Journal of the European Ceramic Society 21 (2001) 2127–2130

www.elsevier.com/locate/jeurceramsoc

Crystal plane influence of the EBIC contrast in zinc oxide varistors

C. Leach *

Manchester Materials Science Centre, University of Manchester and UMIST, Grosvenor Street, Manchester M1 7HS, UK

Received 4 September 2000; received in revised form 23 October 2000; accepted 25 October 2000

Abstract

Scanning electron microscopy (SEM) based remote electron beam induced current (REBIC) microscopy has been used to investigate the electrical characteristics of individual grain boundaries in a zinc oxide based varistor. Although some grain boundaries showed 'bright and dark' contrast consistent with symmetrical, opposed, electric fields on either side of a charged grain boundary, the majority of interfaces were found to be electrically asymmetric showing only *either* bright *or* dark contrast. In these cases, the application of an external voltage bias across the grain boundary of several 10′s of mV was necessary to restore the symmetrical structure. The orientations of grains on either side of grain boundaries showing each of these contrast types were determined using electron backscattered diffraction (EBSD) analysis and the grain boundary plane orientation was established using depth resolved EBIC. It was found that the asymmetry in the electrical structure is governed by the orientations of the grain boundary planes on either side of the interface, demonstrating some crystallographic control of the electrical character of the barrier structure.

Keywords: EBIC; Electrical properties; Electron microscopy; Grain boundaries; Varistors

1. Introduction

The special electrical properties of many polycrystalline electronically conducting electroceramics and wide bandgap semiconductors arise from the behaviour of charged grain boundary planes and the associated space-charge regions.[1] Although the grain boundary structures responsible are primarily due to the incorporation of specific dopants, there is growing evidence that crystallographic aspects of the interfacial structure are important in determining the fine details both of the electrical structure and the behaviour of individual grain boundaries.[2–4] Such factors are particularly relevant in anisotropic crystal systems, such as hexagonal zinc oxide, where many electrical and physical properties are orientation dependant. In these situations, the differing crystal orientations presented on either side of a grain boundary may lead to abrupt changes in important parameters such as the density of states, dielectric constant or band structure, that affect the overall electrical performance.

Varistors are a class of electroceramics that fall into this category. Based on sintered polycrystalline zinc oxide, doped with bismuth and other oxides, they show remarkable non-linear current-voltage characteristics[5] that are controlled by processes occurring at the grain boundaries, with each interface breaking down to a low-resistance state at some critical applied voltage[6]. Within a single device there is known to be some variability in the breakdown characteristics of different grain boundaries.[7]

REBIC microscopy is a form of the conductive mode of operation of the SEM that is widely used to study electrically active grain boundaries in polycrystalline semiconductors and electroceramics.[8–11] Fig. 1 shows the experimental configuration, in which two current collecting electrodes, positioned using a micromanipulator, form ohmic contacts on either side of the area being studied. Under primary beam irradiation, electron-hole pairs are generated within the sample and would normally recombine rapidly. However, if the electron-hole pairs are formed in the space-charge region of a charged grain boundary they are swept up by the associated electric field, giving rise to a current that can be collected by the electrodes, resulting in an EBIC signal. In making quantitative measurements of the EBIC signals generated at

* Tel.: +44-161-200-3561; fax: +44-161-200-3586.
E-mail address: colin.leach@mac.ac.uk

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00186-8

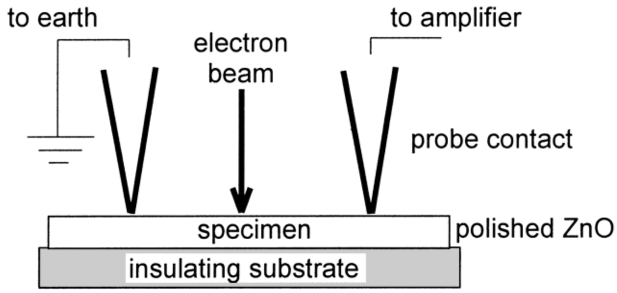

Fig. 1. The sample configuration used for conductive mode microscopy.

electroceramic grain boundaries it is desirable both to maximise the collected current and to be sure of its direction. Thus the current collecting electrodes are ideally positioned immediately to either side of and as close as possible to the grain boundary of interest using the grain boundary-EBIC (GB-EBIC) configuration.[11]

In the case of a symmetrical, charged grain boundary the opposed fields on either side of the interface generate EBIC currents in opposite directions, and so the EBIC contrast appears bright-dark (termed type I contrast in Ref. 9). However, whilst such EBIC contrast is commonly observed in cubic materials with electrically active grain boundaries,[10,11] it is frequently the case for materials with non-cubic crystal structures, such as zinc oxide, that the EBIC signal is suppressed on one side of the interface leaving only a single line, which may be bright or dark (termed type II contrast in Ref. 9). By applying a small voltage bias, of the order of tens of mV, across an electrically active varistor grain boundary, it is possible to change the contrast type from type I to type II and vice versa,[12] suggesting that details of the local microstructure specific to non-cubic crystal systems may affect the symmetry of the electrical behaviour. In this contribution the relationship between crystallographic aspects of the grain boundary structure and the observed EBIC contrast is studied.

