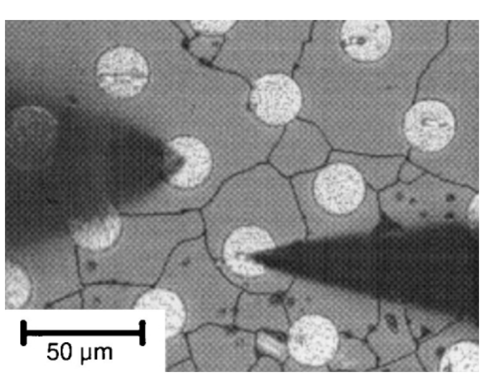

Fig. 1. Optical image of the polycrystalline Fe-doped $SrTiO_3$-sample showing two tungsten tips contacting Ag/$YBa_2Cu_3O_{7-\delta}$-microelectrode on neighbouring grain.

3. Results and discussion

3.1. Distribution of grain boundary properties

Microcontact impedance spectroscopy was used to locally investigate 30 different grain boundaries in a polycrystalline Fe-doped $SrTiO_3$ sample at a temperature of 585 K. A typical electrode configuration is shown in Fig. 1. The distributions of the grain boundary resistances and peak frequencies are shown in Fig. 3. In this context it has to be mentioned that, even with two microelectrodes on adjacent grains, not only the grain boundary between them is under investigation since current paths through neighbouring boundaries also influence the result. A detailed discussion of these interdependences is given in Ref. 9. Hence these histograms cannot directly be transferred into histograms of grain boundary resistivities or widths.[11] From the width of the R_{gb}-, C_{gb}- and ω_{gb}-distributions, however, we can get important information on the uniformity of grain boundary properties.[9]

The resistances and capacitances strongly depend on the corresponding grain boundary areas, which can only be estimated from the visible grain boundary length.

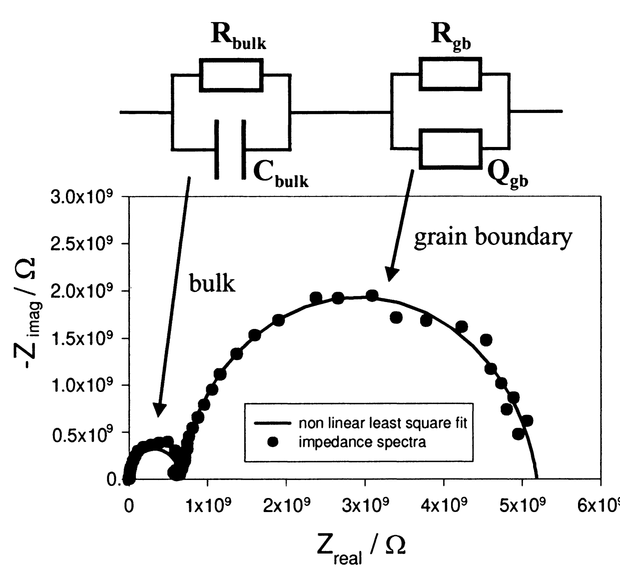

Fig. 2. Typical impedance spectrum measured with two microelectrodes on adjacent grains of an Fe-doped $SrTiO_3$-polycrystal. The equivalent circuit used to fit these spectra is also given.

Therefore, the R_{gb}- and C_{gb}-distributions are somewhat broader than the peak frequency distribution which is much less sensitive to grain boundary area.[9] The relatively narrow peak frequency distribution is a strong indication for a rather homogeneous distribution of grain boundary properties in the Fe-doped $SrTiO_3$ polycrystal. Hence, one could expect that the effective peak frequency from a conventional impedance experiment fits the locally measured distribution. As indicated in Fig. 3b the effective peak frequency (3.0 Hz) is very close to the mean value of the peak frequency distribution (1.2 Hz). The peak frequency values can be used to calculate a mean grain boundary resistivity [Ref. 9] for the microcontact experiments ($\rho_{gb} = 1.6\times10^{10}$ Ωcm) and an effective resistivity for the macroscopic measurement ($\rho_{gb} = 4.1\times10^{10}$ Ωcm) according to

