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Domains with Varying Conductance in Tensile Strained SrMnO₃ Thin Films Using Out-of-Plane Electric Fields

Job J. L. van Rijn,* Ishitro Bhaduri, Majid Ahmadi, Beatriz Noheda, Bart J. Kooi, and Tamalika Banerjee*

Domains and domain wall engineering have been extensively explored in ferroic materials for a range of applications in nanoelectronics and spintronics. Complex oxides exhibiting strongly correlated properties are model platforms for such studies where response to strain or external stimuli such as electric field, temperature and light can be probed. Here, domains in strained SrMnO₃ films, grown on a degenerate semiconductor, allowing for conduction in an out-of-plane geometry, are studied using a combination of microscopy probes. Using conductive atomic force microscopy, electrically isolated domains with varying conductance are found and their temporal evolution is investigated. Further, their formation and microstructure are studied using scanning transmission electron microscopy and secondary electron contrast in scanning electron microscopy. An important contribution is establishing that the observed domains are formed by cracks, driven by inhomogeneous strain relaxation throughout the film, resulting in significantly high strain planes. The potential of secondary electrons to detect domain dependent contrast over a large area, ensuing due to the use of a degenerate semiconductor correlates with the conductive properties of the domains and serves as a new direction to probe domains and domain walls in ferroic materials.

1. Introduction

Domain formation has a prominent role in the functional properties of nanostructures and the ability to move or design domains is proposed for a wide range of applications such as domain-wall-based nanoelectronics[1–3] involving magnetic domain walls in spin valves[4] and spin-based logic[5–7] or conductive ferroelectric domain walls in memristive networks.[8,9] Domain walls in multiferroic materials have additional functionality due to the magnetoelectric coupling hypothesized to allow for magnetic control of ferroelectric domain walls and vice versa.[10,11] Complex oxides serve well as model systems for the study of domains and domain walls due to their strongly correlated properties.[12–14] Their dependence on crystal structure is of interest due to the high degree of tunability it entails, for instance by applying strain in thin films.[15–17] The complex oxide SrMnO₃ (SMO), taken as a model system in this work, is predicted, based on first principles studies, to exhibit a strain-induced multiferroic phase which persists up to room temperature for tensile strains higher than ∼5%[18–20] and a giant magnetoelectric cross-caloric effect.[20] The onset of the ferroelectric phase above ∼2% strain originates from the in-plane displacement of the body-centered Mn cation in the perovskite unit cell. Since both the ferroelectric and the superexchange-mediated magnetic order[21,22] originate from the Mn cation, strong magnetoelectric coupling is expected.[20] The study of antiferromagnetic order in strained SMO films has revealed a domain structure with easy anisotropy axes parallel to the predicted <110> polarization directions.[23–25] The ferroelectric character of strained SMO has been investigated using second harmonic generation, showing the emergence of a polar state in 1.7% tensile-strained films.[26,27] Additionally, strained SMO films have been studied with scanning transmission electron microscopy (STEM), reporting atomic displacements concomitant with a ferroelectric polarization.[28] However, it has proven to be challenging to synthesize strained and stoichiometric SMO films without significant strain relaxation. This can occur by the formation of oxygen vacancies, effectively increasing the cation size. For strained SMO films, this is determined to be strain-dependent.[29,30] In addition, SMO films grown on SrTiO₃ have shown to form cracks, which create strong strain gradients resulting in a flexoelectric polarization in the substrate.[31,32]

In this work, we report on another type of domains in SMO with varying conductive properties, which are electrically isolated. Such domains have previously been reported on SMO films grown on insulating LSAT substrates and have been studied using electrostatic force microscopy and cAFM with a bias applied in an in-plane geometry.[26,33] In these reports,
Figure 1. Electrical characterization of 24 nm SMO on Nb:STO using cAFM. In (a), the measurement setup is drawn. Temperature dependent $I(V)$ measurements using the PtIr tip in contact are shown in (b). In (c), the positive bias regime is fitted with a thermionic emission model. The AFM image ($5 \times 5 \mu m^2$) in (d) shows a height map displaying topographic lines along the crystallographic directions [100] and [010]. The corresponding current map in (e) reveals domains with varying conductance. The image in (f) is a zoomed-in current scan ($0.5 \times 0.5 \mu m^2$).