2. Method

Zinc oxide powder, doped with 1.0 wt.% bismuth oxide and 0.5 wt.% antimony oxide, was prepared by a mixed oxide route, compacted and sintered at 1100°C for 2 h. One face of the sintered pellet was polished using a water based slurry of γ-Al_2O_3 powder and the sample mounted onto an electrically isolated stub for conductive mode imaging in a Phillips 525 SEM using a beam energy of 15 keV and a beam current of 2 nA. Tungsten current collecting electrodes were positioned directly onto the sample surface using a micromanipulator and the collected signal amplified using a Keithley 428 current amplifier. Electron backscattered diffraction (EBSD) analysis was carried out using a Jeol JSM 6300 fitted with a Nordif CCD camera and HKL Channel+ software.

3. Results and discussion

Fig. 2a is a zero bias GB-EBIC image of the varistor grain boundary in which the current collecting electrodes are positioned on either side of the interface. The grain boundary shows characteristic ‘bright-dark’ type I contrast, which is due to opposed EBIC currents generated in the space-charge regions on opposite sides of a charged grain boundary plane. On applying a positive voltage bias to the right hand electrode, the electrostatic barrier height on the right hand, reverse biased, side of the interface is increased, and on the left hand, forward biased, side of the interface it is decreased. When +40 mV is applied, the bias voltage is sufficient to flatten the bands on the left side of the interface and the dark EBIC contrast is lost due to the suppression of the charge separating field. The grain boundary consequently shows bright type II contrast (Fig. 2b). Similarly, by applying a voltage bias of −40 mV flat band conditions are achieved on the right hand side of the interface and the bright EBIC contrast is suppressed, modifying the

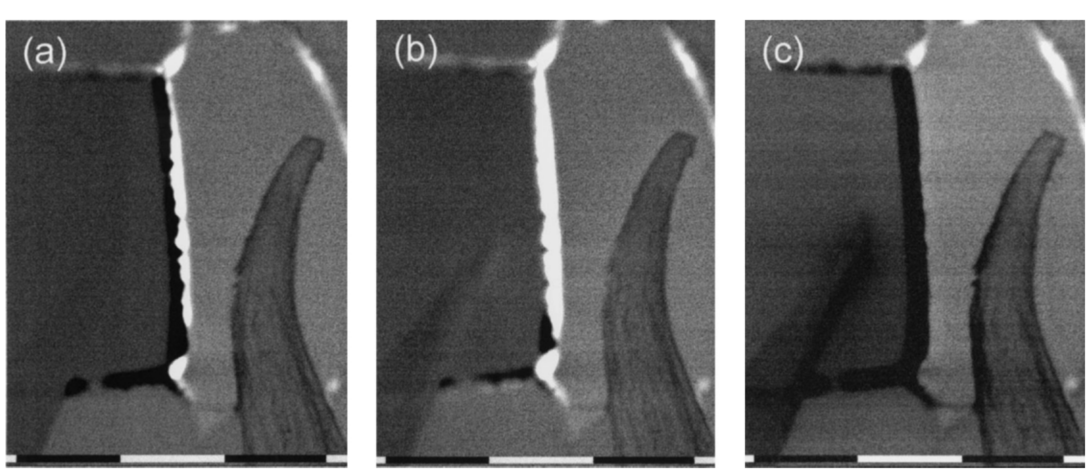

Fig. 2. EBIC images of type I varistor grain boundary with (a) zero, (b) +40 mV and (c) −40 mV bias applied. (scale bars = 10 μm).

form of the EBIC signal to dark type II contrast (Fig. 2c).

Fig. 3a is a zero bias GB-EBIC image of another grain boundary within the varistor. In this case the grain boundary shows bright type II contrast. When a bias of −90mV was applied, the symmetrical barrier structure was restored, causing the grain boundary to show type I contrast (Fig. 3b). Fig. 3c is a zero bias GB-EBIC image of a third varistor grain boundary, this time one showing dark type II contrast. In this case a positive bias of +50 mV bias was required to restore the symmetrical band structure and cause the interface to display type I contrast (Fig. 3d).

