

Grain boundary barrier breakdown in niobium donor doped strontium titanate using *in situ* electron holography

Kevin D. Johnson and Vinayak P. Dravid^{a)}

Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

(Received 17 September 1998; accepted for publication 18 November 1998)

The electrical activity of numerous electroceramics originates with space charge potential across internal interfaces. Space charge formation and the resultant potential barrier at interfaces are believed to be responsible for many interesting and useful properties of electroceramics, ranging from nonlinear current–voltage characteristics to enhanced dielectric properties. Direct current electrical measurements of individual grain boundaries in Nb donor doped SrTiO₃ bicrystals reveal a highly resistive and nonlinear behavior compared to single crystals. The origin of this nonlinear resistance has been examined with electron holography, observing both static and dynamic attributes of the internal potential. In the static case with no applied current, the grain boundary potential barrier height was measured to be about 0.45 V. During the application of a high current, this potential barrier was suppressed, presenting the first direct real space evidence for breakdown of an internal grain boundary barrier. © 1999 American Institute of Physics. [S0003-6951(99)04704-X]

The electrical transport properties of polycrystalline electroceramics can be explained in terms of two distinct components, current transport through grain boundary regions and transport through grain interiors. Grain interior (single crystal) behavior is described by the linear response of ionic or electronic charge carriers to an applied voltage. The grain boundary regions, however, often present a barrier to charge flow in the form of an internal potential that transforms nonlinearly under an applied electric field, giving rise to unique electrical properties such as varistor behavior and high dielectric capacitance.¹ This internal grain boundary potential results from charge distribution, consisting of accumulated grain boundary defects and compensating space charge defects.^{2–4} In electroceramics, charged defects include both intrinsic ionic defects and extrinsic dopant additions, resulting in donor or acceptor states within the energy band gap. The overall electrical properties are determined by both the type of charge carriers, controlled by the grain interior defect chemistry, and the dynamics of the grain boundary potentials. The dynamic modification of space charge and the resultant potential barriers under applied current/voltage is the basis of nonlinear electronic properties. To better understand how the nanoscale defect distributions affect macroscopic electrical properties the characteristics of single grain boundaries in Nb donor doped model SrTiO₃ bicrystals have been investigated.

Nb doped SrTiO₃ is of interest because of the nonlinear grain boundary electrical behavior of the bicrystals. Direct current (dc) electrical measurements on both single crystals and bicrystals reveal a much higher resistance due to the grain boundary. Bicrystals also show varistor behavior, defined as a rapid decrease in the grain boundary resistance above a threshold voltage, towards the single crystal resistance. This nonlinear behavior is attributed to the breakdown of internal grain boundary potentials, first described for an

n-type semiconductor as back-to-back potential barriers.⁵ In order to directly observe this internal potential, the technique of electron holography has been employed. Electron holography is a field emission transmission electron microscope (TEM) technique that records the electron wave function phase difference between coherent beam electrons and exit electrons that are perturbed by the specimen. A confined internal potential such as along a charged grain boundary is detected as a difference in the electron phase at the interface compared to the shift resulting from perturbations by the grain interior. The magnitude, sign, and width of this phase shift profile directly correspond to the magnitude, sign, and width of the internal potential field. Frabboni *et al.* first demonstrated the validity of electron holography as a technique to measure internal interface potentials by accurately measuring the potential shift associated with a silicon based *p–n* junction.⁶ Subsequently, electron holography has been used in an investigation of the internal potential associated with nominally pure and acceptor doped strontium titanate grain boundaries.⁷ The off-axis electron hologram production and reconstruction routines followed in this work closely adhere to that of previous research, and the reader is referred to this reference for more complete information on these routines.⁸ Applying these methods in the present study, the static internal potential of the Nb doped bicrystals was determined to be positive and of magnitude of about 0.45 V. To examine the dynamic redistribution of this internal potential, *in situ* electron holography was employed showing that at 1 mA of applied current the internal potential barrier was completely reduce to the background level.

