Optimisation of superconducting thin films by TEM

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Abstract

High-resolution electron microscopy is used to study the initial growth of different REBa2Cu3O7−δ thin films. In DyBa2Cu3O7−δ ultra-thin films, deposited on TiO2 terminated SrTiO3, two different types of interface arrangements occur: bulk–SrO–TiO2–BaO–CuO–BaO–CuO2–Dy–CuO2–BaO–bulk and bulk–SrO–TiO2–BaO–CuO2–Dy–CuO2–BaO–CuO–BaO–bulk. This variable growth sequence is the origin of the presence of antiphase boundaries. In Nd1−xBaxCu3O7−δ thin films, antiphase boundaries tend to annihilate by the insertion of extra Nd-layers. This annihilation is correlated with the flat morphology of the film and the absence of growth spirals at the surface of the Nd-rich films.

Keywords: High resolution electron microscopy; REBCO-superconductors; Interface arrangement; Antiphase boundary

1. Introduction

A key area for optimising the properties of planar HTSC junctions is the microstructural characterisation, including the study of the interface, of HTSC thin films.

Although X-ray standing wave measurements [1] suggest the existence of a variable interface stacking for YBa2Cu3O7−δ on SrTiO3 (STO), previous transmission electron microscopy (TEM) studies reported a single type of atomic stacking at the interface: bulk–SrO–TiO2–BaO–CuO2–Y–CuO2–BaO–CuO–BaO–bulk [2]. These observations, however, were made on annealed STO substrates, where the atomic surface layer of STO can be either SrO or TiO2 (mixed termination). Here the initial growth of a DyBa2Cu3O7−δ (DBCO) ultra-thin film grown on TiO2 terminated STO is studied by high-resolution electron microscopy (HREM) and the layer sequence of the first DBCO unit cell is determined at different positions of the film.

A variable interface stacking can lead to the formation of antiphase boundaries (APB’s). These may end at dislocations and induce growth spirals at the surface of the film, which is disadvantageous since a smooth film surface is one of the most important requirements for growing planar HTSC junctions.

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Although APB’s can be observed in Nd-rich NdBa$_2$Cu$_3$O$_{7−δ}$ (NBCO) thin films, no growth spirals occur at the surface, resulting in very smooth films. This makes the Nd$_{1+3x}$Ba$_{2−x}$Cu$_3$O$_{7−δ}$ family a very interesting alternative for thin film applications. Using HREM, we studied the local structure of a stoichiometric and a Nd-rich NdBa$_2$Cu$_3$O$_{7−δ}$ film and correlated the results with surface morphology measurements obtained by scanning tunneling microscopy (STM).

2. Experimental

DBCO ultra-thin (approximately 6 nm) films were grown by PLD on a (001) STO substrate, having a miscut-angle of less than 0.2° and an atomically smooth single terminated TiO$_2$ surface [3]. Both the Nd-rich and stoichiometric NBCO thin films were grown by d.c. magnetron sputtering on (001) STO substrates. The ceramic targets were NdBa$_3$Cu$_3$O$_{7−δ}$ (stoichiometric NBCO) and Nd$_{1.12}$Ba$_{1.08}$Cu$_3$O$_{7−δ}$ (Nd-rich NBCO).

Cross-section (CS) and plan view (PV) samples for TEM were prepared by ion milling. For HREM a Jeol 4000EX was used. Image simulations were carried out using the Mac Tempas software.

3. Results and discussion

3.1. DyBa$_2$Cu$_3$O$_{7−δ}$ ultra-thin films

HREM is performed along the perovskite cube directions; i.e. along [100] or [010] of the DBCO film. Imaging the film and the substrate both under ideal conditions is not straightforward since the substrate-film lattice mismatch (about 2%) causes local bending of the film. The most prominent defects occurring are APB’s with displacement vector $\mathbf{R} = \frac{1}{3} [110]$.

This type of APB was already observed earlier in thin REBCO films grown on STO, and its occurrence was attributed to the presence of unit cell steps (0.39 nm) at the STO substrate [2,4]. In the present study, however, no surface steps at the substrate were noticed.

In principle, 12 arrangements are possible for the STO–DBCO interface: STO can end with SrO or TiO$_2$ and the DBCO unit cell contains 6 different (001) layers. However, due to the surface treatment of the substrate, the surface atomic layer of STO is known to be a TiO$_2$ layer. This limits the number of possible interface stackings to 6. Since both materials have a perovskite (related) structure, we can assume that the perovskite stacking will be maintained. Since the substrate has a B site (TiO$_2$) termination, the first layer of the film is expected to be an AO layer in order not to disturb the perovskite stacking.

This rules out the possibility of a CuO$_x$ layer next to the TiO$_2$ layer and limits the number of possible interface configurations to 3. Fig. 1 shows a detailed HREM image of the interface for a very small sample thickness. Image simulations indicate that the cations are imaged as dark dots and the oxygen columns as bright dots. The substrate–film interface is indicated by two arrowheads; an APB is present in the middle of the figure.

Intensity scanning along the vertical [001] axis allows to determine the first layer of the DBCO film (see inset of Fig. 1). This layer was found to be

![Fig. 1. The substrate–film interface is indicated by two arrowheads: (1) In the middle of the picture, an APB is present (marked by arrow 2). In this area, slight bending of the atomic (001) planes can be seen. Line scans along the [001] direction are shown for both sides of the APB. Image simulation are shown as insets. For the left side of the APB model A was simulated (parameters used: $d = 2.4$ nm, $δ = -24$ nm) and the simulation on the right side of the APB is based on model B (parameters used: $d = 3.2$ nm, $δ = -24$ nm).](image-url)
at the same level on both sides of the APB, excluding a step at the STO surface as the reason for the APB formation.