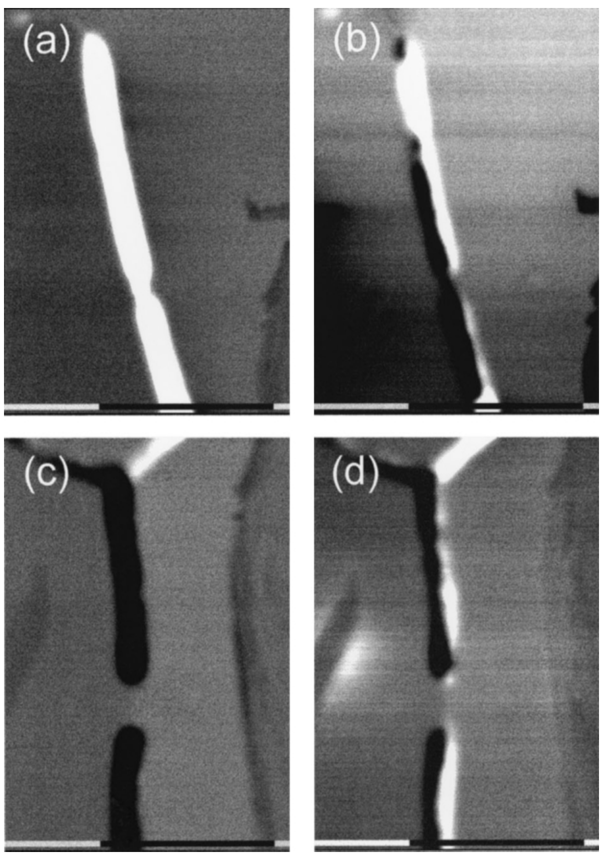

Fig. 3. (a),(b) EBIC images of bright type II varistor grain boundary with (a) zero and (b) −90 mV applied. (c),(d) EBIC images of dark type II varistor grain boundary with (c) zero and (d) +50 mV applied. (scale bars = 10 μm).

Thus, by applying an appropriate voltage bias to an interface showing type I contrast the band structure can be modified such that type II EBIC contrast is observed. Likewise, interfaces showing type II contrast can be modified to show type I contrast under bias, indicating that the electrical structures present at these interfaces are related.

In order to relate the differences in zero bias EBIC contrast at these interfaces to the grain boundary structures, detailed crystallographic measurements were made. In a previous study[4] EBSD analysis was used to compare both the lattice and the basal plane misorientation across a number of interfaces showing types I and II contrast. Similar distributions in misorientation were found in both cases, preventing a simple correlation being made between contrast type and misorientation. In the present study this work is extended by considering the crystallographic orientations of the crystal faces presented on either side of the grain boundary plane. These were calculated by combining the grain orientations on either side of the grain boundary plane, established using EBSD analysis, with the orientation of the grain boundary plane, determined using depth resolved EBIC (DREBIC) microscopy.[13]

DREBIC microscopy is a novel technique that uses a range of beam energies to excite the grain boundary at different depths below the sample surface. If the grain boundary is inclined there is a consequential offset in the EBIC signal from which the slope of the grain boundary plane may be determined.

The crystallographic axes of the zinc oxide grains on either side of the grain boundary, together with the poles to the grain boundary planes were plotted in stereographic projection, enabling the crystal faces forming either side of the grain boundary plane to be identified. Fig. 4 shows this information in the form of pole figures, based on a (00.1)–(10.0)–(21.0) standard triangle onto

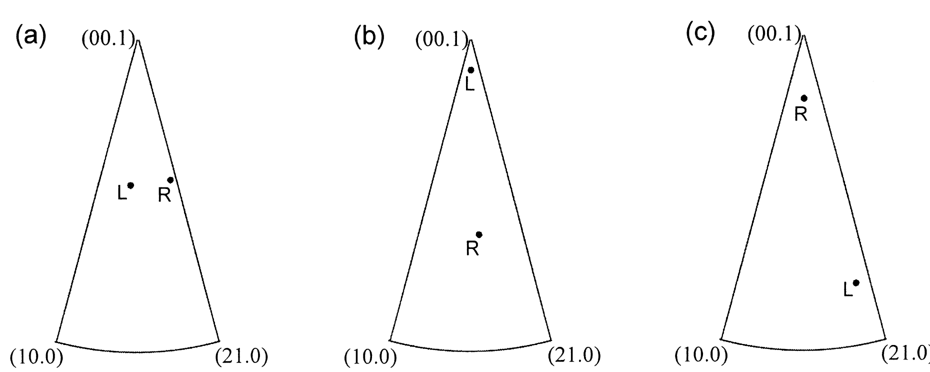

Fig. 4. Pole figures showing the orientations of the crystal faces forming the right (R) and left (L) hand sides of the grain boundaries studied here with (a) type I, (b) bright type II and (c) dark type II contrast.