the electric isolation between domains is stated to originate from oxygen vacancies that form in domain walls. In contrast, we chose 0.5 wt% Nb-doped SrTiO$_3$ (Nb:STO) semiconducting substrates which applies a high tensile strain of 2.6% and allows for an application of bias in the out-of-plane geometry. The high Nb doping concentration in SrTiO$_3$ ensures an optimum pathway for the electric current in this configuration for this degenerate semiconductor. This facilitates the probing of single domains, resulting in a clear secondary electron emission contrast when performing scanning electron microscopy (SEM), associated with the varying surface charging and conductance. The domain edges, as studied by the thin film topography, evolve as a function of time even in ambient conditions. Furthermore, we demonstrate the electric isolation to originate from cracks and study the atomic structure in the SMO films, revealing high-strain planes with surprisingly large strains up to 38%.

2. Results and Discussion

2.1. Conductance of Domains in Strained SrMnO$_3$

The SMO films are grown on TiO$_2$ terminated Nb:STO substrates with a doping concentration of 0.5% using pulsed laser deposition (PLD). The growth is monitored in-situ using reflection high-energy electron diffraction (RHEED) and the corresponding RHEED oscillations are shown in Figure S1 (Supporting Information). The presence of well-defined intensity oscillations indicates layer-by-layer film growth, from which we determine a film thickness of 24 nm. After growth, the sample is annealed in-situ for 1 h at 600 °C at an oxygen pressure of 900 mbar, with the aim of minimizing the formation of oxygen vacancies to maintain the stoichiometry and preserve the epitaxial strain. The surface topography and conductive properties of the film are simultaneously studied using cAFM measurements utilizing a PtIr tip, visualized in Figure 1a. After bringing the tip in contact with the sample using a force of around 10.5 nN, local $I(V)$ measurements are conducted, shown in Figure 1b,c. The $I(V)$ curves have a marked asymmetry, which is attributed to the semiconducting nature of Nb:STO; under negative bias, the metal/insulator/semiconductor junction formed by PtIr/SMO/Nb:STO is forward-biased, allowing greater transport of majority carriers across the barrier. The increased conductance at higher temperatures is consistent with the insulating nature of SMO and excludes avalanche breakdown behaviour. To determine the dominant conduction mechanism governing transport, we took a closer look at the positive bias regime, considering multiple transport models including Fowler–Nordheim tunneling, Poole–Frenkel emission and thermionic emission. Thermionic emission and Poole–Frenkel emission gave best fits to the experimental data. The fits corresponding to thermionic emission are shown in Figure 1c. The current–voltage relationship for both the modified thermionic emission and Poole–Frenkel emission can be described by

$$I(V) = I_0(T) \frac{V}{V_0} \exp\left(\frac{\sqrt{V}}{V_0}\right)$$  \hspace{1cm} (1)
where $T$ is the temperature (K), $V_0$ is a term accounting for the electric field distribution within the dielectric film and $I_p$ is a temperature-dependent current term whose exact identity is dependent on the specific transport model being used, as explained in Section S2 (Supporting Information). We note that for the negative bias regime, the modified thermionic emission and Poole–Frenkel emission models also fit the best. Given that the $I(V)$ measurements were conducted above room temperature and that SMO films are known to incorporate defects, the electrical transport is mediated either by thermionic or Poole–Frenkel emission, evidenced by the detailed analysis of the fitting to the experimental data as shown in Section S2 (Supporting Information).

The surface topography, shown in Figure 1d, displays a unique pattern with straight lines formed along the [100] and [010] crystallographic directions. The corresponding current map shows remarkable contrast that reveals rectangular domain structures with varying conductance. These domains, with sizes around 0.1 $\mu$m², are also formed along the [100] and [010] crystallographic directions, in striking similarity to the lines observed in the topography scans. The emergence of the current contrast implies that the domains are electrically isolated. We observe a correlation between the size and the conductance of the domains, with larger domains being more conductive. This size-dependent conductance is attributed to the amount of mobile charges within each domain.[26]

While some topographic lines coincide with the domain boundaries, each domain appears to encompass multiple topographic lines. This is shown by the magnified current map in Figure 1f, displaying no significant contrast across the lines, indicating that these lines lie within the same domain. Notably, the conduction at the topographic lines themselves is greatly reduced. The domain boundaries have surface traces in the [100] and [010] directions; however, the domain boundary structure along the [001] in the film is not clear from the surface topography only. To understand the nature of these domains with varying conductance, we further discuss the following key-points: domain formation, microstructure and temporal evolution.

