

Chapter 2

Substrate-Film Lattice Engineering for the Growth by Spin Coating of *c*-Axis and Non-*c*-axis BSCCO HTS Epitaxial Thin Films

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Abstract For the fabrication of new devices taking advantage of interface phenomena, growth of thin films with different orientations is necessary. Epitaxial thin films of *c*-axis type (001) Bi-2201, (001) Bi-2212, and (001) Bi-2223 and of non-*c*-axis type (115) Bi-2201, (117) Bi-2212, and (119) Bi-2223 were grown by spin coating and subsequent annealing on single-crystal substrates of SrTiO₃, MgO, or LaAlO₃ with (001) and (110) orientations, respectively. We show that lattice matching relationship between the substrate and the film is the key condition for the orientation control in Bi–Sr–Ca–Cu–O thin films obtained by this route. This is similar to Bi–Sr–Ca–Cu–O films grown by vapor deposition methods. Therefore, it is concluded that the growth method is not essential for the orientation control of the film. However, for the epitaxial growth it is necessary to ensure a high mobility of the atomic species at the substrate-film interface and for the spin-coated films this criterion suggests the presence of a liquid at the interface during annealing. Our films have shown specific structural features and occurrence of impurity phases or orientations. Further research is required.

Our work suggests that the growth by spin coating or by related chemical methods of high-quality epitaxial oxide thin films is a promising research direction.

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2.1 Introduction

Electronics devices and sensors are important for different applications. Development of this field is closely related to the progress in the thin films and crystal growth. Thin films show convenient stacking and integration features. Today, industrial electronics is based on 2D surfaces and from this point of view thin films are ideal elements to build new devices and applications. At the same time, in the last 10–15 years, new effects and physics were demonstrated at the interfaces. In this case, 2D-stacked thin films generating composite interfaces and heterostructures are also very useful.

Different materials show anisotropy. Different properties on different crystallographic directions provide new possibilities for the device and sensor fabrication. Under these circumstances growth of epitaxial thin films with certain orientations versus substrate can promote advantages such as enhanced possibilities for the optimization of functional characteristics, generation of new functions, or easier integration and fabrication of devices.

High-temperature superconductors (HTS) are layered perovskite materials built of superconducting and non-superconducting alternate blocks (Fig. 2.1). Non-superconducting blocks play the role of charge reservoir, while Cu–O planes of the superconducting blocks are the easy transport path of the super carriers. Out-of-plane transport is also possible and, along the *c*-axis direction, HTS can be described as an array of superconductor-insulator-superconductor tunneling junctions, the so-called Josephson junctions. Therefore, the structure of an HTS can also be

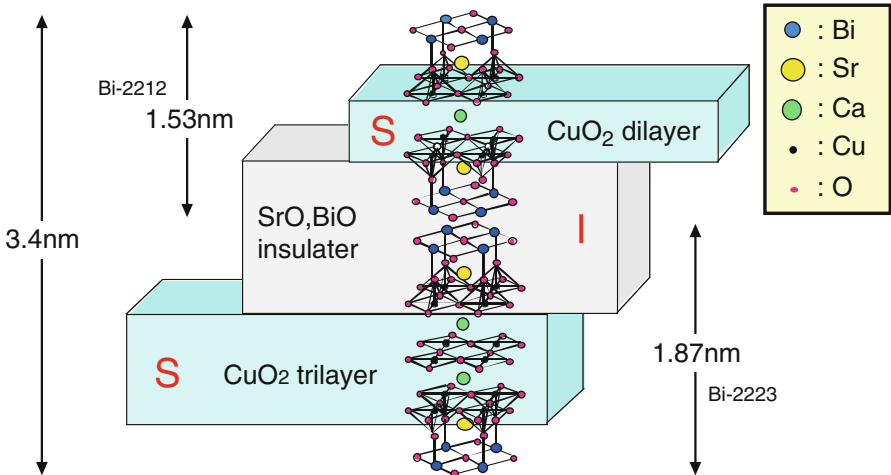


Fig. 2.1 HTS *c*-axis type heterostructure composed of half *c*-axis Bi-2212 and Bi-2223 HTS phases and forming a SIS Josephson junction

described as an intrinsic heterostructure showing Josephson junction tunneling properties. Similar SIS Josephson junctions can also be built artificially, by stacking layers in the *c*-axis direction. These heterostructures composed of epitaxial *c*-axis thin films are however just a simple case and more complex heterostructures using *c*-axis and non-*c*-axis thin films can be imagined. New types of heterostructures can lead to new devices' design involving new types of interfaces, and this may generate new functions as already mentioned. Therefore, growth of non-*c*-axis thin films opens new possibilities for both fundamental and applied electronics and this deserves a special attention.

