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Atomic scale elemental mapping of light elements in multilayered perovskite coatings

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ABSTRACT

Spherical aberration corrected transmission electron microscopes offer unprecedented capabilities in materials structural characterization down to atomic resolution. Electron energy loss spectroscopy (EELS) – spectrum imaging (SI) and annular bright field (ABF) imaging allow to simultaneously identify both the position and nature of the atomic species in a crystalline material. These techniques, along with conventional high-resolution transmission electron microscopy are particularly useful in heterostructures interfaces like epitaxial multilayers characterization, for identifying possible atomic interdiffusion at sub-nanometric scale. This paper presents the structural and compositional microanalysis down to atomic resolution of an epitaxial $BaTiO_3/SrRuO_3/SrTiO_3$ ferroelectric heterostructure using complex complementary analytical electron microscopy techniques. The atomic arrangement of both heavy and light atomic species across the interfaces in the $BaTiO_3/SrRuO_3/SrTiO_3$ heterostructures is revealed.

1. Introduction

The film substrate or film–film interfaces were found to play a crucial role in layers growth mechanisms and in their subsequent characteristics [1]. The stress/strain effects induced in epitaxial films by the substrate, vacancies, dislocations, are responsible for local structural changes, which are of paramount importance in complex materials such as ferroelectrics, ferromagnetics, multiferroics. Among the performing techniques capable of providing evidence at the atomic scale about the structure and configuration of interfaces, atomic-resolution imaging has been considered throughout the times as one of the major goals of the various microscopy techniques in materials science, be it scanning probe microscopy (atomic force microscopy, scanning tunneling microscopy) or electron microscopy. Transmission electron microscopes are able to provide atomic resolution images in two different operating modes: fix parallel electron beam and scanned focused electron beam. The image formation mechanisms and, consequently, the image acquisition devices are different for the two modes. In the parallel beam mode, known as high-resolution transmission electron microscopy (HRTEM), the obtained atomic-resolution image is the result of multiple interference between the diffracted electron beams emerging from the thin crystalline object. The so called "phase image" shows periodic fringes (maxima and minima of intensity) in perfect agreement with the crystalline interplanar distances in the analyzed thin object, which are named lattice fringes. However, the brightness, position and fine structure of the lattice fringes depend basically on the excitation current of the objective lens (defocus) and the sample thickness. The correct interpretation of such images, e.g. the correct assignment of maxima or minima of intensity to certain atomic species present in the crystal structure can only by performed by using specialized image simulation programs. In the scanning transmission electron microscopy (STEM) mode, the focused electron beam is scanned across the thin specimen, while an annular detector collects the electrons scattered through an angle of typically >50 mrad (~3°) by the atomic species in the specimen. The obtained image, named annular dark field (ADF) image, maps the local intensity of the forward scattered electrons. Atomic resolution in such images was possible after field-emission gun addition to the STEM [2]. Moreover, the scattering cross-section is proportional to the atomic number squared Z^2 of the scattering atom in the specimen. Therefore, an atomic resolution STEM image may provide basic chemical structural information, since one can easily distinguish heavy atoms (columns of atoms, actually) from relatively lighter atomic species in the specimen (mass-thickness contrast). Imaging single atoms with the help of an STEM has also been proven since 1970 when individual heavy atoms of Th and U on a thin carbon membrane have been observed [3]. The atomic-resolution imaging capabilities of the modern TEMs have been considerably

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improved with producing increasingly brighter and stable electron beam sources such as the Field Effect Gun (FEG, Cold FEG) and especially with developing the spherical aberration corrector (C_s corrector) inserted into the beam-forming lens system (probe-corrected microscope, STEM mode) or into the image-forming lens system (image-corrected microscope, HRTEM mode). Analytical techniques such as electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) come to complete the configuration of one of the most powerful microstructural and compositional instruments, the analytical transmission electron microscope. Combining high-brightness electron beam sources with state-of-the-art EELS or EDS analytical units installed on a C_s-corrected TEM can take even further the atomic resolution imaging capabilities of the modern TEMs: not only can one image isolated heavy atoms, but also light elements such as oxygen [4], lithium [5] or even hydrogen [6] can be directly identified onto high-resolution STEM images of thin crystalline specimens. Moreover, chemical maps can be created going down to atomic resolution [7]. Getting structural and chemical information at atomic resolution is nowadays of paramount importance in nanoscience and nanotechnology when analyzing, for instance, nanometric multilayers, epitaxial heterostructures or core-shell nanoparticles.

