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A REBIC and CL study of interfaces in a zinc oxide based varistor

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Conductive mode (CM) and cathodoluminescence (CL) microscopy techniques were used to study grain boundary structures in a zinc oxide based varistor, doped with 0.5 mol % Bi_2O_3 and 0.5 mol % Sb_2O_3. By combining these two techniques specific details of the electrical and luminescence properties of individual interfaces could be characterised. CM imaging clearly showed the presence of potential barriers at the grain boundaries. The same grain boundaries were regions of strong CL emission. It is suggested that the dominant CL emission at grain boundaries in this material originates from self-excitation centres at impurities and/or defects within the structure rather than the direct recombination of electron-hole pairs across the forbidden band gap. © *1999 Kluwer Academic Publishers*

1. Introduction

Grain boundaries in polycrystalline semiconductors and ceramics frequently carry a space charge due to the presence of interface states, introduced either as a result of the local crystallography or as a consequence of the segregation of dopants introduced during processing [1]. The presence of space charge results in built in fields at the grain boundaries that are responsible for many of the special properties seen in electronically conducting ceramics [2]. For example, zinc oxide varistors show highly non-ohmic behaviour when subjected to high voltage transients, with individual grain boundaries breaking down to a low resistance state when a threshold voltage, usually between 2 and 4 V, is exceeded [3, 4]. As such they find application as power surge arresters [5].

Remote electron beam induced current (REBIC) microscopy is a scanning electron microscope (SEM) based variant of the conductive mode, and is used to observe effects due to barrier structures within a semiconducting material. In using this mode, two electrical contacts are attached to the sample surface on either side of the region of interest and the current flowing between them as the primary electron beam rasters the surface is amplified to form the image (Fig. 1). In electrical ceramics, two effects may be observed; a brightness gradient between the electrodes with steps at resistive barriers, sometimes termed resistive contrast imaging, and electron beam induced current (EBIC) contrast caused by the separation of electron-hole pairs generated by the incident electron beam by the built-in fields at grain boundaries [6–8]. Previous SEM studies of zinc oxide based varistors and additive free zinc oxide ceramics have shown grain boundary contrast indicative of built-in field effects at some grain boundaries [7, 9, 10].

Cathodoluminescence (CL) is the term used to describe the emission of light as a result of electron bombardment. When carried out in the SEM, CL occurs by the radiative recombination of beam induced electron-hole pairs, and can be classified into intrinsic and extrinsic emissions. Intrinsic, or fundamental, emission occurs when conduction band electrons and holes from the valence band recombine radiatively, whereas extrinsic, or activated, emission involves electronic transitions between energy levels specific to a given impurity atom or defect. In this regard, transition metals, well known for their coloured salts, are particularly effective at generating additional states locally [11]. In zinc oxide it is reported that intrinsic luminescence occurs in a blue to near UV band and also that extrinsic emission occurs throughout the visible range, in particular with overlapping bands centred on the green, orange and yellow regions of the spectrum. These are attributed in the main to zinc and oxygen interstitials or vacancies [12–15] arising as a consequence of the processing conditions.

In this study a combination of conductive mode and cathodoluminescence microscopy was used to investigate the REBIC and CL properties of specific grain boundaries in zinc oxide based varistors in order to establish details of the electrical structure of specific interfaces.

2. Method

The varistor sample used in this study was sintered from a powder prepared by a standard mixed oxide route, and contained 99 mol % ZnO, 0.5 mol % Bi_2O_3 and 0.5 mol % Sb_2O_3. A compact was prepared by uniaxial pressing and sintered in air for 4 h at 1200 °C, heating and cooling at 100 °C/h. The sintered pellet was then ground flat and the surface polished using a water based slurry of 0.3 μm alumina powder.

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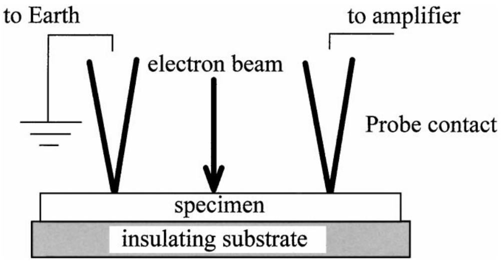

Figure 1 The sample and electrode configuration used in this study for conductive mode imaging.