Growth of the thin films is performed by a chemical route, namely by spin coating. Chemical routes are gaining in popularity due to low manufacturing costs. They are also convenient for deposition of coated Km-long epitaxial *c*-axis superconducting tapes. These tapes, called "second-generation conductors" to differentiate them from the first-generation tapes produced by the "powder-in-tube" method, are made of REBa₂Cu₃O₇ superconductor, with RE being a rare earth element such as Y, Sm, or Gd. A much lower number of articles are devoted to coated tapes or thin films [1–6] fabricated by chemical routes of other HTS.

For the first time we have succeeded in orientation control of Bi₂Sr₂CuO₆ (Bi-2201) and obtaining non-*c*-axis oriented film of (115) Bi-2201 [7, 8]. In this chapter we present growth aspects of *c*-axis and non-*c*-axis epitaxial spin-coated thin films in the Bi–Sr–Ca–Cu–O (BSCCO) HTS system. We explore the possibilities to obtain high-quality thin films with potential for electronics applications.

2.2 Experimental

(001) SrTiO₃ (STO), (001) MgO, or (001) LaAlO₃ (LAO) substrates were used for the growth of (001) Bi₂Sr₂Ca_{*n*-1}Cu_{*n*}O_{*x*} (*n* = 1, 2, 3) thin films. Non-*c*-axis thin films of (115) Bi₂Sr₂CuO₆ (Bi-2201), (117) Bi₂Sr₂CaCu₂O₈ (Bi-2212), and (119) Bi₂Sr₂Ca₂Cu₃O₁₀ (Bi-2223) were grown on (110) STO. Substrates and thin films with indicated orientations show convenient lattice matching. Examples of the relationship between the substrate and the *c*-axis or non-*c*-axis films are presented in Fig. 2.2. We used substrates produced by Furuuchi Chem. Co., LTD. The coating solution was supplied by Kojundo Chem. Lab. Co., LTD. Spin coating was performed at 3,000 rpm for 30 s and it was repeated five times. As-prepared films were preheated in the air at 500 °C for 5 min. A final heat treatment was performed for different thermal regimes.

Structure of the thin films was measured by X-ray diffraction (XRD) using a Rigaku diffractometer (Cu_{Kα} radiation). Microstructure was observed by scanning electron microscopy (SEM) using a Hitachi High-Tech Fielding Co., S-3400N microscope. Resistance with temperature was measured in-plane by standard four-probe method using silver paint contacts.

