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The measurement and interpretation of electrostatic potential profiles across grain boundaries in strontium titanate

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Abstract: Results from a systematic Fresnel contrast (in-line electron holography) study of a large number of grain boundary potentials from undoped, donor-doped and acceptor-doped polycrystalline strontium titanate samples are summarised. An assessment is made of whether the measured variations in potential can be used to provide information about space charge distributions at the boundaries, or whether they are instead dominated by local changes in composition, density and specimen thickness. The effects on the measured contrast of both specimen preparation for transmission electron microscopy and irradiation by the high-energy electron beam are also discussed.

1. Introduction

Electroceramics are used in many solid state electrical devices such as transistors, varistors and ferroelectric memories. Their electrical characteristics, and in particular their conduction properties, are controlled by potentials at grain boundaries. These potentials often arise from the inherent ionic character of electroceramics. In these materials, atomic disorder, such as that found at a grain boundary, causes local variations in charge. In strontium titanate, $SrTiO_3$, the grain boundaries are intrinsically negative. At equilibrium, the excess charge at each boundary must be compensated; in doped samples this occurs by segregation or depletion of the dopant to or from the grain boundary. In the case of $SrTiO_3$, acceptor dopants such as Fe, Na and Mn segregate to grain boundaries, whereas donor dopants such as Nb and La are depleted [1]. The net result is a potential barrier at each boundary, with a region of space charge extending on either side.

The existence of space charge at grain boundaries in perovskite materials such as $SrTiO_3$ was originally predicted in work performed in the 1960s on barium titanate, and has been recently investigated experimentally in the literature using electron holography. However, most of these published studies have involved the characterisation of a small number of grain boundaries, some of which are 'special' boundaries in bicrystals. Few comparisons of experimental results from doped boundaries with undoped control samples have been performed. Here, we present and discuss recent experimental results from a systematic Fresnel contrast (in-line electron holography) study of a large number of grain boundary potentials from a variety of polycrystalline strontium titanate samples. The aim of this work has been to establish whether or not space charge distributions at grain boundaries can be extracted reliably from the measured potentials.

2. Results and Discussion

Segregation and the formation of a potential barrier at a grain boundary are two aspects of the same phenomenon. Therefore, if the presence of segregation or depletion can be established then the formation of space charge can be inferred. Energy-filtered transmission electron microscopy (EFTEM) elemental maps obtained from acceptor-doped and donor-doped $SrTiO_3$ examined in this work suggest that segregation of Na acceptor dopants and depletion of La donor dopants occurs, as shown in Fig. 1.

It is also possible to measure the potentials at grain boundaries directly in the TEM using either off-axis electron holography or Fresnel contrast analysis (in-line electron holography). Fresnel contrast analysis is sensitive primarily to high spatial frequency variations in the potential. The technique involves the acquisition of a defocus series of images of a grain boundary. To a good approximation, the contrast of the fringes that form at the interface contains information about the magnitude and shape of the change in potential, while the fringe spacing contains information about its width. A representative set of fringes obtained from a grain boundary in acceptor-doped $SrTiO_3$ is shown in Fig. 2, alongside corresponding experimental and simulated intensity profiles. The images used for Fresnel contrast analysis were all recorded on a FEI Tecnai F20ST field emission gun TEM operated at 200 kV.