$$\rho_{gb} \approx \frac{1}{\varepsilon_{gb}\omega_{gb}}. \quad (1)$$

The permittivity of the grain boundary (ε_{gb}) was assumed to correspond to the bulk permittivity ε_{bulk} obtained from the bulk semicircle at 585 K ($\varepsilon_{bulk} \approx 230\varepsilon_0$). From the resistivity, the space charge potential of a double Schottky barrier at the grain boundary, which is considered to be responsible for the pronounced grain boundary resistivity [Ref. 12], can been calculated. For microcontact and macroscopic impedance measurements nearly identical values for the space charge potential were deduced: 630 and 680 mV, respectively

A similar comparison has been performed with respect to the electrically active width of the grain boundary (w_{gb}). From the C_{gb}-distribution and estimated grain boundary areas a grain boundary width-histogram could be calculated.[13] The mean value of this distribution (60–70 nm) is again close to the value obtained from a brick layer analysis of the conventional impedance measurement (33 nm), via

$$w_{gb} \approx \frac{\varepsilon_{bulk} A_{sample} L_{grain}}{L_{sample} C_{gb}} \quad (2)$$

with A_{sample}, L_{sample} being the area and the thickness of the sample and L_{grain} denoting the average grain size. Some reasons for the slight discrepancies are discussed in Ref. 13.

3.2. Activation energies of grain boundary resistance

Temperature dependent impedance measurements have been performed to obtain the activation energies of grain boundary resistances of "individual" grain boundaries. A typical Arrhenius-plot of the temperature dependence of bulk and grain boundary resistances measured with microcontact impedance spectroscopy is given in Fig. 4a. The bulk (≈ 0.9 eV) and grain boundary (≈ 1.1 eV) activation energies correspond, within the accuracy of the measurement, to the values obtained with macroscopic electrodes and reported in literature.[14,15]