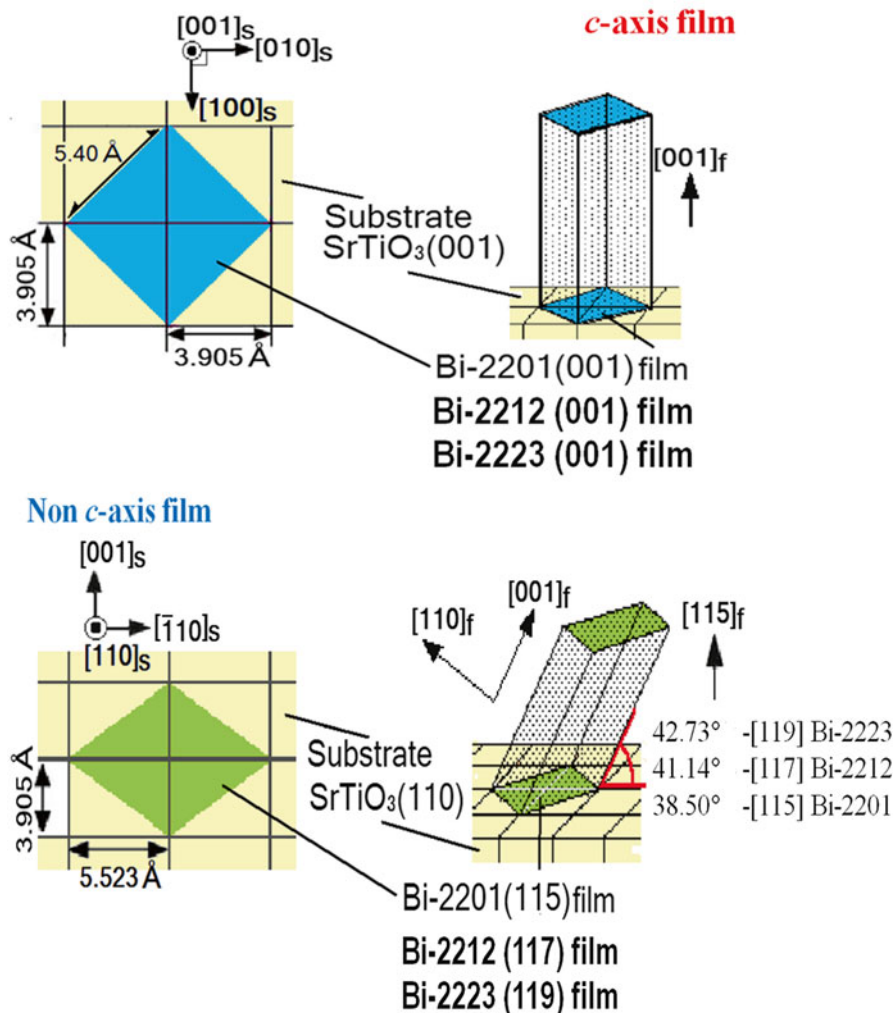


Fig. 2.2 Lattice matching relationship between c -axis and non- c -axis thin films (f) and SrTiO₃ substrate (S)

2.3 Results and Discussion

XRD patterns of the c -axis and non- c -axis films are presented in Figs. 2.3, 2.4, and 2.5 and Figs. 2.6, 2.7, and 2.8, respectively.

For the c -axis thin films (001) peaks are observed (Figs. 2.3, 2.4, and 2.5). The lowest amount of impurity phases and orientations are for the (001) Bi-2201 films. These films form at lower temperatures of 750–820 °C when compared to (001) Bi-2212 or (001) Bi-2223 films for which growth temperatures above 800 °C are necessary.

