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Direct observation of resistive barriers in a $BaTiO_3$ based thermistor

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The remote electron beam induced current technique has been used to form resistive contrast images of the resistive barriers developed in 80 °C thermistor materials. Linescans extracted from the images have been used to calculate the temperature variation of resistivity of selected interfaces within the material. It is seen that the major resistive changes are associated with only a few of the grain boundaries in this material.

1. Introduction

Perovskite phase positive temperature coefficient of resistance (PTCR) thermistors show a characteristic increase in resistivity over a fairly small temperature interval just above the Curie temperature, T_c, making them suitable for use in thermal protection and current limiting devices [1]. It is known that the increase in resistivity is associated with processes occurring at the grain boundaries and several models describing this behaviour have been proposed [2, 3]. In these models an abrupt change in the dielectric constant at the Curie temperature leads to changes in the barrier height and hence the grain boundary impedance. However the fine details of the PTCR effect are still not fully understood [4].

Traditionally, structure averaging techniques, for example bulk resistance versus temperature measurements, are used to characterize PTCR devices but, using this approach, localized property variation due to heterogeneity in the microstructure is not observed. Little work has been carried out to determine the electrical properties of individual grain boundaries, and has been confined to direct measurements made on coarse grained materials using microcontacts [5]. From such experiments it has been concluded that there may be differences in the detail of the PTCR effect at different grain boundaries [4].

In this contribution, we report the application of a scanning electron microscope (SEM) based technique to the study of PTCR materials which permits the simultaneous observation of resistivity variations at many grain boundaries in fine grained material. It uses the conductive mode of the SEM [6] and is termed remote electron-beam induced current (REBIC) [7, 8].

In the REBIC mode electrical contacts are made with the sample as is shown in Fig. 1. Using this configuration, image contrast can be generated in electronic ceramics as a result of several different processes [9]. However, for the purposes of this contribution we are solely concerned with contrast introduced due to resistivity variations in the material, an effect termed resistive contrast imaging [10, 11]. In this case the specimen acts as a current divider with the net current injected by the electron beam flowing either directly through the left contact to earth or through the right contact, the amplifier, then earth with the resultant signal used to form an image on the SEM viewing screen. In an homogeneous material a brightness gradient is observed between the contacts in the REBIC image with variations in sample resistivity manifested as local changes in the gradient. At a given point the detected current, I, is simply related to the magnitudes of the resistive paths to earth through the right and left contacts, (R_L and R_R) via:

$$I = I_0 \frac{R_L}{(R_L + R_R)} \quad (1)$$

where I_0 is the component of the beam current absorbed by the specimen. For a more complete discussion, see Russell and Leach [11].

2. Experimental procedure

A flat section of commercial PTCR thermistor with a T_c of 80 °C was cut and polished. After careful cleaning, an array of closely spaced aluminium contact pads was formed by evaporation using a transmission electron microscopy grid as a mask. The sample was then mounted on to an Oxford Instruments H1001 heating stage for observation in the SEM. Electrical contacts were made on adjacent pads using micromanipulator probes and the collected signal amplified using a Keithley 428 current amplifier.

3. Results and discussion

Sample current–voltage characteristics and REBIC images of the region between the electrical pads were taken in the temperature range 80–140 °C. Fig. 2 shows the variation of low-voltage resistance with temperature, which was calculated from *in-situ* current–voltage characteristics measurements, and

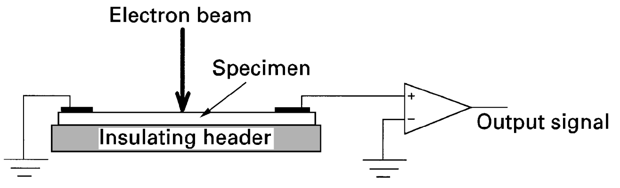

Figure 1 The REBIC configuration used in this study.