Because the size of a (Ba–CuO) block (4.14 Å) is larger than the size of a (Dy–CuO) block (3.39 Å), it is fairly easy, using the line intensity scan, to locate the position of the Dy-layer on both sides of the APB (see Fig. 1). We observed a clear shift of the Dy layer over \( \mathbf{R} = [00 \frac{1}{2}] \) on both sides of the APB, leading to a chemical and structural misfit and unavoidably two different interface configurations. The structural misfit and the change in interatomic spacing at the APB causes a relaxation and a slight bending of the atomic (001) planes close to the APB.

The interface stacking on the left side of the APB is determined to be: bulk–SrO–TiO2–BaO–CuO–BaO–CuO2–Dy–CuO2–BaO–bulk (model A) and on the right side of the APB the following sequence is found: bulk–SrO–TiO2–BaO–CuO2–Dy–CuO2–BaO–CuO–BaO–bulk (model B). Image simulations (insets in Fig. 1) for both models can be matched with the experimental images.

These two interface configurations are observed throughout the complete film. The third possibility: bulk–SrO–TiO2–Dy–CuO2–BaO–CuO–BaO–CuO2–Dy–bulk, was never observed. This can be understood by taking into account the co-ordination environment of the Ti\(^{4+}\) cations. The –SrO–TiO2–Dy–CuO2– stacking sequence would imply an incomplete square-pyramid polyhedron for the Ti cation whereas it is favourably disposed towards an octahedral co-ordination. The absence of oxygen atoms in the Dy layer also results in an increase of the lattice energy associated with the interface due to a repulsion between the highly charged Ti\(^{4+}\) and Dy\(^{3+}\) cations [5].

The miscut-angle of the STO substrate is less than 0.2°, implying that the minimum width of a substrate terrace is 112 nm. Since HREM shows that the average width of an antiphase domain is of the order of 20 nm, unit cell steps at the substrate can impossibly be the only reason for the formation of APB’s. APB’s here are necessarily created during the growth of the film and the consequence of a varying stacking mode at the interface. We therefore propose the following growth model. Initially pyramidal shaped islands are formed. Because of the TiO\(_2\) terminated substrate, the first layer of each island is BaO. The next can be either a CuO\(_2\) or a CuO layer. When neighbouring islands coalesce, APB’s can be created.

3.2. \( \text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta} \) thin films (\( x = 0; x = 0.12 \))

Using STM, very smooth surfaces were observed for Nd-rich NBCO films, while stoichiometric NBCO films show “3D towers” formed by unit cell high (\( c = 1.12 \) nm) terraces along the \( c \)-axis.

HREM shows that both the stoichiometric and the Nd-rich films are of high quality. \( \text{Nd}_3\text{CuO}_4 \) inclusions occur with the same density in both types of films, meaning that the Nd excess in the Nd-rich film is not incorporated by the formation of extra \( \text{Nd}_3\text{CuO}_4 \) precipitates. Compared to the stoichiometric film, far more APB’s (\( \mathbf{R} = [00 \frac{1}{2}] \)), caused by steps at the substrate or by a different interface configuration, are observed in the Nd-rich film. This is not surprising because substitution of Ba by Nd will change the interlayer distance, meaning that more interface configurations become possible. Such APB’s may end at dislocations and induce growth spirals at the surface. In the Nd-rich films, however, no growth spirals are observed, a strong indication that the elimination of APB’s through the formation of dislocations does not occur. A frequent observation in these films is: two APB’s, originating at two different positions at the film-substrate interface and lying more or less in the (100) plane (vertical), meet and annihilate in the (001) plane (horizontal) of the film. An example is shown in Fig. 2. The horizontal part necessarily forms a non-conservative APB; i.e. a difference in chemical composition is induced. Again using a linescan along the [001]NBCO direction, it is possible to analyse the position of the Ba- and Nd-layers. Using this method the stacking sequence across the (001) APB is found to be: \( -\text{BaCuO}_x\text{NdCuO}_x\text{BaCuO}_x\text{BaCuO}_x\text{NdCuO}_x\text{BaCuO}_x\text{BaCuO}_x\text{NdCuO}_x\text{BaCuO}_x; \) i.e. in the horizontal part of the APB an extra (Nd–CuO\(_x\)) layer is inserted (marked by arrowhead 2 in Fig. 2). The
formation of these (0 0 1) non-stoichiometric APB’s is almost certainly related to the absence of growth spirals at the surface of the Nd-rich film and apparently is one way of absorbing the excess Nd. Such a growth mode was already proposed earlier and is supported by the present results [6].

4. Conclusions

Ultra-thin DBCO films show a variable atomic stacking sequence at the interface. Two different interface arrangements are determined: bulk–SrO–TiO₂–BaO–CuO₂–Dy–CuO₂–BaO–bulk and bulk–SrO–TiO₂–BaO–CuO₂–Dy–CuO₂–BaO–CuO–BaO–bulk. This variable stacking sequence will lead to the formation of APB’s. In Nd-rich NBCO films such APB’s can annihilate by the insertion of extra Nd-layers, resulting in very smooth film surfaces.

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