Film-substrate lattice-engineering of HTS thin films

K Endo¹ and P Badica²,³

¹Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology (KIT), 3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan
²National Institute of Materials Physics (INCDFM), Bucharest-Magurele, POB MG-7, 077125, Romania
³University of Mainz, Institute of Physics, Staudinger Weg 7, 55128 Mainz, Germany

E-mail: kendo@neptune.kanazawa-it.ac.jp

Abstract. Materials may show anisotropic properties on different crystal directions and this is also the case of High Temperature Superconductors (HTS). To take advantage of the materials anisotropy one concept of interest is “orientation engineering” in thin films. This can be realized through the control of the film-substrate lattice relationship. Some examples in this regard are presented in this work and through comparative analysis we try to evaluate the viability of this approach and of he encountered problems. It is expected that in the future this approach will generate new nano composite materials with new properties and effects leading to development of new devices with new or improved functionality.

1. Introduction

High Temperature Superconductors attracted much interest from the fundamental as well as practical points of view. Despite this sustained effort, very few applications found their way to our daily life and commercialization.

With the recent development of the nanomaterials and nanotechnologies this field is further expanding with new possibilities on the one hand and other challenges on the other. It is already demonstrated that for some materials, when their size is less than a certain nanolimit, new effects and physics may occur.

For HTS superconductors studies in this direction are just emerging. Synthesis of nanosamples and their characterization face complex problems. However, high quality HTS thin films were demonstrated by several groups. We shall also note that the layered structure of HTS with alternate superconducting and non-superconducting blocks along the c-axis direction is automatically producing a natural (intrinsic) nanocomposite material for which the principles of bottom-end material layer-by-layer building are realized. Of course one can imagine similar artificial heterostructures built by using different materials and such examples are also described in the literature. Often, the approach is to stack the layers in the c-axis direction of HTS, and to take advantage of the Josephson junction (JJ) effect that occurs when a current is applied along c-axis. A simple configuration of a c-axis heterostructure would be with the composing materials of the heterostructure stacked with their c-axes parallel to each other and perpendicular to the surface of the substrate. But one can imagine also different combinations of stacking for a c-axis heterostructure (e.g. (001) for HTS and (111) for non-
HTS), at least theoretically. Nevertheless, building of \( c \)-axis conventional artificial heterostructures showing JJ effect is not easy since the coherence length of HTS is low, of about 2 nm, and this is resulting in necessity to grow non-superconducting layers with the thickness of approximately the same or lower values. To solve this problem one possibility would be growth and characterization of non-\( c \)-axis thin films. The most simple non-\( c \)-axis heterostructures are to keep stacking of the layers along \( c \)-axis direction of HTS with this direction being tilted vs. substrate surface. Also more general cases can be imagined.

Taking advantage of the anisotropy of the HTS films or of the HTS based composites has also several other interesting aspects to be considered. For example, different physico-chemical properties on different crystal directions enable new possibilities in materials growth and design. The new \( c \)-axis and non-\( c \)-axis thin films, if realized, may possibly show new properties and effects useful for designing devices with enhanced or new functionality. Furthermore, new types of nanomaterials are expected to be created.

To realize orientation control we applied the film-substrate lattice engineering through the control and selection of a certain substrate-film relationship. Some examples for thin film growth will be presented trying to explore and understand the viability and the problems associated with this idea, similarities in growth, morphology formation and superconducting properties as a first step for further developments.

2. Experimental

Thin films were prepared by metal-organic-chemical-vapor-deposition (MOCVD) [1, 2] using three unique laboratory designed machines, two of horizontal type and one of vertical type. Raw materials were metal-DPM (DPM is abbreviation for di-pivaloyl-methanate and \( M = \text{Sr, Ca, Cu, Ti} \) and \( \text{Bi}(C_6H_5)_3 \) (triphenyl-Bi). The films were \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) (Bi-2223), \( \text{Bi}_2\text{Sr}_2\text{Cu}_4\text{O}_{8} \) (Bi-2212), \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) (Y-123), \( \text{Bi}_4\text{Ti}_3\text{O}_{12} \) (BTO), \( \text{(Sr,Ca)}\text{CuO}_2 \) (SCCO) and \( \text{(Ba,Ca)}\text{CuO}_2 \) (BCCO). Details of growth are presented in our earlier works [3-7]. Substrate for \( c \)-axis growth was \( \{100\} \text{SrTiO}_3 \) (STO), while for non-\( c \)-axis growth was \( \{110\} \text{STO} \). The film-substrate lattice relationships for \( c \)-axis and non-\( c \)-axis thin films are shown in Fig. 1 and 2, respectively.

3. Results and Discussion

AFM images from Fig. 3 taken on \( c \)-axis thin films reveal a 2D layer-by-layer growth mechanism. There are also some deviations as for (001) Y-123 and (001) BTO film showing sometimes some tendency for spiral growth mode (significantly lower for BTO). For \( c \)-axis thin films terraces may occur and also dot-like precipitates-segregates. The growth direction for the (001) films is \( c \)-axis that is perpendicular to the surface of the substrate (Fig. 4a).