### 2.2. Formation and Structure of Conductive Domains

To investigate the microstructure of the domains, high-angle annular dark field (HAADF)-STEM scans have been performed on the thin SMO films. Figure 2a presents a cross-sectional HAADF-STEM image where the perovskite crystal structure of both the film and the substrate are evident. The well-defined interface between SMO and Nb:STO indicates a high-quality interface and film growth. Additionally, in Figure 2a, clear, observable cracks parallel to the (100) and (010) can be distinguished that physically separate the SMO domains, indicated by the white arrows. The distance between the cracks in the shown image is 120 nm, comparable to the distance between topographic lines in Figure 1. From this, we conclude that the observed topographic lines are a surface manifestation of these cracks that exist in the film. Since the conductive domains can encompass multiple topographic lines, we conclude that not all cracks are domain boundaries. Only those cracks that both connect laterally and reach the substrate vertically, form domain boundaries. The domain boundaries are cracks formed along the (100) and (010) planes which isolate the domains electrically, enabling contrast in the conductive domains.

Another feature observed in the STEM image is the appearance of high-strain planes, indicated by the red arrows in Figure 2a. To study this, the local strain distribution is analyzed for the region indicated by the red box in the HAADF-STEM image, see Figure 2c. The high-strain plane consists of Mn atoms, as identified by their lower intensity. To investigate the in-plane strain, both for Mn and Sr, six rows of atoms along the [010] direction have been analyzed across a high-strain plane; Sr rows are indicated in Figure 2d. The intensity profile is plotted in Figure 2e, displaying a surprisingly large interatomic distance across the high-strain plane. This distance, and the corresponding strain, is calculated by analyzing the atomic positions, shown in Figure 2b. Across the high-strain plane, the interatomic distance between neighboring Sr atoms reaches over 0.52 nm which, when taking the basic SMO perovskite lattice as reference lattice, would translate to an exceptionally high strain of 38%.

The Sr atoms directly next to the high-strain plane display a tensile strain lower than what is expected to arise from the substrate, possibly to compensate for the extremely high strain across the high-strain plane. Further away from the plane, the expected in-plane tensile strain of 2.6%, imposed by the substrate, is recovered. The strain relaxes in an inhomogeneous manner in SMO, preferentially along the cubic crystallographic directions. We propose that these high-strain planes can act as nucleation planes for the formation of cracks. To better understand the origin of the high interatomic strain, the role of oxygen is investigated.

Utilizing integrated differential phase contrast (iDPC) STEM, the oxygen atoms within the same region are imaged. Six rows of Sr-O atoms, marked in the iDPC image in Figure 2g, are used for the analysis. The averaged intensity of these six atomic rows is shown in Figure 2h, normalized to the position of the leftmost Sr atom. By deconvolution of the Gaussian profiles, see Figure S4 (Supporting Information), the intensity of oxygen in the high-strain plane is decreased by approximately a factor of 2. This is a strong indication that oxygen vacancies accumulate in the high-strain plane. The presence of oxygen vacancies locally modifies the orbital structure of the bonds within the unit cell, which possibly explains the high interatomic distances across the high-strain plane. Furthermore, the position of the oxygen atoms is off-centered, which indicates a distortion of the oxygen octahedron. The existence of oxygen vacancies in the high-strain planes supports our proposition that they serve as nucleation planes for crack formation. The oxygen-vacancy rich high-strain planes also possibly increase the local conductance; however, the limited lateral resolution of the cAFM prevents the detection of such behaviour.