The ferroelectric oxide thin films or artificial multiferroics represent typical systems where acquiring structural and compositional information at atomic resolution is crucial for correctly understanding the fine mechanisms controlling, at nanometric scale, phenomena like the electrical polarization switch or the magneto-electric coupling, for applications such as dynamic random access memories (DRAM), field effect transistors (FET), non-volatile ferroelectric random access memories (NvFRAM), micro-electromechanical systems (MEMS), tunable microwave devices etc. [8,9]. Both the fundamental studies and the devices to be further developed rely on heterostructures made up of high quality epitaxial thin films, exhibiting sharp interfaces with the substrate or between the different layers. Ferroelectric materials from the class of perovskite oxides (general formula ABO_3) like $PbZr_xTi_{1-x}O_3$ (or PZT), $BaTiO_3$ (or BTO), $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) are widely used because of their large value of the remnant electrical polarization or their superior piezoelectric properties compared to the classical materials such as ZnO or quartz. The structural similarity of these compounds and the relatively small lattice mismatch between all these structures allows one to grow high quality epitaxial layers on a properly chosen substrate (like $SrTiO_3$) and to play with the strain values in order to finely adjust their electrical properties via the piezoelectric effect. The crystalline structure of these materials consists in packing of BO_6 octahedra containing the A atoms in the spaces between them. The slightest distortion of the BO_6 octahedral frame or relative displacement of the B cations within the octahedral oxygen cages have significant influences on the ferroelectric properties. The magnitude of these structural distortion induced effects and their influence upon the ferroelectric properties is higher in the neighborhood of interfaces, extended defects or in nanometric thin films, under the strain induced by the lattice mismatch. Therefore, the structure and chemistry of the interfaces as well as the strain value and distribution around the interfaces should be carefully analyzed. Clearly identifying the positions of the oxygen atoms opens the possibility to evidence the strain induced distortions of the oxygen octahedral frame or to map the relative displacement of the A-type or B-type cations within this frame, revealing ferroelectric domain walls, local polarization [10]. In this regard, C_s-corrected TEM/STEMs represent an extremely valuable nanoscale characterization tools capable of simultaneously providing, when coupled with analytical techniques such as EELS or EDS, both chemical and structural information at a space resolution below 1 Å [11,12].

Barium titanate ($BaTiO_3$) is among the most studied perovskite systems, being considered as a potential candidate in lead-free ceramic and microelectronic industry. Even though the chemical composition of BTO remains the same from bulk to nanostructures (thin film, nanoparticles, etc.), the applications are different. In bulk state BTO has applications in actuators and sensors, while as thin film BTO has major application in ferroelectric random access memories (FeRAM) [13]. BTO is a ferroelectric material with a rhombohedral perovskite crystal structure at room temperature (S.G. R3m, $a = 0.4004$ nm, $\alpha = 89.87^\circ$ [14]). In BTO, a very important role is played by the oxygen atoms who are involved, along with titanium, in the polarization switching. The ionic displacement in BTO concerns the relative position of the titanium cations within the oxygen octahedra.

Our study concerns epitaxial BTO layers deposited onto single-crystal (0 0 1) $SrTiO_3$ (or STO) substrates using a $SrRuO_3$ (SRO) buffer layer. The SRO layer has a double role in the ferroelectric heterostructures based on BTO. On one hand, SRO is well known for its metallic-like electrical resistivity of the order of $10^{-6}\ \Omega$ m in bulk [15] and epitaxial thin films [16], being frequently used as electrode in multilayered devices. On the other hand, because of its perovskite structure and low lattice mismatch with respect to STO (used as substrate), it enables the further epitaxial growth of perovskite ferroelectric thin films, reducing the strain, which might be induced into the overgrowing layer [17]. An important aspect in BTO/SRO/STO heterostructure is the interface between the layers: STO-SRO and SRO-BTO. The quality of interfaces dictates, further, the quality of the epitaxial heterostructure to be obtained. An atomic interdiffusion or a non-stoichiometry at the interfaces can induce modifications in polarization values, dielectric constants or leakage current [18].

In this paper we comparatively present two methods to visualize the low-Z oxygen atoms: one method based on spectral information at atomic resolution (EELS-SI in STEM mode) and a second method employing a STEM imaging technique based on low-angle electron scattering. Along with conventional and high-resolution TEM observations, these complementary characterization methods performed on epitaxial $BaTiO_3/SrRuO_3/SrTiO_3$ (BTO/SRO/STO) heterostructure for applications in multiferroic devices create a complete picture going down to atomic resolution regarding the morphology, structure and chemical composition of the thin films and the interfaces between them.

2. Experimental

The SRO and BTO layers have been deposited by pulsed laser deposition (PLD) from stoichiometric targets using a KrF* excimer laser (Lambda Physik COMPex 205) with a 248 nm wavelength. Details about the experimental setup and depositions conditions are given elsewhere [19]. Cross-section TEM specimens have been prepared from the as-deposited samples by mechanical polishing down to ca. 30 μm, followed by ion milling in a Gatan PIPS machine at 4 kV accelerating voltage and 7° incidence angle. Low-voltage (2 kV) milling was used as final ion polishing stage in order to reduce the amorphous surface layer enveloping the specimen.

Transmission electron microscopy observations have been performed using a probe-corrected analytical high-resolution JEM ARM 200F electron microscope operated at 200 kV. The microscope is equipped with a Gatan Quantum SE Image Filter for EELS analysis. Atomic resolution images have been recorded in STEM mode (0.08 nm point resolution) using the high-angle annular dark field (HAADF) detector. Annular bright field (ABF) imaging in STEM mode has been used for the direct visualization of the oxygen atoms. Chemical maps at atomic resolution have been obtained by EELS spectrum imaging (SI) in the STEM mode. The specialized routines