Direct observation of potential barrier behavior in yttrium–barium titanate observed by electrostatic force microscopy

S.M. Gheno,* H.L. Hasegawa and P.I. Paulin Filho

Department of Materials Engineering, Federal University of São Carlos, Rod. Washington Luiz, Km 235, P.O. Box 676, 13565-905 São Carlos-SP, São Paulo, Brazil

Received 5 June 2006; accepted 20 October 2006
Available online 8 January 2007

Electrostatic force microscopy (EFM) was used to directly probe, and thereby characterize, both the surface morphology and surface potential of semiconducting barium titanate doped with yttrium. The potential barrier developed at the grain boundaries was determined using EFM with in situ applied voltage up to 8 V. The applied voltage was mapped and the distribution of potential across the sample showed changes in regions that matched the grain boundaries, displaying a constant barrier width of 145.2 nm.

Keywords: Yttrium–barium titanate; Barrier layer; EFM; PTC effect

Ferroelectric materials have been extensively studied over the last 50 years, and insight into the peculiar properties of these materials has led to numerous applications. In these applications different kinds of ferroelectrics have been employed beyond the linearity limit prescribed by the classical theory of piezoelectricity [1–4].

Positive temperature coefficient (PTC) ceramics based on doped barium titanate are ferroelectric polycrystals that exhibit a wide variety of electrical phenomena, and are commonly employed in applications such as sensors and actuators due to their wide variation in electrical resistance as a function of temperature [1,5–8]. A detailed knowledge of the behavior of PTC ceramics is desirable in order to predict the performance and durability of ferroelectric devices. In ferroelectric sensors, linear behavior is usually more important than the strength of the signal; however, in applications such as ferroelectric actuators, nonlinear behavior results from operating at high power [5].

In semiconducting barium titanate-based ceramics, the PTC effect is attributed to the formation of electric potential barriers in the grain boundaries, increasing the electrical resistance. The grain resistivity of donor-doped barium titanate thermistors increases sharply and rapidly with temperature [1,6,8]. These materials display an electrical behavior characterized by an abrupt increase in resistivity as a function of temperature close to the Curie temperature ($T_c$) during the shift from tetragonal to cubic phase when the materials are heated to temperatures above 130 °C [6,8].

Studies of the behavior of individual grain boundaries in thermistors have shown that the magnitude of the PTC effect can vary widely between grain boundaries, with some grain boundaries showing substantial changes in resistance above $T_c$ [8–12].

Several techniques have been used to characterize the PTC effect on grain boundaries [6,8,13–18]. The most widely accepted models attribute the PTC effect to the formation of potential barriers in grain boundaries; these barriers increase the resistivity when temperatures above $T_c$ are reached [15]. PTC behavior depends largely on the material’s microstructure because it is basically a grain boundary phenomenon [6,7,15,16]. However, it has also been observed that the magnitude of the PTC effect at a given grain boundary can be influenced by the geometry of that boundary and, in particular, by the crystallographic misorientation across the interface. Even so, lattice misorientation alone does not, of itself, constrain the degree of freedom sufficiently to fully define the physical structure of a grain boundary. In real materials, the relative importance of each of these parameters in defining the energy of an interface depends on how strongly it influences its physical and electrical structure [8,17,18].
Hayashi et al. [18] proposed a correlation between the magnitude of the PTC effect and the overlapping volume of the two lattices on either side of the grain boundary. They noted that the grain boundary resistivity above $T_c$ increased at a slower rate as the interface coherency increased, prompting the suggestion that the peak height of the grain boundary potential barrier was linked to the grain boundary structure.

Seaton and Leach [7], who analyzed a large number of grains, established the misorientation of a statistically significant number of grain boundaries. The large proportion of coherent grain boundaries, they found, corresponded to about twice the number of randomly oriented grains in all their samples.

The presence of grain boundaries in semiconducting and mixed-conducting oxides influences the material's macroscopic properties to such an extent that these boundary have become a focus of engineering strategies for the development of devices. Thus, the electrical properties of PTC ceramics are influenced by the nature of their grain boundaries [15,16].

In this work the electrical properties of yttrium–barium titanate (Y–BT) ceramics are studied using electrostatic force microscopy (EFM), which allows for local potential measurements while imaging the surface. The investigation and mapping of potential barriers distribution across the Y–BT surface was carried out using atomic force microscopy (AFM)/EFM, varying the applied potential on the surface.