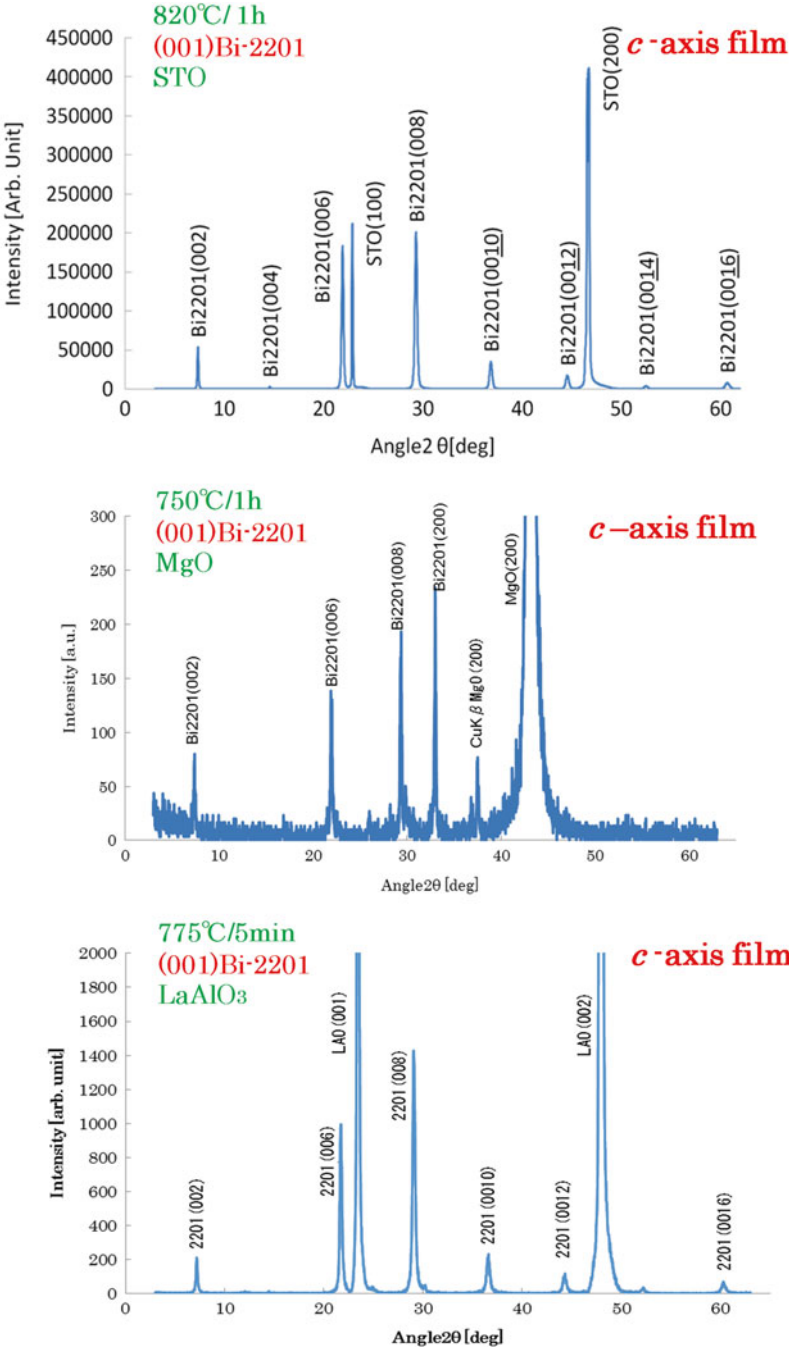


Fig. 2.3 Bi-2201 thin films with *c*-axis orientation obtained by spin coating on (001) STO, (001) MgO, and (001) LAO substrates. Growth conditions are indicated

