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CONTROL OF THE GROWTH MECHANISM OF (119) Bi-2223 SUPERCONDUCTING THIN FILMS. TWO-DIMENSIONAL NUCLEATION GROWTH AND STEP-FLOW GROWTH

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Films of (119) Bi-2223 high-T_c superconductor, potentially useful for future sandwich-stacked structures exhibiting Josephson effect have been prepared by MOCVD on (100) $NdGaO_3$ and (110) $SrTiO_3$ flat and vicinal substrates with different off-angles. It is shown that off-angle is a key parameter in growth control mechanism of the films. In-plane aligned films, with regular morphology and low roughness as well as having maximum zero-resistivity critical temperature of T_{c0}=67.2K and T_{c0}=74K when "single" and "two"- temperature growth routes are used, respectively, have been obtained for high of-angles (20 °). Growth mechanism is changing from a two-dimensional type for the flat substrate to a step-flow one for vicinal substrates.

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1. Introduction

In high-T_c superconductors (HTS) coherence length is much smaller along c-axis than along a- or b- axis directions [1]. Short coherence length on c-axis direction is a crucial problem for HTS-based nanoelectronics devices such as sandwich-stacked structures exhibiting Josephson effect. This is a difficult technical limitation since for the c-axis oriented superconducting layer, non-superconducting layer should be very thin. Superconducting films with a different orientation (non c-axis) can potentially play an important role (non-superconducting layer can be thicker and therefore easier to fabricate Josephson stacked structures). In the previous paper [2] we reviewed the current status of synthesis and processing of Bi-2223 superconductivity ceramic by spray frozen-freeze drying method.

In this paper we report the growth by MOCVD and investigation of the (119) Bi-2223 films. To fabricate the above mentioned structures, besides orientation, surface morphology and superconducting characteristics are key parameters. The paper focuses on growth control for a better quality of the films through a combination of single-temperature, template (two-temperature) routes and the use of substrates with different off-angles (0-20°). Special attention is given to the growth mechanism.

2. Experimental

Films growth has been performed in a cold-wall-type MOCVD equipment with horizontal reaction tube. Same equipment has been used for growth of c-axis Bi-2223 thin films in our previous

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work [3]. The source materials $Bi(C_6H_5)_3$ and $M(DPM)_2$, with M= Sr, Ca and Cu were loaded in vaporizers and individually heated to appropriate temperatures (DPM is abbreviation for di-pivaloyl-methanate). Argon flow has been used to transport vapors to the reaction tube. Gas lines were heated to temperatures higher than those of the vaporizers to prevent condensation of the source materials. Oxygen gas was introduced directly into reactor at a partial pressure of 23 torr. Substrates of (100) $NdGaO_3$ (NGO) or (110) $SrTiO_3$ (STO) flat or vicinal (off angle up to 20°) were placed on an Inconel susceptor and inductively heated at different temperatures (Table 1). The (100) $NdGaO_3$ (NGO) and (110) $SrTiO_3$ (STO) substrates have favorable lattice matching with (119) Bi-2223, i.e. misfit on $[001]_s$NGO/$[001]_s$STO direction of the substrate is 1.25%/-2.17% and on $[010]_s$NGO/$[110]_s$STO directions of 0.4%/1.96%. Symbols S and F are used for substrate and film, respectively. As-grown films on flat or vicinal substrates are gathered in Table 1. Template films were grown at lower temperature for 57 hours and at higher temperature for 83 hours. Switch from one temperature to another has been done in-situ very fast (less than 1min).

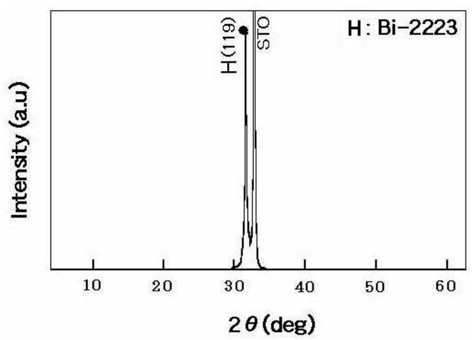
The films were checked for composition and thickness by inductively coupled plasma spectroscopy (ICP).). Composition ratio Bi : Sr : Ca : Cu, normalized to Bi_2, was 2 : 1.8-2.2 : 1.8-2.2 : 2.8-3.4 (by ICP and EDS) and the films thickness was between 500 and 3200 Å. The films have been characterized by x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM/EDS) and electrical transport (R(T)) measurements (four-probe method). For R(T) measurements the current has been applied parallel and perpendicular (// and ⊥ notation) to the $[001]_s$ azimuth of the substrate's surface.

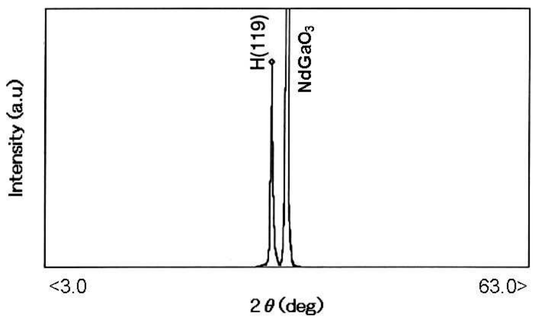
3. Results and discussion

Table 1. Samples, substrates and off-angles, growth temperatures, critical temperature at zero resistance (T_{c0}), when measuring current is applied // and ⊥ to the $[001]_s$ substrate's azimuth.