Morphology of the non-\( c \)-axis thin films (Fig. 3) is very similar to each other and consists of roof-range-like-shaped grains, in-plane aligned. This morphology is very different from that of the \( c \)-axis thin films. However, the growth mechanism in the case of non-\( c \)-axis thin films is also a 2D layer-by-layer growth along \( c \)-axis. The difference is that the growth direction, that is parallel to \( c \)-axis, is inclined and is making a certain angle with the surface of the substrate (Fig. 4b). The value of this angle is around 45° for our thin films. When two growing symmetrical neighboring fronts merge, they form the specific roof-like-shape grains.

AFM also suggests that films are in-plane aligned. As already introduced in the previous paragraphs, this is obtained for different film materials on \( \{100\} \) and \( \{110\} \) STO substrate for \( c \)-axis and non-\( c \)-axis thin films respectively. Furthermore, for \( c \)-axis as well as non-\( c \)-axis thin films grown on substrates other than STO, when applying the same principles of the lattice relationship, similar results were obtained. We conclude that the principles of films-substrate relationship play a major role in controlling film orientation. These principles are rather general and do not depend significantly on the material of the substrate or of the film. This provides a powerful tool for thin films orientation and anisotropy engineering.
Figure 1. Film-substrate lattice relationship for (100) STO and (001) Bi-2223 or (001) BTO.

Figure 2. Film-substrate lattice relationship for different non-c-axis thin films.
**Figure 3.** Atomic Force Microscopy (AFM) images of different films on (001) and (110) STO. Substrates were flat substrates with low miscut angles (typically less than 1°).
It is worthy to note that in some cases as-prepared HTS non-c-axis thin films do not have the best properties and X-ray diffractions may show the presence of impurity phases and orientations. To improve roughness and morphology uniformity, zero-resistance critical temperature, $T_c0$, transition width and to obtain single phase and orientation with a single and sharp (i.e. without steps) resistivity-temperature transition into superconductivity state it was demonstrated in our works [3] that careful optimization of the growth conditions is necessary.

Other useful parameter to improve and control the quality of the films is the miscut-angle of the substrate that shifts the growth mechanism from 2D layer-by-layer growth to a step-flow growth [3]. This has a positive effect to decrease roughness and to improve the morphology uniformity (there are no roof-range-like grains) and single phase and orientation features, all of them leading to a better superconducting characteristics. Growth of non-c-axis thin films on miscut substrates through the step-flow growth mechanism proceeds in the similar way as for the flat substrate in the sense that the growth direction is c-axis and it is inclined versus the surface of the substrate, but the difference is that there are no opposite symmetrical growth fronts to merge and to form the roof-range-shape grains: front growth directions for all the grains are parallel and the grains start to grow from the inner edge of the stepped miscut profile of the substrate, since this is the place where the free energy is minimized and, hence, nucleation can preferentially occur.

Template method and interrupted growth methods were also very efficient to improve the quality of the films [3, 8]. Nevertheless, electrical properties measured with the current applied along the grains length were generally better than when the current was applied perpendicular. The difference was significantly higher for the films on flat substrates [3]. This is perhaps due to the intrinsic anisotropic nature of HTS and the characteristics of the non-c-axis films morphology (with roof-range-like-grains for films on flat substrates) with some high angle dissipative boundaries through which the perpendicular current has to pass. Some details and their understanding and not clear [3] and more investigations in this direction are needed. From a practical point of view it results that just application of the film-substrate lattice engineering principles are not enough to grow top quality thin films and complex and individual optimization process should be undertaken for each film’s case.

Figure 4. Schematic drawing of the growth for (001) and (117) BTO thin films.
4. Conclusion
Principles of film-substrate engineering are shown to be a powerful tool for growth control and orientation in thin films of HTS. Different c-axis and non-c-axis thin films were obtained and a comparative analysis revealing similarities and differences in the growth, morphology and properties are presented. Emphasis is made on understanding the problems as a necessary step for further developments towards higher quality of the presented films or to further growth of new structures. Results are promising, but much more research is necessary to optimize growth processes. To do that a complex and individual approach is required.

Acknowledgements
PB acknowledges partial support from Alexander von Humboldt Foundation.

References
[1] Endo K, Hayashida S, Ishiai J, Matsuki Y, Ikedo Y, Misawa S and Yashida S, 1990 Jpn. J. Appl. Phys. 29 L294
[2] Endo K, Yamasaki H, Misawa S, Yoshida S and Kajimura K, 1992 Nature 355 327
[3] Endo K and Badica P, 2002 Proc. SPIE Int. Soc. Opt. Eng. 4811 130
[4] Endo K and Badica P, 2005 IEEE Trans. Appl. Supercond. 15(2) 3066
[5] Endo K, Badica P and Itoh J, 2003 Physica C 386 318
[6] Endo K and Badica P, 2004 Physica C 408-410 904
[7] Endo K and Badica P, 2007 Supercond. Sci. Technol. 20 S430
[8] Endo K, Badica P, Sato H and Akoh H, 2006, Supercond. Sci. Technol. 19 S221