Yttrium-doped barium titanate was obtained by mixing 0.3% yttrium nitrate ($Y(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 99.8%, AESAR, with BaTiO$_3$ powder with $\frac{\text{Ba}}{\text{Ti}} = 0.95$ (TAM ceramics)). The mixture was made in an aqueous solution and dried to a powder, which was then ground and compacted into pellets. Y–BT pellets (10 mm in diameter) were made by pressing the powders at 25 MPa in an uniaxial press, drying and then sintering in air at 1350°C for 2 h. After the sintering, the Y–BT pellet samples were polished and thermally etched at 1250°C for 18 min using a heating rate of 2°C min$^{-1}$.

EFM experiments were performed using an AFM microscope, model nanoScope IIIa from digital instruments equipped with an extender electronics module (Veeco Instruments, Santa Barbara, CA). Topographical measurements and surface potential data were obtained using the two-pass technique (Lift Mode). In this configuration, the tip (operating in TappingMode), scans a topographical line, then lifts to a predefined height for a second scan, during which it detects variations in the frequency of the oscillating cantilever, measuring the surface potential over the same line at a constant distance from the sample. Imaging was carried out in ambient conditions. The electrical potential at the sample surface was quantified in a combination of AC noncontact mode (TappingMode) and constant sample-tip separation mode (Lift Mode). A NSC15 tip (MikroMasch) was used in all the experiments. A separation distance of 75 nm between the tip and the sample was chosen in order to minimize the effect of the van de Waals forces while allowing the monitoring of the long-range electrostatic forces. Electrostatic force gradient images were obtained by monitoring the shifts in phase and frequency between the oscillations of the biased AFM cantilever and those of the piezoelectric driver as a function of bias voltages applied to the cantilever. The initial EFM imaging conditions were: interleave frequency drive, 25 Hz; integral gain, 0.35; proportional gain, 2.5. The images of surface potential and barrier layer were obtained by applying 0, 4 and 8 V in situ to the sample.

Figure 1 shows an XRD pattern of the Y–BT. This sample containing tetragonal-BaTiO$_3$ is easily identifiable by the peak splitting (e.g. (002) and (200) reflections). In addition to the tetragonal reflections of barium titanate, a peak (∼5, 3, 1) of monoclinic Ba$_6$Ti$_{17}$O$_{40}$ is also visible, which is a common feature in nonstoichiometric BaTiO$_3$ ceramics containing excess TiO$_2$ and sintered at temperatures above the lowest eutectic point of 1332°C [19]. However, no peak broadening due to the nonuniform strain introduced by surface grinding is visible.

Figure 2 shows the characteristic PTC curve. The electrical resistivity of Y–BT at temperatures below 85°C behaves like that of any semiconductor with a negative temperature coefficient. A sharp PTC effect of three orders magnitude starting at ∼85°C and ending at ∼130°C was observed. In this region the resistivity increased exponentially with the temperature. This abrupt increase in resistivity was attributed to the shift from tetragonal phase (ferroelectric) to cubic phase (paraelectric), which is evidence of the PTC effect. The ferroelectric domains, which short-circuited the grain boundary, disappeared gradually as the temperature rose. Low resistivity at high temperatures is caused by desorption of chemisorbed oxygen atoms at the grain boundaries upon heating, which diminishes the potential barrier height. Thus, chemisorbed oxygen is consumed and conducting electrons are released, lowering the potential barrier and degrading the PTC effects [20].

The topography and EFM images were recorded simultaneously to characterize the local ferroelectric properties. Figure 3 depicts the topographic AFM image of Y–BT, revealing a microstructure with clearly defined grains and grain boundaries.

Figure 4 shows the EFM images corresponding to the topographical image of Y–BT obtained by AFM and shown in Figure 3. The sample was subjected to a range of voltages from 0 to 8 while the EFM scan was performed at a lift height of 20 nm.

![Figure 1. X-ray diffractogram of yttrium–barium titanate.](image-url)
Figure 4(a) shows the EFM image without the applied voltage gradient, showing no features when compared with Figure 3. Figure 4(b) and (c) shows EFM images with voltage steps from 4 and 8 V applied to the samples surface. These EFM images clearly show the raising of potential barriers as the applied field gradient increased.

Some grain boundaries began to appear at 4 V (Fig. 4(b)). At 8 V (Fig. 4(c)) the grain boundaries became clearly visible and were found to be congruent with the topographical image depicted in Figure 3.

The dark regions appearing in Figure 4(b) and (c) are associated with semiconductor material, indicating that the grains are current conductors, while the bright regions are insulating regions associated with grain boundaries. These images were formed because, as the voltage increased, the probe began to be repelled in the grain boundary regions. This is congruous with theories developed to explain the PTC behavior observed in doped barium titanate, and indicates that the PTC effect is related to the barrier formed at the grain boundaries in response to segregation of acceptor and donor dopants.