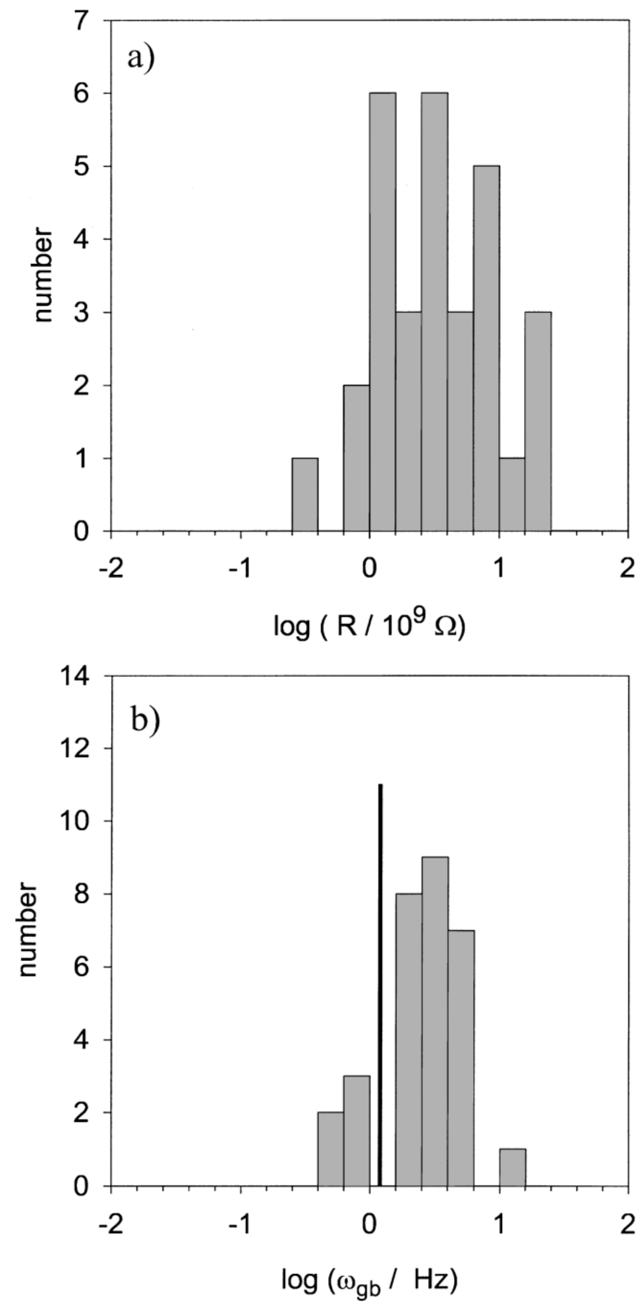

Fig. 3. Histograms of the (a) resistances and (b) peak frequencies of the grain boundary semicircles measured at 30 individual grain boundaries (measurement temperature 585 K). The solid line in (b) represents the peak frequency from a macroscopic measurement.

3.3. Bias dependent grain boundary resistivities

The bias dependence of the impedance spectra measured at "individual" grain boundaries revealed a strong decrease of the grain boundary resistance with increasing bias as expected for resistances due to space charge

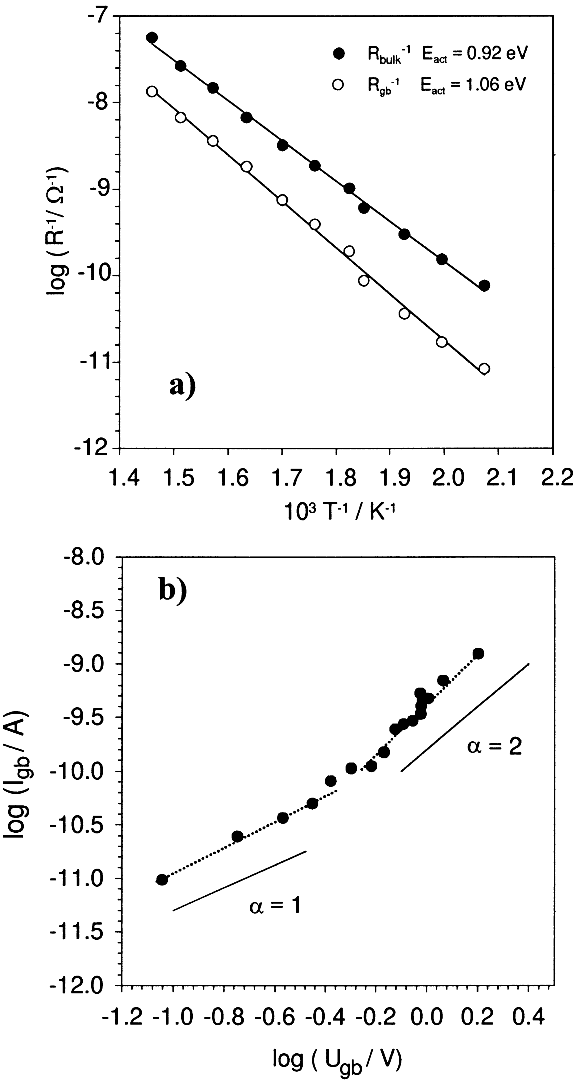

Fig. 4. (a) Arrhenius–plot of the temperature dependence of the inverse bulk and grain boundary resistances and (b) logarithmic plot of the current-voltage relation obtained with microelectrodes on adjacent grains.

layer effects. In the logarithmic plot of the current-voltage curve calculated from the impedance data two regimes, namely an ohmic regime (non-linearity factor $\alpha \approx 1$) at low bias (< 0.35 V) and a nonlinear regime with $\alpha \approx 2$ at higher bias are observed (Fig. 4b). This is again in accordance with results obtained by time-dependent macroscopic current-voltage measurements on polycrystalline acceptor-doped $SrTiO_3$.[12]

