Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 30 (2010) 1761–1764

www.elsevier.com/locate/jeurceramsoc

Technical note

Electrical characterization of ZnO multilayer varistors on the nanometre scale with conductive atomic force microscopy

Martin Schloffer[a,*], Christian Teichert[b], Peter Supancic[a,c], Andrei Andreev[b], Yue Hou[b], Zhonghua Wang[a]

[a] *Institut für Struktur- und Funktionskeramik, University of Leoben, Franz-Josef-Str. 18, A-8700 Leoben, Austria*
[b] *Institut für Physik, University of Leoben, Franz-Josef-Str. 18, A-8700 Leoben, Austria*
[c] *Materials Center Leoben, Roseggerstrasse 12, A-8700 Leoben, Austria*

Received 12 October 2009; received in revised form 1 December 2009; accepted 4 January 2010
Available online 27 January 2010

Abstract

The conductivity of ZnO–varistor ceramics has been analyzed with conductive atomic force microscopy (C-AFM) under atmospheric conditions by measuring the current at different voltages and positions in zinc oxide-based multilayer varistors (MLVs). It is possible to detect individual ZnO grains on the polished sample surface in the AFM topography mode as well as in the two-dimensional current images. Additionally local current–voltage (*IV*) curves revealed details of the electrical behaviour of the material. To correlate the laterally resolved current image with grain orientations, electron backscattering diffraction (EBSD) has been performed. Beside the well-known varistor behaviour specific influence of the local microstructure has been found.

Keywords: ZnO; Varistors; Electrical conductivity; Grain boundaries; C-AFM

---

1. Introduction

Metal-oxide varistor ceramics based on ZnO with certain additives (e.g. bismuth and antimony oxide) exhibits excellent non-linear current voltage characteristics. The grain boundaries (double Schottky barriers), acting with typical switching voltage of 3–3.5 V,[1] are responsible for that extraordinary macroscopic materials behaviour. These materials are widely used in commercial components for overvoltage protection, where the switching level ranges from a few volts to MV. Especially in the low-voltage range, the quality of individual grain boundaries is crucial for the components' behaviour, since most of the functional barriers are connected in parallel. Therefore it is necessary to understand the switching behaviour of single grain boundaries and the influence of the microstructure in detail.

Modern scanning probe microscopy based techniques (for example electrostatic or piezoresponse force microscopy) allow to study electric properties of ferroelectric and piezoelectric materials on the nanometre scale.[2] With respect to local measurements of conductive properties, points contacts[3,4] as well as scanning surface potential microscopy[5] have been applied.

Here, we use conductive atomic force microscopy (C-AFM) operating in contact mode,[6] to investigate the topography and current response with respect to a given microstructure. In contrast to previous applications of the technique with emphasis on grain boundaries,[7] we focus on the local conductivity, which resolves twin crystals also. The identical surface region has been inspected subsequentially with electron backscattering diffraction (EBSD) to get information of individual crystal orientations. This allows an interpretation of the obtained two-dimensional (2D) current images. Additionally local current–voltage (*IV*) curves were recorded at points of special interest, like both parts of twins.

2. Experimental setup and samples

Commercial MLV-components (Bi_2O_3 doped ZnO with Ag/Pd inner electrodes) were polished in a way to enable electrical inspection close to an inner electrode layer (see Fig. 1).

---

[*] Corresponding author. Tel.: +43 3842 402 4109; fax: +43 3842 402 4102.
E-mail addresses: martin.schloffer@stud.unileoben.ac.at (M. Schloffer), phs@unileoben.ac.at (P. Supancic).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.01.005

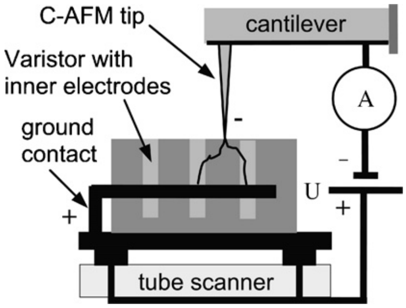

Fig. 1. C-AFM setup for measurements of multilayer varistor samples; all inner electrodes were connected with the ground.