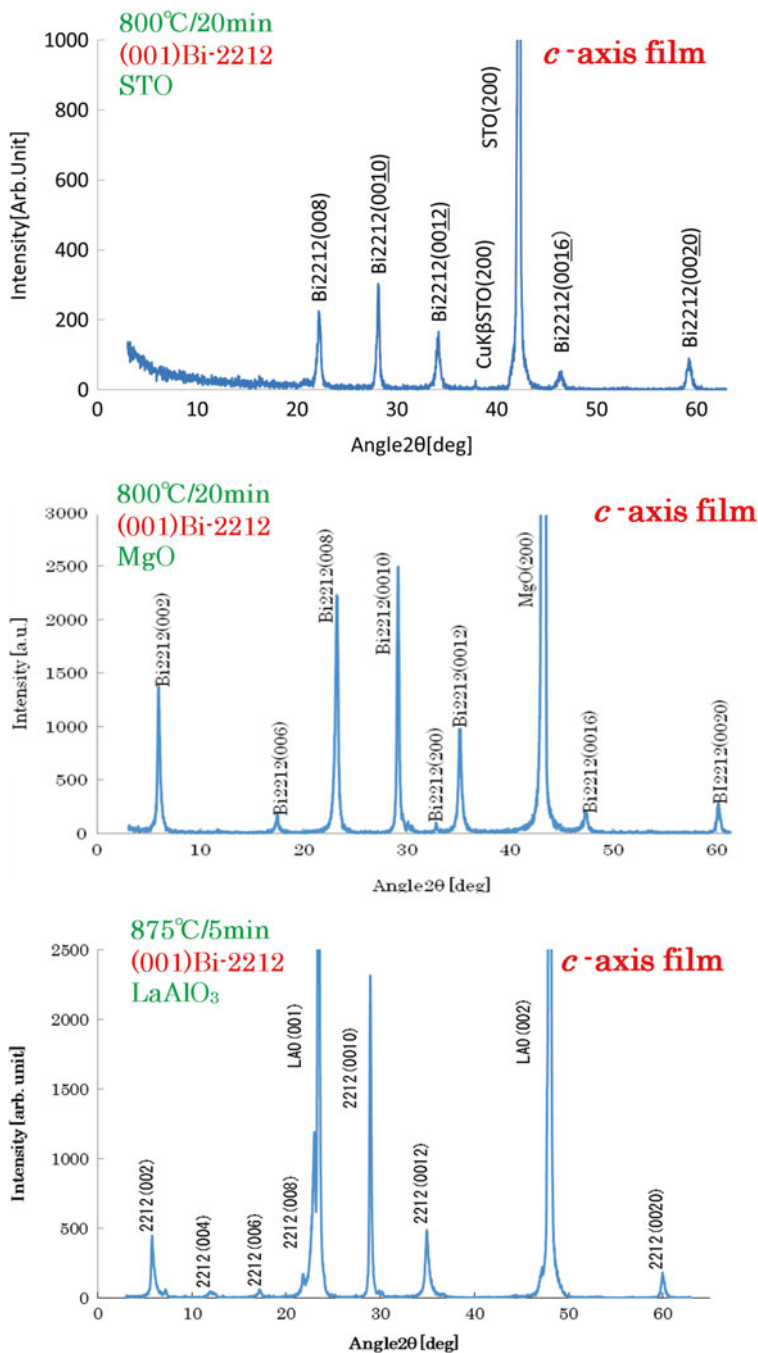


Fig. 2.4 Bi-2212 thin films with c-axis orientation obtained by spin coating on (001) STO and (001) MgO substrates. Growth conditions are indicated

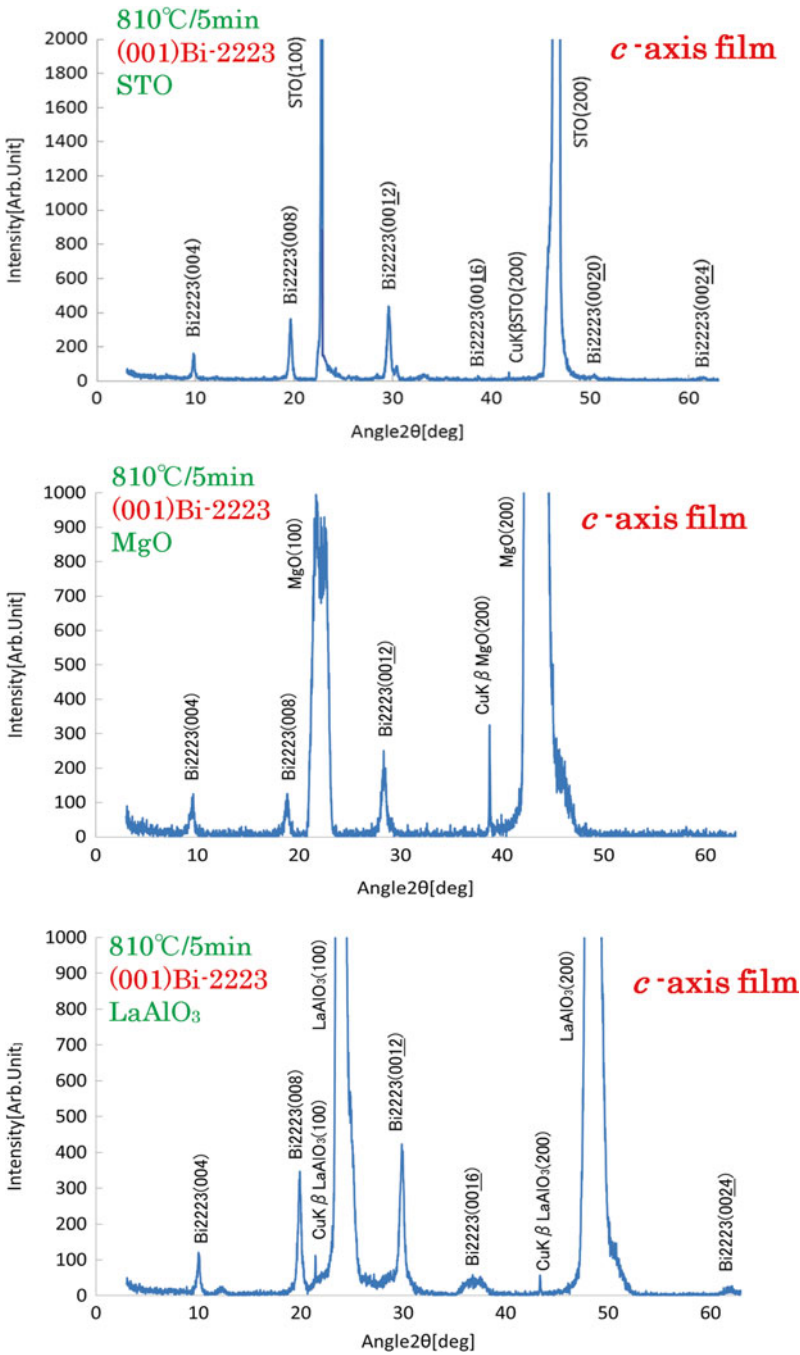


Fig. 2.5 Bi-2223 thin films with *c*-axis orientation obtained by spin coating on (001) STO, (001) MgO, and (001) LAO substrates. Growth conditions were the same