4. Conclusions

Microcontact impedance spectroscopy has been used to analyze the distribution of electrical grain boundary properties in an Fe-doped $SrTiO_3$ polycrystal. The measured distribution of peak frequencies of the grain boundary semicircle is rather narrow, which is a strong indication for a rather homogeneous distribution of the grain boundary resistivities. The values measured with microelectrodes have been compared with the mean values obtained by conventional impedance measurements with macroscopic electrodes. Satisfactory agreement between the resulting resistivities and thicknesses was found. It can, therefore, be concluded that the brick layer model used to evaluate the grain boundary properties from the conventional impedance measurements is a reasonable approximation to obtain mean values of grain boundary properties in polycrystalline Fe-doped $SrTiO_3$.

References

1. Greuter, F. and Blatter, G., Electrical properties of grain boundaries in polycrystalline compound semiconductors. *Semicond. Sci. Technol.*, 1990, **5**, 111–137.
2. Daniels, J., Härdtl, K. H. and Wernicke, R., The PTC effect of barium titanate. *Philips Technol. Rev.*, 1978, **38**, 73–82.
3. Mauczok, R. and Wernicke, R., Ceramic boundary-layer capacitors. *Philips Technol. Rev.*, 1983, **41**, 338–346.
4. Gerblinger, J. and Meixner, H., Fast oxygen sensors based on sputtered strontium titanate. *Sensors and Actuators B*, 1991, **4**, 99–102.
5. Bonanos, N., Steele, B. C. H. and Butler, E. P., Applications of Impedance Spectroscopy. In *Impedance Spectroscopy*, John Wiley and Sons, New York, 1987, pp. 191.
6. Fleig, J., The influence of non-ideal microstructures on the analysis of grain boundary impedances. *Solid State Ionics*, 2000, **131**, 117–128.
7. Rodewald, S., Fleig, J. and Maier, J., Resistance degradation of Fe-doped $SrTiO_3$ investigated by spatially resolved conductivity measurements. *J. Am. Ceram. Soc.*, 2000, **83**, 1969–1976.
8. Rodewald, S., Fleig, J. and Maier, J., Measurements of conductivity profiles in acceptor doped strontium titatante. *J. Eur. Ceram. Soc.*, 1999, **19**, 797–801.
9. Fleig, J., Rodewald, S. and Maier, J., Microcontact impedance measurements of individual highly resistive grain boundaries: general aspects and application to acceptor-doped $SrTiO_3$. *J. Appl. Phys.*, 2000, **87**, 2372–2381.
10. Fleig, J., Jamnik, J., Maier, J. and Ludvig, J., Inductive loops in impedance spectroscopy caused by electrical shielding. *J. Electrochem. Soc.*, 1996, **143**, 3635–3641.
11. Rodewald, S., *Local electrochemical characterization of conductivity inhomogeneities in Fe-doped $SrTiO_3$*. PhD thesis, University of Stuttgart, 1999.
12. Vollmann, M. and Waser, R., Grain boundary defect chemistry of acceptor-doped titanates: high field effects. *J. Electroceramics*, 1997, **1**, 51–64.
13. Rodewald, S., Fleig, J. and Maier, J., Microcontact impedance spectroscopy at single grain boundaries in Fe-doped $SrTiO_3$. *J. Am. Ceram. Soc.*, in press.
14. Denk, I., Claus, J. and Maier, J., Electrochemical Investigations of $SrTiO_3$ Boundaries. *J. Electrochem. Soc.*, 1997, **144**, 3526–3536.
15. Denk, I., Münch, W. and Maier, J., Partial conductivities in $SrTiO_3$: bulk polarization experiments, oxygen concentration cell measurements, and defect-chemical modelling. *J. Am. Ceram. Soc.*, 1995, **78**, 3265–3272.