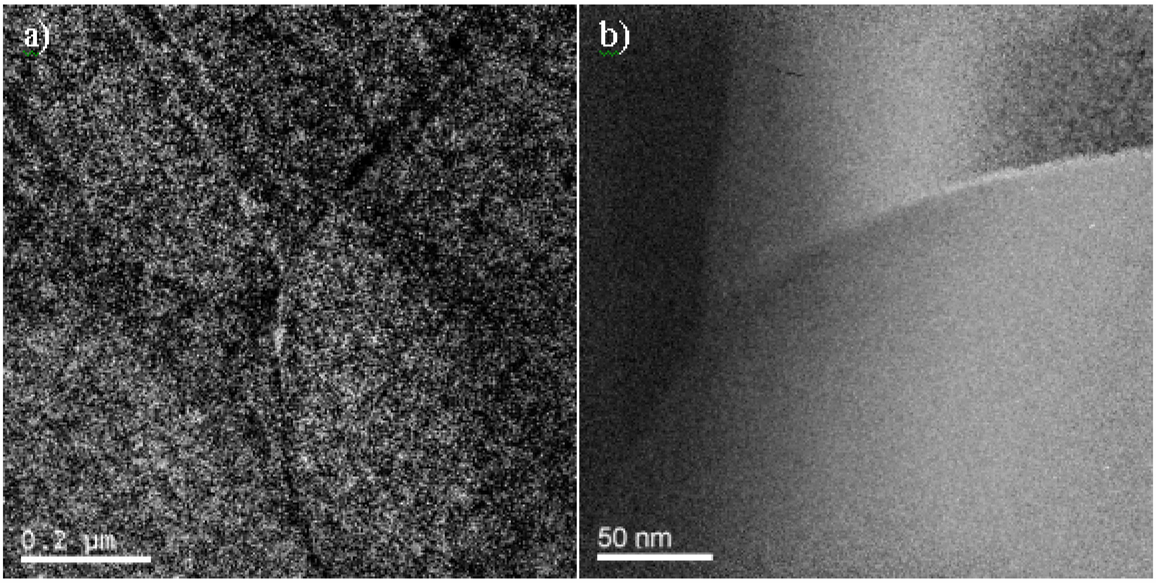

Figure 1. EFTEM elemental maps acquired from (a) donor-doped $SrTiO_3$ and (b) acceptor-doped $SrTiO_3$, showing donor (La) depletion and acceptor (Na) segregation at the boundaries.

Samples of acceptor-doped, donor-doped and nominally undoped $SrTiO_3$ were examined. The space charge contributions to the potential were expected to take the form of a well in the acceptor-doped material, a barrier in the donor-doped material and a shallow well in the undoped material. In each case, multiple measurements were taken from several grain boundaries. The measured potential barrier heights are summarised in Fig. 3. The significant result obtained was that all of the measurements took the form of potential wells, with distributions that are statistically indistinguishable: despite the expected differences in the space charge contributions to the potential between the different $SrTiO_3$ samples, the data in Fig. 3 shows that there is no measurable difference in measured potential barrier heights between acceptor-doped, donor-doped and undoped material.

The mean inner potential contribution to the local change in potential at a boundary can be calculated from the equation

$$V_0 = \frac{h^2}{2\pi m e \Omega} \sum f_{el}(0)$$

where V_0 is the mean inner potential, h is Planck's constant, m is the rest mass of an electron, e is the charge of an electron, Ω is the volume of a unit cell and $f_{el}(0)$ are the electron scattering factors at zero angle of the constituent atoms or ions [2]. The measured variation in potential can be interpreted in terms of a change in density at the grain boundaries, thickness or segregation. Analysis shows that the experimental results summarised in Fig. 3 could be explained by a 7 % reduction in density at the grain boundaries, a 2 nm change in specimen thickness or 0.2 at% segregation or depletion. It is most likely that the measurements result from a combination of these factors and space charge [3]. If present, the space charge contribution is likely to be the smallest of these factors, and is obscured by the other effects.

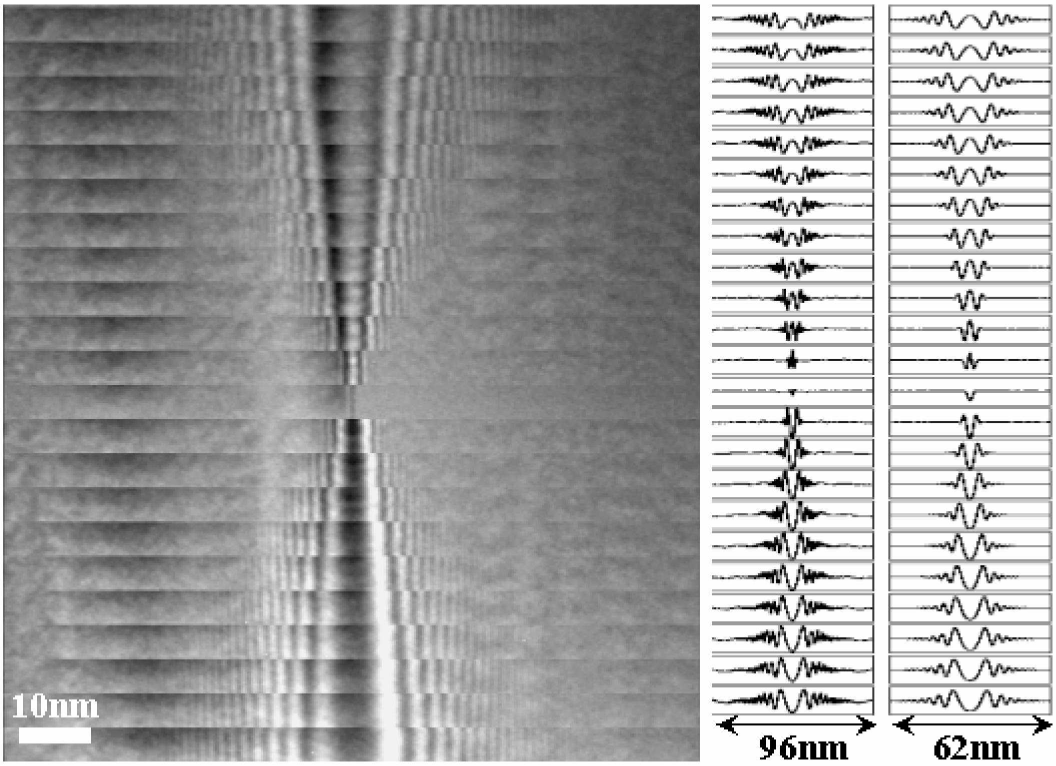

Figure 2. A representative defocus series of images taken from a grain boundary in Na-doped $SrTiO_3$, alongside corrresponding experimental and best-fitting simulated fringe intensity profiles. The series extends by 19 μm on either side of Gaussian focus in 1.91 μm steps. This region is approximately 70 nm thick.