To quantify the minimum error in the elimination of topographic signals in the potential gradient image, a comparison was made of the topographic image and the potential gradient image at the interface of some grain boundaries. Since there is no lateral applied voltage, the features at the grain boundaries increase as the repulsive forces increase between the grain boundary and the force probe.

The image contrast in Figure 4 emphasizes the fact that the increase of contrast in the field gradient image is due not to the topographical structure but to effects of the local electric field. An increase in the voltage applied to the samples surface corresponds to an increase in the local field gradient. In either case, the results shown in Figure 4 imply that the voltage drop at the grain boundary spreads extensively into the grain. The measured barrier thickness was 145.2 nm, which is close to the values reported in the literature [18,21,22].

The resistivity anomaly of the barrier layer depends on both the geometry and the activation energy required to surmount the height of the potential barrier. The resistivity anomaly of the barrier layer is due to a decrease in carrier density rather than in carrier mobility. The depletion of free charge carriers applies in the same way to volume and barrier layers.

The resistivity anomaly can be treated quantitatively, according to Heywang’s theory [1]. We therefore propose a band diagram for Y–BT (Fig. 5) where the defects at the grain boundary produce a trap density \((N_i, \text{cm}^{-2})\) distributed over a certain energy range. In BaTiO\(_3\) grains, electron donors embodied in the lattice dissociate quantitatively above the ambient temperature. Our results demonstrate that both donors and
acceptors segregate in the boundary region, in agreement with Heywang [1] and Desu and Payne [15,16].

Defects and diffusion effects suggest that the potential barriers originating at the grain boundaries are due to regions of barium-rich vacancies that are electrically compensated by electron donors (oxygen diffusion along grain boundaries). However, acceptor and donor dopants are assumed to be uniformly distributed throughout the grains and grain boundaries and the acceptor effects are due to their activation energies. Dopant mass transport is driven by differences in the surface and interface energies, which lead to nonuniform distribution of dopants and, as such, need not be symmetric around the boundary. Activation energies depend on polarization in the ferroelectric region, and the formation of high electrical resistance regions at grain boundaries produces potential barriers. Space charges are developed in the vicinity of grain boundaries due to the flow of electrons from the conducting grains to the vicinity of the high resistance area (grain boundaries) [1,15,16].

Diffusion studies and chemical defects [1,15,16] suggest that the potential barriers in grain boundaries originate from layers with barium-rich vacancies or areas that form grain neighborhoods during cooling from high temperatures. It is assumed that the donors in these layers are completely compensated by barium vacancies. However, donor or acceptor dopants are assumed to be uniformly distributed throughout the grains and grain boundaries and the acceptor effect is only interpreted through their energy levels.

If the traps in the grain boundary are activated, some of the carriers contributed by the donor atoms in the grain may be trapped at the grain boundaries, thus producing a region of space with the opposite polarity. The thickness and resistivity of the space charge region, and the grain boundary resistive region, can then limit the sample’s conductivity. The results obtained here with EFM are only in partial agreement with Desu and Payne’s theory [15,16], since we did not find any variation in barrier layer width.

Moreover, a uniform barrier was only observed at high resistive grain boundary layers surrounding semiconducting grains, resulting in a potential barrier due to the equilibration of Fermi levels. Therefore, space charges will develop in the vicinity of grain boundaries in response to the flow of electrons from the core of the semiconducting grain to its highly resistive boundary. Space loads develop in the neighborhood of the grains’ applied voltage due a flow of electrons starting from inside the semiconducting grains to regions of high resistivity in their vicinity. This transition has been explained in terms of a constant width layer of the space load, independent of grain size [13–16].

Our EFM results provide strong support to explain the PTC effects in Y-BT ceramics, showing the formation of a potential barrier in grain boundary regions and a resistivity layer associated with space charge regions. Despite our detailed discussion of all the physical details obtained with the aid of the grain boundary barrier layer model, it should be emphasized that the surface states have only been introduced phenomenologically and that very little is known about their nature. This justifies the assumption that the chemical conditions at the grain boundary play an important role in the surface states, based on the fact that Y-BT ceramics display a resistivity anomaly of three orders of magnitude. The calculated width of the potential barrier is 145.2 nm.

We gratefully acknowledge CNPq (Brazil) for its financial support of this research and the National Synchrotron Light Laboratory (LNLS) (Campinas, SP, Brazil) for the AFM/EFM analyses.