### 2.3. Time Dependence of the Crack Formation

Cracks have previously been reported to form during growth of SMO at higher temperatures.[31,32] In this work, we report on an unexpected temporal evolution of crack formation at ambient conditions for highly strained SMO thin films. A time-dependent
Figure 2. Investigation of the strain state within the high-strain planes using STEM. In (a), a HAADF-STEM image of the SMO/Nb:STO heterostructure is shown along the [100] zone axis. The red and white arrows indicate the high-strain planes and developed cracks respectively. In (c), the image used to analyze the strain is shown, where the red box indicates the analyzed area. In (d), six horizontal Sr rows are indicated, which are analyzed to investigate the local strain. The displacement and strain is shown in (b) for both the Sr atoms and the Mn atoms from the region in (c). In (e) and (f), an overview of the averaged Mn and Sr positions are shown. In (g), the green Sr-O lines display the region used for the analysis of the iDPC image. In (h), the average Sr-O intensity is shown, normalized to the first Sr atom position. The oxygen intensity in the high-strain plane is clearly lower, indicative of oxygen deficiencies.

topography study is performed to track the crack evolution, see Figure S5 (Supporting Information). In Figure 3a,b, two AFM scans at different time instances are shown, revealing that the density of cracks has significantly increased after 24 h. The time here is defined as the time from removal of the sample from the PLD chamber. The density of the cracks is approximated by counting the number of topographic lines crossing the vertical axis, defined by the blue dashed line. The time-dependence of the crack density is shown in Figure 3c, from which it can be observed that the crack density seems to converge between 1 and 30 days to around 4 μm⁻¹. At this crack density, the total strain energy is sufficiently reduced such that further crack formation is unrequired. To validate the temporal dependence of the strain state in the sample, reciprocal space maps (RSM) are taken around the (103) peak, both 14 days and 36 days after growth, shown in Figure 3d. We note that the film peak is aligned with the substrate peak, both possessing an in-plane lattice parameter of 0.39 nm, indicating an epitaxially strained film. However, the RSM after 36 days displays a significant diffusion of the SMO (103) peak toward the bulk lattice parameter of SMO, confirming the time-dependent strain relaxation. The more diffuse character of the substrate peak indicates that the strain relaxation has also compromised the substrate structure with the cracks developing into the STO substrate, as observed in Figure S6 (Supporting Information).

2.4. Domain Dependent Secondary Electron Contrast

In a complementary set of measurements, we further extend our analysis of the domain characteristics in SMO by employing SEM by detecting the emission of secondary electrons (SE) in an SMO
Figure 3. Time dependence of the strain relaxation and crack formation. In (a) and (b), topography images are shown at 6.5 hours and 24 hours after growth. Height lines crossing with the vertical white lines are counted and plotted as a function of time in (c). The (103) reciprocal space maps in panel (d) indicate the strained state of the SMO film. The strain relaxation increases with time as is evident from the two reciprocal space maps.

film. The resulting image is shown in Figure 4a, displaying a distinct contrast from which both cracks and domains can be identified. SE contrast is expected for topographic features, explaining the observation of cracks. In the zoom-in Figure 4b, cracks, domain boundaries (DB) and domains are indicated. The contrast in the detected SE for the different domains, however, is unexpected and here we discuss its origin. For insulating materials, the secondary electron emission yield (SEYY) is dependent both on the primary electron energy $E_{PE}$ and on charging effects at the interface.\[35,36\] Negatively charged surfaces are known to result in a brighter region due to the acceleration of the emitted SE towards the detector.\[37\] In Figure 4a, we observe that the relative SE intensity of the domains is correlated with their size, similar to the domains in cAFM (Figure 1). Based on this, domain contrast could arise from varying conductance, considering that a higher conductance would result in an increased discharging of the surface. In this case, larger domains, being more conductive, are expected to discharge the surface resulting in a decreased SEEY. However, we observe the opposite trend with larger domains being brighter, excluding varying discharging as the main contrast generating mechanism.

We therefore propose other possible mechanisms which would explain the observed contrast. SE detection is dependent both on the generation of secondary electrons and on the escape probability of the generated secondary electrons. The peak yield of insulators is typically larger than metals due to the absence of electron–electron scattering, resulting in a larger escape depth.\[38\] Nevertheless, depending on the PE energy, materials can appear brighter due to lower binding energies. Varying binding energies thus could give rise to both varying conductance and generation of SE’s. Additionally, modified transport properties imposed by the SMO/Nb:STO interface such as the existence of a Schottky barrier could affect the domain-dependent electron transport and in turn the SEEY. We note that the formation of oxygen vacancies could impact the electron affinity. An inhomogenous distribution of these defects could also give rise to domain dependent contrast. Furthermore, we note that for this sample, although the cracks have more deviations from the in-plane crystallographic directions [100] and [010], the preferred direction of the domain edge seems to be parallel. A different Nb:STO substrate morphology could be a reason for these deviations.