Four probe electrical tests were used to characterize the grain boundary electrical response and, for comparison, the single crystal behavior. The 0.5 wt % Nb doped SrTiO₃ bicrystal samples were purchased from Nikko Trading Corporation, San Jose, CA. Assuming Nb only replaces Ti atoms, the 0.5 wt % Nb corresponds to about 1 at. % replacement of Ti by Nb. The misorientation of the grain boundary was specified as 36.8° about the [001], producing a Σ5, (310)

^{a)}Electronic mail: v-dravid@nwu.edu

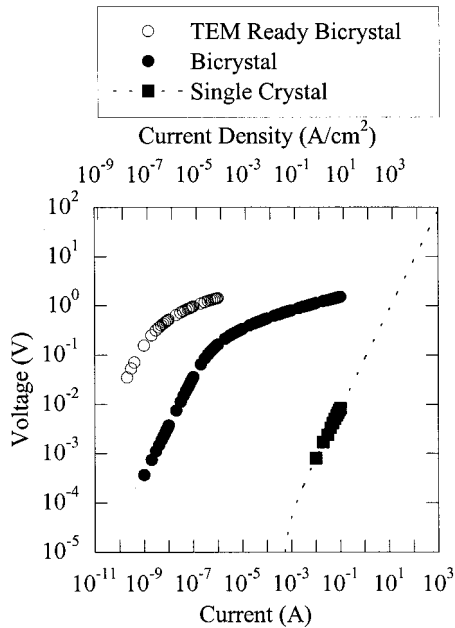


FIG. 1. The dc electrical measurements compare the behavior of Nb doped SrTiO₃ bicrystal (●), single crystal (■), and TEM ready bicrystal (○) samples. The dotted line indicates a linear fit to the single crystal data. The current density values only apply to the bulk samples.

symmetric tilt grain boundary. The addition of Nb to SrTiO₃ results in *n*-type semiconducting behavior with nearly two orders of magnitude higher conductivity than nominally pure SrTiO₃ ceramics.⁹ To make electrical measurements on these bicrystals, Ni or Ag was used as a contact material. Four collinear contact pads were created by thermal evaporation of the metal through a shadow mask onto a well-polished surface. The single crystal measurements were recorded from one of the bicrystal grains. The four probe dc current–voltage (*I*–*V*) measurements for a bicrystal and single crystal samples are shown in Fig. 1. From Fig. 1 it is apparent that the single grain boundary has decreased the current flow by greater than six orders of magnitude over single crystal values in the low voltage regime. While the single crystal behavior remains linear, the bicrystal shows a rapid drop in resistance above a threshold voltage of about 0.1 V. The nonlinear resistance behavior can be described by a coefficient of nonlinearity given by $\alpha = d \log I / d \log V = \sim 7.8$. Compared to $\alpha = 15\text{--}35$ for commercial devices based upon polycrystalline SrTiO₃, this parameter is low.¹ However the single grain boundary response provides a model system for studying the nanoscale effects that underlie the macroscopic electrical properties.

The primary nanoscale phenomena of interest are the size, shape, and dynamic response of the grain boundary potential. As described above, electron holography provides the means to examine these details, and therefore a method was developed to provide electrical connection to a bicrystal specimen for TEM observation. For these *in situ* experiments, a bicrystal specimen was prepared by conventional dimple and ion mill routines, and then two nickel contact pads were deposited by thermal evaporation. To these nickel contact pads 20- μm -diam silver wires were attached with silver paste. After a low temperature anneal ($\sim 120^\circ\text{C}$) to

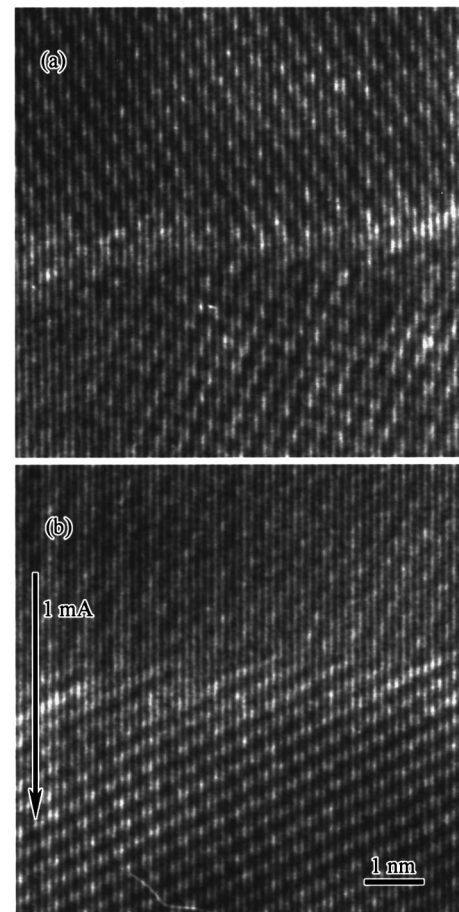


FIG. 2. Electron holograms are shown of the static grain boundary region (a) and the same region as current is applied (b). Despite the high *in situ* current, the quality of the holography fringes and the high resolution lattice is maintained.

cure the silver paste, the sample was placed in a custom electrical TEM holder, and the silver wire was soldered onto metal contact posts on the holder near the specimen cup. Feedthroughs on the rear of the holder, exterior to the microscope vacuum, allow electrical equipment to be connected. Figure 1 also displays two probe current–voltage data from the bicrystal specimen connected to the electrical holder. This *I*–*V* curve is important because it establishes that the bicrystal varistor behavior is maintained in the as prepared TEM specimen. The discrepancy from the four probe measurements is most likely a result of contact resistance, convoluted with the bicrystal behavior for two probe measurements. However, it should be noted that the general shape of the curve is identical to that of the four probe measurements.