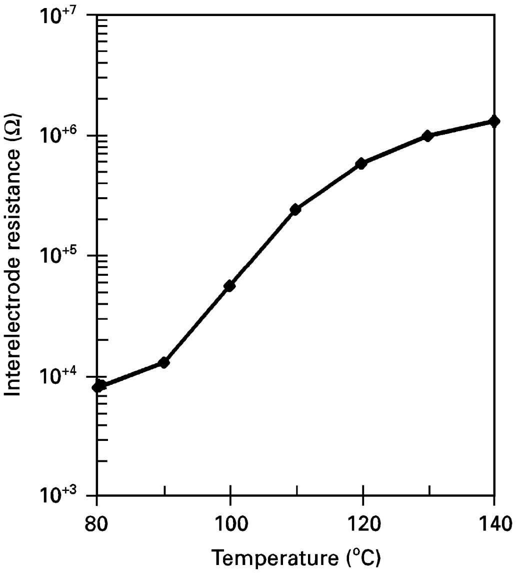

Figure 2 Temperature variation of interelectrode resistance.

reproduces a section of the characteristic PTCR curve for this material.

Fig. 3(a and b) are typical REBIC images of the material taken at 110 °C and 140 °C respectively, with the corresponding secondary electron image shown in Fig. 3c. In each image, signal steps corresponding to high resistivity interfaces are superimposed on a baseline of increasing brightness. In general, the contrast steps are not observed at all grain boundaries and, from comparison of Fig. 3(a and b), do not develop uniformly as the temperature is increased. This suggests that the grain boundary resistivity transition does not occur homogeneously across the whole microstructure. For example a step, visible in the 110 °C image at the top of Fig. 3a (labelled-'S'), is not observed in the 140 °C image (Fig. 3b), because the resistance of that particular interface no longer represents a significant proportion of the overall resistance of the sample, i.e., other interface resistances dominate the overall response.

We can more accurately describe the development of the sample resistance with temperature by considering the evolution of a REBIC linescan across a section of the microstructure as a function of temperature. Such a sequence, spanning the gap between the two electrical contact pads along the line A-A′ on Fig. 3c, is presented in Fig. 4. In these linescans the signal intensity at any point along the linescan varies with the cumulative resistance along the line profile, as described earlier. The ordinate of each of these linescans is presented in such a way that the constant of

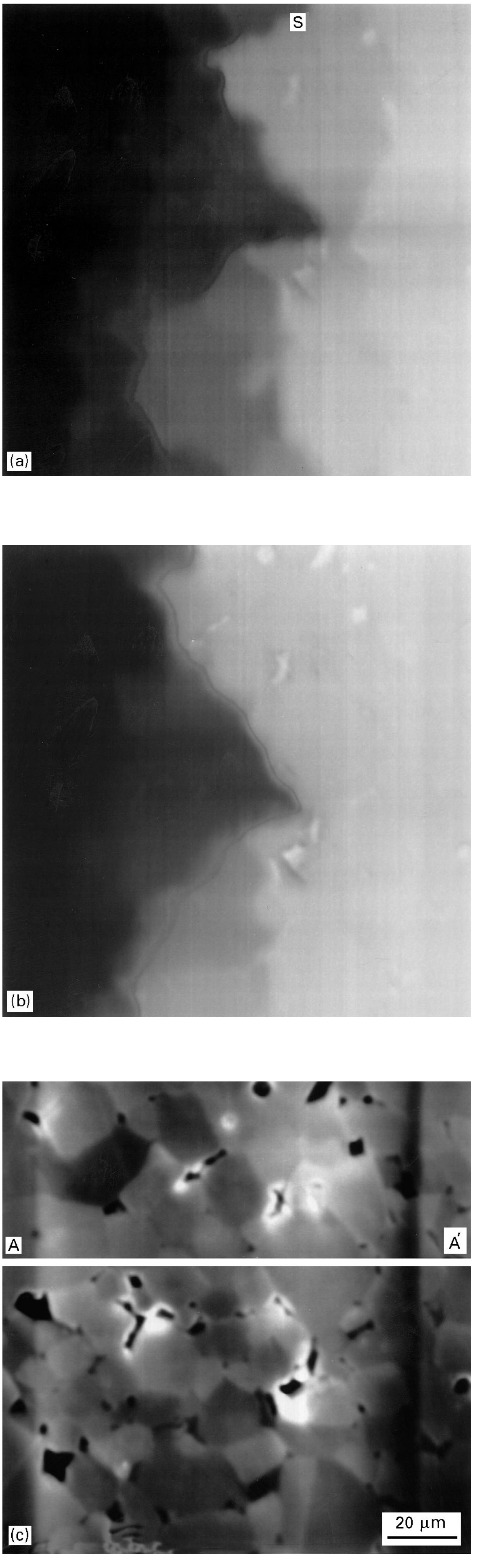

Figure 3 Resistive contrast images collected at (a) 110 °C and (b) 140 °C. The corresponding SE image is shown in (c).