which the poles to the crystallographic planes forming the left and right hand faces of each of the grain boundaries presented in Figs. 2 and 3 have been plotted. For the grain boundary showing type I EBIC contrast under zero applied bias (illustrated in Fig. 2a), the poles to both the left (L) and right (R) hand grain boundary planes lie at a similar angle from the *c*-axis (Fig. 4a). In the case of the interface showing bright type II contrast (illustrated in Fig. 3a), the poles to the left and right hand grain boundary planes lie at different angles from the *c*-axis, with the left hand grain boundary plane lying closer to the *c*-axis (Fig. 4b). Conversely, for the interface showing dark type II contrast (illustrated in Fig. 3c), the pole to the grain boundary plane forming the right hand side of the interface lies closer to the *c*-axis (Fig. 4c).

From these examples it can be seen that there is a strong correlation between the orientation of the crystal planes presented on either side of the grain boundary and the observed EBIC contrast; similarly oriented planes giving rise to type I contrast whilst grain boundary planes with significantly different orientations show bright or dark type II contrast according to which side of the interface the plane closest to the (00.1) pole lies.

4. Conclusions

A relationship between crystallographic aspects of the structure of a varistor grain boundary and its electrical behaviour has been observed for the first time. An asymmetry in the EBIC signal was related to the orientations of the crystal faces presented on either side of the grain boundary. This behaviour is not currently taken into account in models of varistor performance.

References

1. Moulson, A. J. and Herbert, J. M., *Electroceramics*. Chapman and Hall, London, 1997.
2. Ernst, F., Kienzle, O. and Rühle, M., Structure and composition of grain boundaries in ceramics. *J. Eur. Ceram. Soc.*, 1999, **19**, 665–673.
3. Kataoka, N., Hayashi, K., Yamamoto, T., Sugawara, Y., Ikuhara, Y. and Sakuma, T., Direct observation of the double Schottky barrier in niobium-doped barium titanate by the charge-collection current method. *J. Am. Ceram. Soc.*, 1998, **81**, 1961–1963.
4. Russell, J. D., Halls, D. C. and Leach, C., The relationship between crystal misorientation and conductive mode contrast of grain boundaries in additive free zinc oxide. *J. Mater. Sci.*, 1997, **32**, 4585–4589.
5. Matsuoka, M., Non-ohmic properties of zinc oxide ceramics. *Jpn. J. Appl. Phys.*, 1971, **10**, 736–746.
6. Clarke, D. R., Varistor ceramics. *J. Am. Ceram. Soc.*, 1999, **82**, 485–502.
7. Tanaka, S. and Takahashi, K., Voltage-current characteristics of single grain boundary of zinc oxide varistors and the effects of additives. *Key Eng. Mat.*, 1999, **157–158**, 241–248.
8. Russell, J. D. and Leach, C., Problems associated with imaging resistive barriers in BaTiO3 PTC ceramics using the SEM conductive mode. *J. Eur. Ceram. Soc.*, 1995, **15**, 617–622.
9. Russell, J. D., Halls, D. C. and Leach, C., Grain boundary SEM conductive mode contrast effects in additive free ZnO ceramics. *Acta Mater.*, 1996, **44**, 2431–2436.
10. Russell, G. J., Robertson, M. J., Vincent, B. and Woods, J., An electron beam induced current study of grain boundaries in zinc selenide. *J. Mater. Sci.*, 1980, **15**, 939–944.
11. Palm, J. and Alexander, H., Direct measurement of the local diffusion length of grain boundaries by EBIC without a Schottky contact. *J. Phys. IV, Colloq. C6,* Suppl. to *J. Phys. III*, 1991, **1**, 101-106.
12. Leach, C., The effect of voltage bias on the EBIC contrast at varistor grain boundaries. *Interface Science,* 2000, **8**, 383–396.
13. Leach, C., SEM based estimation of the grain boundary plane orientation in zinc oxide varistors using conductive mode microscopy. *Scripta Mater.*, 2000, **13**, 529–534.