Upon confirming that the electrical behavior is maintained in the electron transparent bicrystal, electron holograms were recorded of the grain boundary region with and without an applied current. The motivation of this particular experiment was to determine the internal potential in the breakdown regime, defined by the bicrystal electrical data. In Fig. 2 electron holograms without applied current and with 1 mA of applied current are displayed for comparison. It is evident that the *in situ* applied current does not destroy either the holography fringes or the high resolution lattice image of the grain boundary region. Because the bicrystal is symmetric tilt and the interface plane has been tilted parallel to the

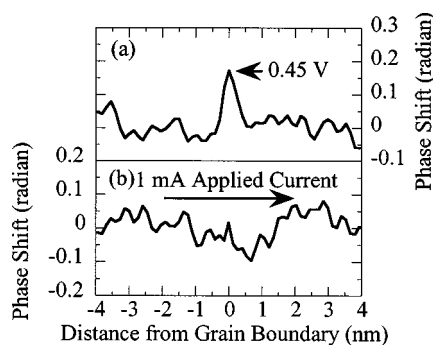


FIG. 3. After reconstructing the holograms in Fig. 2, a phase shift peak is detected for the static grain boundary (a) but with applied current the peak is absent (b), indicating barrier breakdown.

incident beam, the dynamic diffraction on neither side of the grain boundary is expected to be identical, which is important for obtaining the phase shift due solely to the internal potential at the grain boundary.

Upon reconstruction of the holograms, a phase image is produced revealing the relative shift in electron phase across the grain boundary region. Figure 3 displays a comparison of phase shift profiles for the static and applied current cases, after deconvolution of linear thickness dependence due to the specimen geometry. In the static case, a small positive phase shift peak is centered on the grain boundary plane. This peak was found to return after the applied current was removed. While the relative peak shape and size is comparable to previous static case measurements,¹⁰ the absolute magnitude of this particular peak may have suffered somewhat due to high current applied previously. The profile with 1 mA of *in situ* applied current, however, shows no appreciable phase shift peak above the background level, even though this background was found to have an increased slope relative to the static case in accord with the magnitude and direction of the measured electric field. The immediate deduction is that the positive phase shift peak, representing the grain boundary internal potential barrier to current transport, is leveled with 1 mA of applied current. This is the first direct real space evidence for dynamic grain boundary potential behavior in accord with macroscopic electrical measurements of barrier breakdown.

Further analysis of the phase shift profile for the static case allows the magnitude of the internal potential to be extracted from the phase shift peak height. The magnitude of the potential, $V(x)$, is related to the phase shift, $\Delta\Phi(x)$, by

$$V(x) = \frac{\Delta\Phi(x)\hbar c\sqrt{E_{KE}(E_{KE} + 2m_0c^2)}}{e(E_{KE} + m_0c^2)t},$$

where E_{KE} is the energy of the beam electrons, 200 keV, m_0c^2 the electron rest energy, and t is the specimen thickness in nanometers. Assuming a thickness of 50 nm, the static case phase shift profile is shown to have a peak of about 0.17 rad, corresponding to an internal potential magnitude of about 0.45 V. The estimate for the specimen thickness seems to be a reasonable upper limit, as greater thickness would produce incoherent scattering and a complete loss of the holography fringes. Improvement in the signal to noise ratio is expected with the installment of a new field emission tip, providing greater coherency and higher current density.

This *in situ* experiment has demonstrated the viability of using electron holography to explore dynamic internal potential effects in electroceramics. Four probe electrical measurements showed the varistor behavior of the single grain boundary in niobium doped strontium titanate bicrystals. Electron holography on a static grain boundary revealed a positive phase shift peak centered on the grain boundary plane, corresponding to an internal potential of about 0.45 V. In accord with barrier breakdown, *in situ* applied current resulted in a leveling of this phase shift peak. Further experiments are now in progress to determine the *in situ* response of the potential barrier for a range of applied currents in an effort to map out the nanoscale grain boundary barrier characteristics of varistor behavior.

This research is supported by the U.S. Department of Energy-Basic Energy Sciences (DOE-BES), under Grant No. DE-FG02-92ER45475. Thanks also goes to contract monitor Dr. Helen Kerch.

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