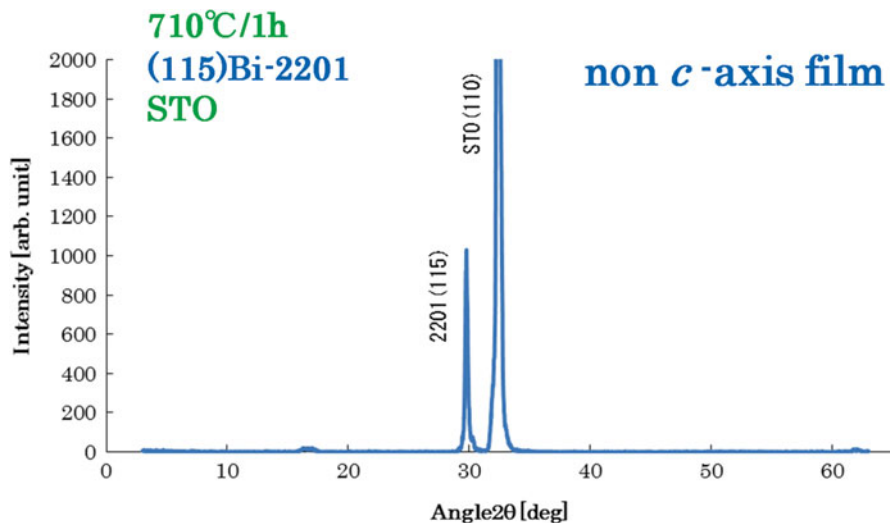


Fig. 2.6 Bi-2201 thin film with (115) orientation obtained by spin coating on a (110) STO substrate

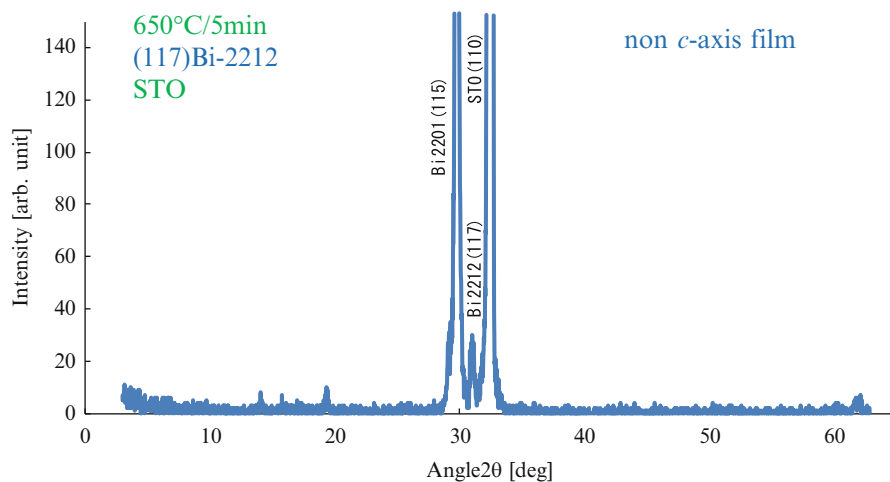


Fig. 2.7 Bi-2212 thin film with (117) orientation obtained by spin coating on a (110) STO substrate

One observes that the influence of the substrate type is relatively low, meaning that the material of the substrate plays a minimal role, while the lattice mismatch relationship between the film and substrate is essential for the growth of the film. However, for the control of the film quality, growth conditions should be optimum so that the crystal quality is high, the roughness is small, the film lacks impurity phases and orientations, and superconducting properties are optimum.