C-AFM measurements were performed under ambient conditions in contact mode with a Digital Instruments Nanoscope IIIa Multimode microscope using an AS-130("J") scanner with $125\,\mu\text{m} \times 125\,\mu\text{m}$ maximum lateral scan size. The voltage applied to the samples was varied from 0 to +10 V. A home-made amplifier[8] allows measurements in the 200 pA range with a peak-to-peak noise level of 30 fA.[9] As probes, CDT-CONTR silicon cantilevers (Nanosensors$^{\text{TM}}$) with p-doped diamond coating on the tip were used. The typical macroscopic tip radius of curvature is below 100 nm. However, the grains of the polycrystalline diamond coating allow a resolution below 20 nm.[10] The scan speed for acceptable spatial resolution must stay below $15\,\mu$m/s for 512 data points in one scan line. Electron backscattering diffraction (EBSD) and scanning electron microscopy (SEM) have been performed with a commercial unit (LEO 1525, ZEISS), the latter after HF etching and sputtering the surface with gold on the same investigated areas.

3. Results and discussion

Fig. 2 shows a typical region of a varistor sample recorded by C-AFM in topography mode (a), in current mode at constant voltage (b), and the corresponding SEM image (c) after etching.

The height differences in the topographic image reflect the wear resistance (abrasion) against the polishing aids, which is significantly influenced by the hardness but also by the crystal orientation of the different microstructural phases. Additional information on grain structure can be obtained by the current image (Fig. 2b). Spinel and Bi–O phase show no detectable currents (bright, see e.g. position 1). The ZnO grains exhibit different, but homogeneous current levels, which allow to distinguish individual grains. As in the topographic image even parts of twins can be discriminated (e.g. positions 3 and 4).

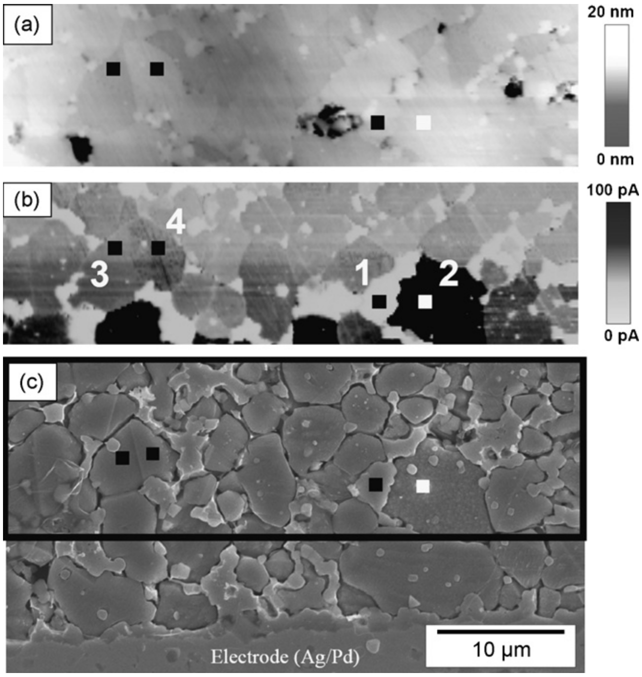

Fig. 2. Overview of a polished MLV-area of $50\,\mu\text{m} \times 12.5\,\mu\text{m}$. (a) Topographic AFM image and (b) simultaneously recorded 2D current image at +10 V. The SEM image of the etched surface (c) shows a slightly larger area to visualize the distance to the adjacent Ag/Pd inner electrode (the framed region corresponds exactly to the scanned areas in (a) and (b)). The spots for acquiring IV curves are marked by numbered squares.

Quantitative information on the electrical characteristics is obtained by local IV curves. Conventionally, such curves are measured by sweeping through a given voltage range at the desired position.[8] Since such a measurement is strongly influenced by the local surface conditions it is not representative for the whole grain. Therefore, we apply here the following, rather time consuming procedure: a series of current images is recorded at various voltages (i.e. 0 to +10 V in steps of 1 V) and the current values are averaged at certain positions on an area of $1\,\mu\text{m} \times 1\,\mu\text{m}$. Reassembling this data leads to a discrete IV curve which is representative for a given domain. The results of four characteristic positions (numbered 1–4) are presented in Fig. 3. IV curves are only presented for positive sample bias, since for the opposite voltage, after a few seconds of scanning time, a material modification occurs resulting in loosing discrimination of the individual ZnO grains.