To further study the dependence of the SEEY on the conductive properties of the domains, the Nb:STO substrate was biased using a voltage supply while detecting the SE, shown in Figure 4d–f. The domain dependent contrast is clear upon applying 0 V bias or a −10 V bias, as this allows for the negative potential at the SMO surface, accelerating the SE towards the detector. When applying a positive potential of +10 V to the Nb:STO, the overall surface potential of the SMO surface is decreased due to an increased discharging, effectively lowering the contrast. We conclude that SEM secondary electron detection is effective in determining the varying conductive properties of the SMO domains. Although cracks have previously been imaged in SMO using a SEM, no domain dependent contrast was observed.\[31\] The crucial element in revealing the domain...
Figure 4. Imaging of a 24 nm SMO/Nb:STO sample using SEM. In (a), the domains with varying conductance are visible by the secondary electron emission contrast, as visualized in (c). In (b), a zoom-in of (a) is shown, indicating cracks, DBs and domains. In (d–f), SE SEM images are shown when the Nb:STO substrate is biased using a voltage of −10 V, 0 V, and +10 V, respectively. The change in contrast dependent on the voltage bias direction.

dependent contrast in the SEEM is the degenerate semiconductor Nb:STO substrate, since this allows for a well defined out-of-plane conduction path for each domain determining the surface charge. Our work showcases the potential of using SE detection to detect varying conductive domains in such oxide insulators.

3. Conclusion

In this work, we report on the emergence of varying conductive domains in tensile strained SMO films grown on 0.5% doped Nb:STO substrate. This degenerate semiconductor as a substrate allows for a well defined out-of-plane electric field application. The electrical properties vary for each electrically isolated domain within the SMO, as characterized by cAFM. We show for the first time that the domains are formed by cracks driven by strain relaxation processes. An in-depth TEM study of the 24 nm thick SMO film reveals that the strain relaxes inhomogeneously such that high-strain planes with in-plane strains up to 38% are found, stabilized by the reduced oxygen concentration. The high-strain planes provide insight in the strain relaxation process for complex oxide heterostructures in general. We hypothesize that the physical properties of these high-strain planes could deviate significantly from the thin film properties. Furthermore, we show that the time-dependent evolution of cracks takes place even in ambient conditions. Finally, we demonstrate domain dependent contrast imaged by secondary electron detection which is correlated with the conductive properties of the domains. A semiconducting substrate facilitates imaging large surface areas of such domains acting like nanocapacitors in strained oxides.

4. Experimental Section

The 0.5% Nb-doped Strontium Titanate substrates were prepared using a Buffered Hydrofluoric acid treatment to acquire a TiO2 terminated surface, before annealing at 960 °C in a 300 sccm oxygen flow. The SMO films were grown using PLD with a fluence of 2 J cm−2 at a temperature of 800 °C, in a 0.05 mbar oxygen environment during growth. After growth, the sample was annealed in situ for 1 h at 600 °C at an oxygen pressure of 800 mbar, minimizing the formation of oxygen vacancies to maintain the stoichiometry. The cAFM measurements were performed in an Asylum Research Cypher ES AFM, utilizing a PtIr tip with spring constant 0.03 N m−1 and applying a force of 10.5 nN. The measurements were done in a closed environment in a small Ar flow to minimize humidification or other interactions with the environment.

The STEM studies were performed using a Thermis Z microscope. HAAADF-STEM and iDPC-STEM imaging modes were used simultaneously. STEM lamellae were extracted from samples using a Helios G4 CX dual beam system with a Ga focused ion beam. In the TEM analysis, the position of the atoms was determined by using gaussian fits and averaging over the six atom rows. The position of the atom was normalized by the position of the most left atom in the row. Field emission (FE) Helios G5 SEM with FE e-gun with in-lens detector in immersion mode was used for imaging the surface of the samples by collecting secondary electrons. To electrically isolate the sample from the SEM stage, the metallic plate on which the sample was mounted was attached to a sapphire disk using silver paste. A co-ax cable was used to connect the metallic plate to the power supply to externally bias the Nb:STO substrate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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