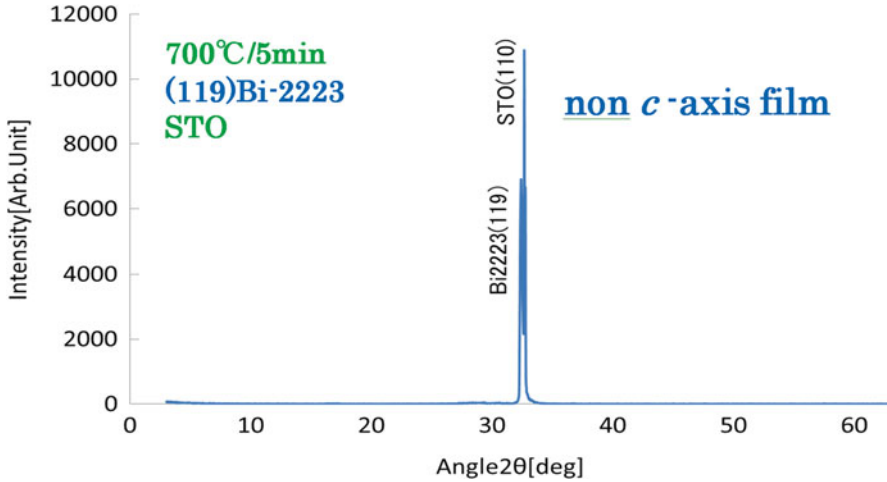


Fig. 2.8 Bi-2223 thin film with (119) orientation obtained by spin coating on a (110) STO substrate

A specific feature of the *c*-axis thin films reported in this work is that often some diffraction (001) lines of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ ($n = 1, 2, 3$) superconducting phases such as (002), (006), and others cannot be always observed in the diffraction patterns (Figs. 2.3, 2.4, and 2.5). This may suggest a certain specific structural behavior for the spin-coated films, but more investigations are necessary. It is likely that a more pronounced tendency in this regard is shown by the (001) Bi-2223 spin-coated thin films (Fig. 2.5).

The non-*c*-axis films grow at lower temperatures than for the *c*-axis films. In the non-*c*-axis films impurity phases and orientations can easily occur (Figs. 2.6, 2.7, and 2.8). At the moment of writing this chapter, the non-*c*-axis (117) Bi-2212 films grown for different conditions and on different substrates always show the presence of (115) Bi-2201 (Fig. 2.7) or of other phases and orientations. On the other hand, thin films from Figs. 2.6 and 2.8 of (115) Bi-2201 and (119) Bi-2223, respectively, can be regarded as being approximately of a single phase and orientation.

In our previous works we have grown *c*-axis and non-*c*-axis excellent films by metal organic chemical vapor deposition (MOCVD) or metal organic molecular beam epitaxy (MOMBE). Growth details of the MOCVD or MOMBE thin films and heterostructures are briefly reviewed in our article [9]. When using the same substrates, the resulting orientation of the films grown by MOCVD or MOMBE was identical with the orientation of the spin-coated films. The lattice relationship between the substrate and the thin film proved to be a strong tool to induce the thin film orientation. Remarkably, this principle does not depend on growth technology. Films obtained by MOCVD, MOMBE, or spin coating show similar growth tendencies from the phase and orientation viewpoints. However, supply of the atomic species and supersaturation play an important role and situations might be very different

when using vapor growth methods such as MOCVD or MOMBE and solid–liquid ones such as spin coating followed by a subsequent crystallization. In the case of vapor deposition methods such as MOCVD or MOMBE, atomic species arriving on the substrate are supplied sequentially. First-arriving species migrate on the surface and condensate. Islands and, at a certain moment, a complete thin film layer are generated. On the first-formed layer newly arriving species will generate the next layer. It is easy to understand that in this case we deal with a layer-by-layer growth. This image is simplified and the crystal chemistry of the material is also important. This means that layers are not necessarily atomic planes and in fact for our MOCVD or MOMBE growth they are made of the smallest building elements. For the BSCCO HTS phases, building blocks are half c -axis unit cell of the Bi-2201, Bi-2212, or Bi-2223 phases. Therefore, stacking of half c -axis unit cells in the c -axis direction generates layers and the film. A special note is required for the non- c -axis films. Namely, while for c -axis films, c -axis is perpendicular on the substrate's surface, for the non- c -axis thin films the c -axis is inclined with an angle α close to 45° . More precisely, depending on the phase, α takes slightly different values of 38.5° , 41.14° , and 42.73° for (115) Bi-2201, (117) Bi-2212, and (119) Bi-2223, respectively. Apart from this particular feature, c -axis and non- c -axis thin films can be considered to grow by a similar layer-by-layer growth. Going back to spin-coated BSCCO thin films, in this case, atomic species are not supplied sequentially as for MOCVD. Since we obtained similar orientation results as for MOCVD thin films, it is thought that the spin-coated films start to crystallize from the substrate's surface to the outer free surface of the film. This result is strongly supported by the fact that films are epitaxial. Although not perfect, one can observe in Fig. 2.9 the morphology of the (115) Bi-2201 film showing bar-like grains that are mostly following one