A typical TEM sample of $SrTiO_3$ has a thickness of approximately 100-200 unit cells. Surface amorphisation during ion beam milling is thought to create equipotential layers on both specimen surfaces. These layers in turn affect the spatial distribution of the potential inside the specimen [4]. The passage of the high-energy electron beam through these samples is known to generate electron-hole pairs, which may affect the potential in the sample [5]. Both of these effects may contribute to the absence of a measured space charge contribution to the samples examined here. Therefore, the key to the successful measurement of variations in space charge may lie in the development of a transmission electron microscope specimen preparation technique that allows such effects to be minimised reliably, and the bulk properties of the boundaries to be maintained in electron-transparent specimens.

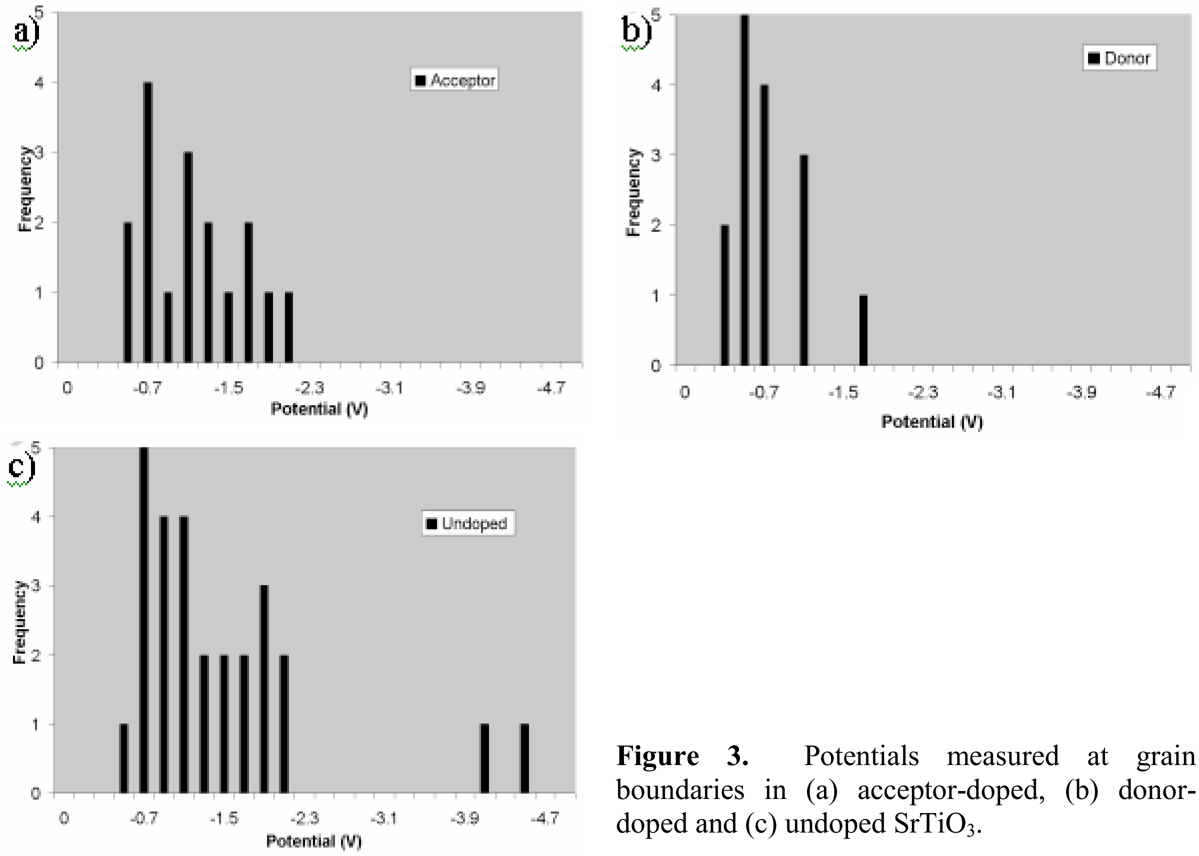

Figure 3. Potentials measured at grain boundaries in (a) acceptor-doped, (b) donor-doped and (c) undoped $SrTiO_3$.

3. Conclusions

The aim of this research was to characterise potential barriers at grain boundaries in $SrTiO_3$ using TEM. EFTEM maps show the expected dopant distributions in the three dopant regimes. However, grain boundary potentials measured across the different doping regimes are the same to within experimental error. The measured potentials are highly unlikely to be dominated by the effects of space charge.

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