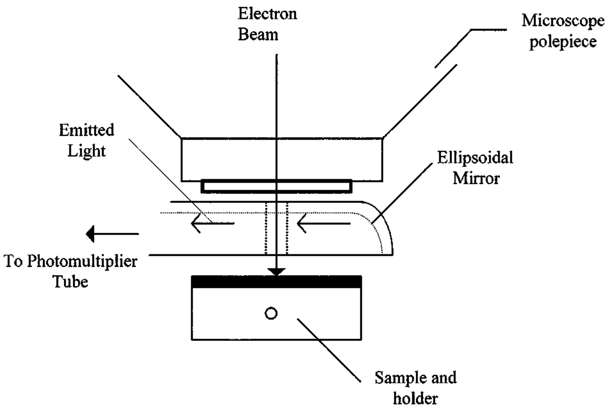

Figure 2 Details of the SEM based cathodoluminescence system.

The sample was mounted on an insulating stub and conductive mode imaging was carried out using a Phillips 525 SEM. Electrical contact to the sample was made through micromanipulator controlled electrodes that were placed directly onto the sample surface. The collected signal was amplified using a Keithley 428 current amplifier and used to form the image.

CL images of the same area were made using a JEOL 6400 SEM fitted with an Oxford Instruments CL302 cathodoluminescence detection system, which uses a silver plated parabolic light collector placed directly above the sample, with the region of interest at one focus, to direct the emitted light onto a monochromator and photomultiplier. The monochromator can be adjusted so that the amplified signal used to form images can contain all the emitted light (panchromatic imaging) or merely a small band of wavelenghts (monochromatic imaging) (Fig. 2). In this study the collected CL signal was used to form a panchromatic image.

3. Results

Micrographs of the area of the varistor selected for study are presented in Fig. 3: (a) is a back-scattered electron image, (b) a conductive mode image and (c) a CL image. The deep scratches clearly visible on the backscattered electron image (Fig. 3a) were caused (intentionally) by the micromanipulator controlled electrodes and act as reference markers.

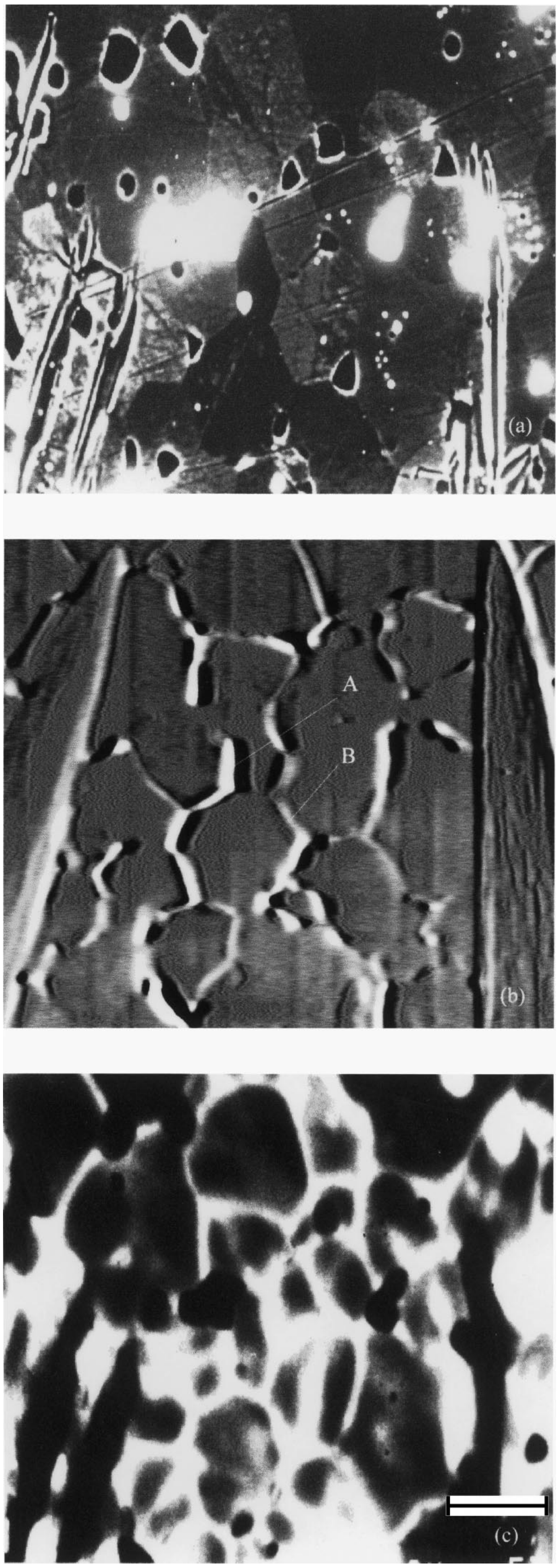

Figure 3 SEM images of the ZnO-based ceramic used in this study. (a) a backscattered electron image; (b) a REBIC image of the area outlined in (a); and (c) a CL image. (scale bar = 20 μm).