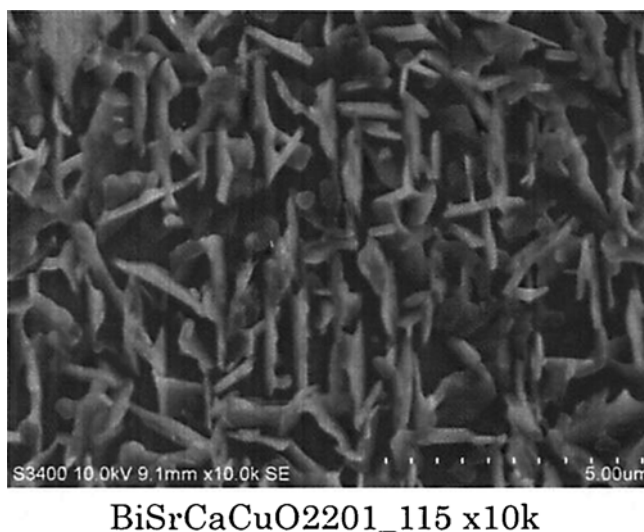


Fig. 2.9 SEM image of the (115) Bi-2201 thin film obtained by spin coating

orientation (vertical in Fig. 2.9) according to substrate-film lattice relationship. Some grains with an in-plane orientation at 45° are also visible and twins are formed. There are also apparent grains with an in-plane orientation at 90° . It was not possible to distinguish their type. Crystallization of the spin-coated film starting from the substrate's surface generates few interesting questions. Heating of the films was performed in a conventional electrical furnace meaning that flow of the heat is from the outer to inner part of the sample and the developing thermal gradient would be with a lower temperature in the center of the substrate-film sample. But, to crystallize the sample from the inner to outer part of the sample, the thermal gradient should be opposite; that is, in the center of the sample temperature should be higher. Another aspect related to the development of the epitaxial film in the spin-coated or in other films is that at the interface between the film and the substrate, conditions for the mobility of the atomic species should be active. Otherwise epitaxial growth is hindered. Considering that thermal treatments for the crystallization of the spin-coated films are short of less than an hour when compared to tens or hundreds of hours necessary to form BSCCO HTS phases by solid-state reaction routes, we anticipate that a liquid phase ensuring high mobility of the atomic species at the substrate-film interface is involved during annealing in the crystallization processes of our spin-coated thin films. If the conditions of mobility are active, in the case of our spin-coated thin films a higher mobility and, hence, a higher crystallization temperature are required for the growth of epitaxial *c*-axis thin films than for homologous non-*c*-axis thin films. The situation is similar as for the other growth techniques MOCVD or MOMBE. This observation also strongly supports the presence of a phase with high atomic mobility at the substrate-film interface. During heating of the spin-coated film, thermal features of the substrate and of the film, specifics of the organic and inorganic intermediates in the spin-coated films such as their reaction, decomposition, and melting/wetting behavior should be further investigated.

Thin films of Bi-2201 were insulating. Thin films of (001) Bi-2212 have shown superconductivity with $T_c(R \rightarrow 0) = 70.5$ K. Measurements of the other films are in progress.

2.4 Conclusion

Thin epitaxial films with *c*-axis (001) and non-*c*-axis (i.e., 115, 117, 119) orientations of Bi-2201, Bi-2212, and Bi-2223 were grown by spin coating on (001) or (110) STO, MgO, or LaAlO₃ single-crystal substrates, respectively. Films show similar growth tendencies as for the other vapor deposition methods. Regardless of the deposition method, to induce orientation the substrate-film matching relationship plays a key role. From the comparative analysis of the growth of the spin-coated films and the films obtained by vapor deposition methods, the presence of a liquid-like phase with high atomic mobility at the substrate-film interface during annealing of the spin-coated films is anticipated. As-prepared spin-coated films

show in some cases some specific structural features or the presence of undesirable impurity phases or orientations. Further research is required.

Our results suggest that spin coating is a promising cheap method for the growth of epitaxial BSCCO thin films with potential for electronics applications. Exploration of the growth of other perovskite oxides for electronics by spin coating also deserves attention.

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