For the spinel (Nr. 1), no current was detectable in the entire voltage range. At position 2 in the large (mono-domain) ZnO grain, a typical non-linear IV curve has been measured. Between grain Nr. 2 and the adjacent electrode is only one grain boundary (see Fig. 2c), but the corresponding switching voltage is below the well-known "ideal" varistor voltage of about 3.5 V. Such a scatter of the IV characteristics of individual grain boundaries has been reported in literature.[11] Between the twin half's Nr. 3

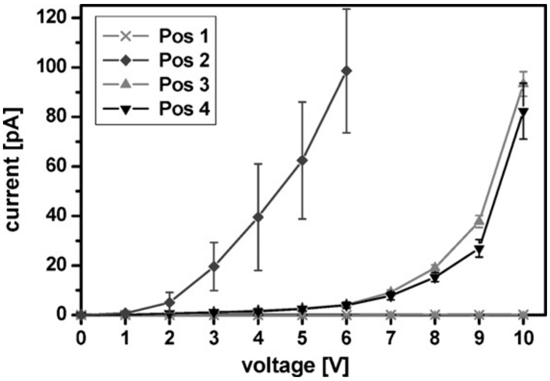

Fig. 3. *I–V* characteristics at the spots 1–4 marked in Fig. 2. The error bars correspond to the standard deviation of measured currents at individual pixels.

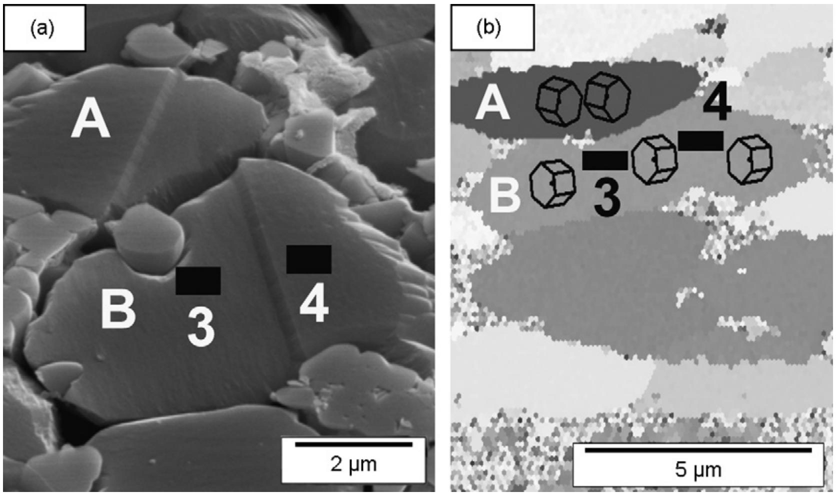

Fig. 4. (a) SEM image of the twin crystal under 50° (twin detail from Fig. 2) after heavy etching. (b) Crystal orientations determined with EBSD (tilted by 70°). Both twin crystals visible, A and B exhibit the same orientation in their half's. The numbers denote the spots for recording IV curves of the twin.

and 4 and the electrode, there are two grain boundaries visible on the polished surface (see Fig. 2c) resulting in a switching voltage in the range between 6 and 7 V. Actually, the IV curves are slightly different in a certain voltage range[12] (i.e. around +9 V) for positions 3 and 4.

In Fig. 4a, an SEM image of the heavily HF-etched surface of the grain containing positions 3 and 4 and its neighbours is shown. The twin boundaries of the grains marked with A and B can be recognized by a surface step.[13] The corresponding EBSD-plot with information on the crystal orientations of the originally unetched sample (Fig. 4b) reveals for both grains a homogeneous orientation on the whole section. This can be attributed to the well-known degeneracy for 180° antiparallel crystal domains, which are of the dominate type in ZnO varistor ceramics.[12] The EBSD analysis reveals that the polar axis of the twinned crystal is 45° tilted with respect to the section plane, while the crystal at position 2 is perpendicular. This might explain the scatter of switching voltages of individual grains, which should be also influenced by the relative orientation of adjacent grains. The small difference of the IV curves between positions 3 and 4 might be attributed to the different work functions of the polished surface plane in contact to the tip.