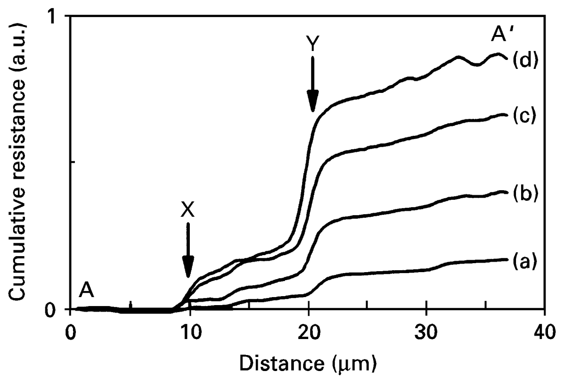

Figure 4 Plots of cumulative resistance versus distance across line A-A′ in Fig. 3c at (a) 110 °C, (b) 120 °C. (c) 130 °C and (d) 140 °C.

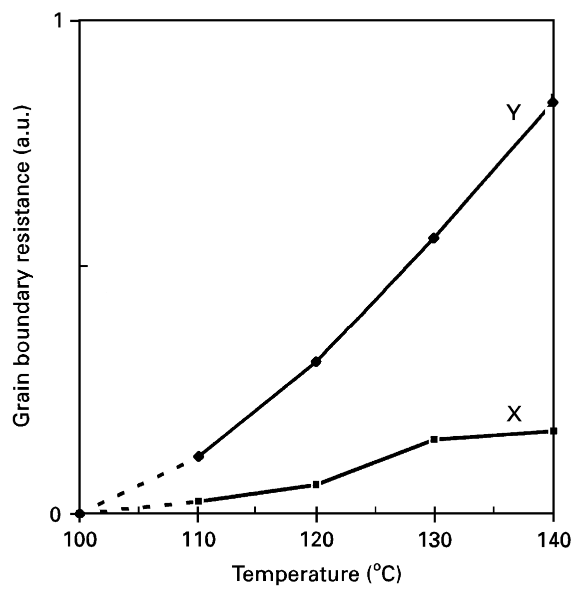

Figure 5 The variation with temperature of grain boundary resistance estimated from the step heights in Fig. 4.

proportionality relating signal strength to resistance is common to all the lines. This was arrived at by firstly normalizing the contrast range of each linescan and then scaling it by a factor equal to the inter-electrode resistance at that temperature (which was read from Fig. 2). The advantage of presenting the data in this way is that a given step in the graph represents the same resistance change in each of the linescans.

The resultant plots can be considered as a sequence of lines of steadily increasing gradient upon which steps are superimposed at points X and Y. The increase in the overall gradient with temperature reflects the gradual increase in sample resistivity. Although the linescans cross several interfaces, it is clear that in this material the major resistance increase with temperature is due to processes occurring at just two interfaces, labelled X and Y, where large steps in the contrast gradient have developed. These steps increase in size with increasing temperature and also become steeper, which is consistent with the development of a high resistivity barrier at a narrow interface.

From the development of step height at these interfaces, it is possible to estimate the temperature variation of grain boundary resistance. Such data are presented in Fig. 5. It can be seen that the behaviour of each interface is distinct and both responses clearly contrast with the behaviour of the majority of interfaces in this material where a large resistance step is not observed.

In this material it can therefore be seen that the overall PTCR characteristics are dominated by effects occurring at just two of the interfaces along the path of the linescan. Thus the PTCR behaviour of this material is controlled by the behaviour of a relatively small proportion of the grain boundaries which exhibit large resistance changes with temperature.

These observations concur with the observations of other workers who have suggested that the bulk PTCR effect is not described by a single grain boundary characteristic response, but that there may be several responses dependent on the interfacial structure. It is therefore important for the continued development of PTCR materials that their local behaviour is studied rather than placing reliance on bulk averaged property determinative techniques in order that ineffective, or undesirable structures can be eliminated.

4. Conclusions

Resistive contrast imaging has been used to demonstrate that the development of resistive barriers in PTCR thermistors is heterogeneously distributed through the microstructure.

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