The CM image (Fig. 3b) shows EBIC contrast, in the form of strong bright and dark lines coincident with certain grain boundaries. Using the nomenclature of [10], the contrast effects observed are of type I, arrowed (A) and consisting of a pair of parallel bright and dark lines, and type II arrowed (B) and consisting of a single bright or dark line.

The CL micrograph (Fig. 3c) shows that the bright CL contrast is more intense at the grain boundary regions than the grain interiors, indicating an increased density of radiant recombination centres close to the grain boundaries. Surface damage appears in dark contrast, indicating that either the lattice disruption has quenched the CL emissions or the surface roughness causes sufficient scattering as to make it impossible for the light to escape the surface locally.

4. Discussion

The grain boundary regions of this sample appear as sites of strong EBIC contrast as well as enhanced CL emission. The strong EBIC contrast is indicative of charge separation at well developed barrier structures at the ceramic grain boundaries, and is consistent with accepted varistor models. The predominance of type I contrast, consisting of parallel bright and dark lines at the grain boundary is indicative of a symmetrical structure with equivalent barriers on either side of the grain boundary. For a more detailed description of conductive mode contrast in electrical ceramics, and a discussion of the factors giving rise to these contrast effects the reader is referred to previous publications [7, 8, 10, 16].

The features seen in the CL images from this study are similar to the contrast effects observed by Löhnert and Kubalek from the near surface regions of their sample [17]. Deeper within their sample, they observed a reversal in contrast whereby the grain boundaries showed in dark contrast relative to the grain interiors. The increased density of radiant recombination centres close to the grain boundaries in the near surface region was interpreted as due to the effects of transitions between extra states as a result of a local oxygen excess. Well below the surface the pellet was considered oxygen deficient, possibly as a result of reduction of the zinc oxide during binder burn out [18] leading to dark grain boundary contrast. In a more recent study [19], CL spectra of the grain boundary and grain interior of a sintered undoped zinc oxide were compared. In this case the grain boundaries were dark relative to the grain interiors, but showed EBIC contrast. It was found in this case that the reduction in CL intensity close to the grain boundaries was due to a reduction in the intensity of the intrinsic peak.

Intrinsic CL emission requires the radiative recombination of beam induced electron-hole pairs whereas the processes giving rise to EBIC require that electron-hole pairs generated by external excitation drift apart in the electric field without recombination. It might be expected that if one of these processes were active at a given grain boundary then the other process may be inhibited. It is clear that at many of the grain boundaries examined in this study, built-in fields are leading to charge separation with resultant EBIC contrast. We may therefore conclude that the increased intensity of CL emission in these regions compared with the grain interiors cannot be due to intrinsic emission. Instead it is caused by radiative transitions between energy states introduced as a result of dopants or defects acting as luminescence centres, which have segregated to the grain boundaries rather than being distributed evenly through the sample. This conclusion is in agreement with the observations of Löhnert and Kubalek [17], who attributed the increase in luminescence to transitions between localised states introduced as a result of an increase in oxygen content at grain boundaries. In the case of the materials studied here, additional dopants have been added in order to promote the varistor action and may themselves act as self-excitation centres at the grain boundary.

5. Conclusions

By combining REBIC and CL analysis techniques, detailed information about the electrical structure of individual grain boundaries in zinc oxide varistors has been obtained. Both EBIC and CL contrast were observed at individual grain boundaries within the varistor. The EBIC contrast demonstrates the existence of well developed grain boundary potential barriers consistent with the accepted varistor models. The strong CL emission observed at the varistor grain boundaries is due to transitions between localised additional states, introduced either around lattice defects or as self-excitation centres within dopants, and not the direct recombination of beam induced electron-hole pairs across the bandgap.

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