4. Summary and conclusion

By a combination of C-AFM- and SEM/EBSD-techniques it is possible to correlate IV characteristics of individual grains and grain boundaries in ZnO varistors to their crystallographic orientation and their position with respect to the metal electrode. For a given polished area, 2D C-AFM images allows to distinguish all different phases in the varistor microstructure: Spinel, Bi_2O_3 phases, and the ZnO matrix. The IV curves recorded by a special sampling technique could be attributed to one and two active grain boundaries. The deviations of the switching voltages from the ideal value of 3.5 V confirms the significant influence of microstructural grain orientations. The same is valid for twinned crystals. The combination of complementary nanometre characterization techniques operating on the same sample location, as developed here, will enable detailed studies of the barrier parameters (e.g. height, charge densities, etc.) of grain boundary-controlled ceramics in the future. In a next step it is planned to carry out detailed studies going beyond this technical note, e.g. the demonstrated sensibility to twin grains will be of special importance to quantify the influence of orientation differences of adjacent grains.

Acknowledgements

Mr. T. Feichtinger (EPCOS, Austria) is highly acknowledged for providing MLV-samples for these experiments. Mrs. D. Luef (Erich-Schmidt-Institut für Materialwissenschaft of the "Österreichische Akademie der Wissenschaften", Austria) is gratefully acknowledged for supporting the work at the SEM/EBSD.

References

1. Clarke DR. Varistor ceramics. *J Am Ceram Soc* 1999;**82**(3):485–502.
2. Alexe M, Gruvermann A. *Nanoscale characterization of ferroelectric materials—scanning probe microscopy approach*. Berlin: Springer; 2004.
3. Fleig J, Pham P, Sztulzaft P, Maier J. Inhomogeneous current distributions at grain boundaries and electrodes and their impact on the impedance. *Solid State Ionics* 1998;**113–115**:739–47.
4. Fleig J, Rahmati B, Rodewald S, Maier J. On the localized impedance spectroscopic characterization of grain boundaries: general aspects and experiments on undoped $SrTiO_3$. *J Eur Ceram Soc* 2010;**30**(2):215–20.
5. Huey BD, Bonnell DA. Nanoscale variation in electric potential at oxide bicrystal and polycrystal interfaces. *Solid State Ionics* 2000;**131**(1–2):51–60.
6. Olbrich A, Ebersberger B, Boit C. Conducting atomic force microscopy for nanoscale electrical characterization of thin SiO_2. *Appl Phys Lett* 1998;**73**(21):3114–6.
7. Gheno SM, Kiminami RHGA, Morelli MM, Bellini JV, Filho PIP. An AFM/EFM study of the grain boundary in ZnO-based varistor materials. *J Am Ceram Soc* 2008;**91**(11):3593–8.

8. Kremmer S, Teichert C, Pischler E, Gold H, Kuchar F, Schatzmayr M. Characterization of silicon gate oxides by conducting atomic force microscopy. *Surf Interface Anal* 2002;**33**(2):168–72.
9. Kremmer S, Peissl S, Teichert C, Kuchar F. Conducting atomic-force microscopy investigations on thin silicon gate oxides: influence of tip shape and humidity. In: *Proceedings of the 28th international symposium for testing and failure analysis, Phoenix*. Materials Park, OH: ASM International; 2002. p. 473–82.
10. Kremmer S, Wurmbauer H, Teichert C, Tallarida G, Spiga S, Wiemer C, et al. Nanoscale morphological and electrical homogeneity of HfO_2 and ZrO_2 thin films studied by conducting atomic-force microscopy. *J Appl Phys* 2005;**67**(7):1–7 [074315].
11. Tanaka S, Takahashi K. Direct Measurements of voltage–current characteristics of single grain boundary of ZnO varistors. *J Eur Ceram Soc* 1999;**19**(6–7):727–30.
12. Haskell BA, Souri SJ, Helfand MA. Varistor behavior at twin boundaries in ZnO. *J Am Ceram Soc* 1999;**82**(8):2106–10.
13. Jo W, Kim S-J, Kim D-Y. Analysis of the etching behavior of ZnO ceramics. *Acta Mater* 2005;**53**(15):4185–8.