Sample	Substrate		Off-angle (°)	Growth temperature (°C)	$T_{c0//}$ (K)	$T_{c0\perp}$ (K)
N1	$NdGaO_3$	Flat	0	520/20h	-	-
N2			0	520/160h	-	-
N3			0	600	$T_c^{onset}{}_{//}$=45	-
N4			0	700	$T_c^{onset}{}_{//}$=110	-
N5			0	800	22.5	6.5
N6			0	810	-	-
N7			0	610+670	-	-
S1	$SrTiO_3$	Flat	0	560	14.9	12.8
S2			0	630	31	27.5
S3			0	600+670	-	47.6
V1		Vicinal	10	610	45.5	-
V2				630	-	-
V3			15	610	57	-
V4				630	-	-
V5			20	610	68	67.2
V6				630	36.8	-
V7				670	<9.2	-
V8			5	610+670	40.4	-
V9			10	610+670	61.1	-
V10			15	610+670	66.7	-
V11			20	610+670	74.5	74

In our first experiments on (119) Bi-2223 films we have tried to optimize growth temperature (350-820°C) and time. Despite much effort, the quality of the film was rather poor. By XRD several impurity phases and orientations (most often c-axis Bi-2212, Bi-2223 and (119) Bi-2212 phases) were detected. Full transitions into the superconducting state were not always attained, down to 4K (Table1). The phase/orientation stability versus growth temperature was approximately the same for NGO and STO substrates. Higher temperatures and longer times induced formation of bigger grains, increasing the roughness of the films as well as improving transport properties. On the other side less impurities have been found for the films grown at intermediate temperatures (around 600°C). Our results suggest processing by a template method (two-temperature growth). Our samples N7 and S3 grown by this approach have shown to be single phase (Fig.1a, b), with better superconducting characteristics (Table 1), but at the same time consisting of large grains.





a b

Fig. 1. XRD patterns for the (119) Bi-2223 thin films, grown by template method on: a) flat STO (sample S3) and b) NGO substrate (sample N7 from Table 1).

The morphology of the films grown on a flat substrate is presented in Fig. 2. Grains of mountain-range shape are in-plane aligned parallel to the $[001]_s$ azimuth. The growth mechanism is the conventional 2D one, usually observed in the c-axis oriented films [4]. But, in this case the c-axis direction is not perpendicular, but tilted with a certain angle α to the substrate's surface. The growing, neighboring inclined fronts will merge in a twin-like geometry, i.e. the observed grains with mountain-range shape. We have used term - twin - only to emphasize that there is an angle, boundary and arrangement between domains and it has nothing to do with the classic definition of twins. The angle (α) determined experimentally from the AFM images between the tilted surface of the mountain and substrate's surface coincides to the theoretical (47.3° for the (119) Bi-2223) value.

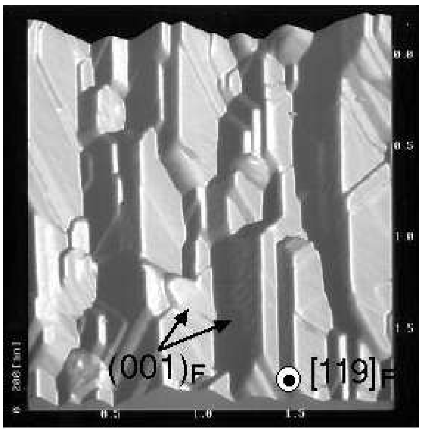


Fig. 2. AFM image (2 μm × 2 μm) of the (119) Bi-2223 film grown by template (two-temperature) method on flat STO (sample S3 from Table 1).

Presented morphology has the disadvantage of being rough in order to attain better superconducting properties and to form single phase/orientation. At the same time the films are not perfectly uniform. Some secondary germination and growth on the two tilted surfaces of the mountain grains can be observed especially when mountain grains are large as for the "two-temperature" route (Fig. 2). Roughness and uniformity are limitative factors in the case of sandwich type devices. For the secondary germination the following explanation can be given: when grains become large the atoms arriving on the tilt surfaces of the mountain-grains will have to cover long distance by migration to form a new layer. In this case, growth defects/imperfections can act as germination centers for the new incomplete layers. These layers will be parallel to the tilted surface of the mountain grains, but they will look like separate grains. The growth mechanism is similar to the 2D one presented in detail for our c-axis Bi-2223 thin films grown on flat substrates [4].

Another observation is that reported critical temperatures for the Bi-2212 and Bi-2223 phases are 90K and 110K, respectively, i.e. much higher than in our (119)-oriented films (Table 1, flat substrates). For (001) Bi-2223 thin films we have reported zero-resistivity critical temperatures of 97K and excellent transport critical current densities [5].

Considering these two-observations, it is clear that there is much room for improvement of our films and a different morphology is necessary. For this purpose understanding and control of the growth mechanism is important. In our paper [3] we have shown that for (001) Bi-2223 films the higher the off-angle of the substrate (i.e. vicinal) is, the higher quality is obtained. We have decided to apply this result to our (119) Bi-2223 films.

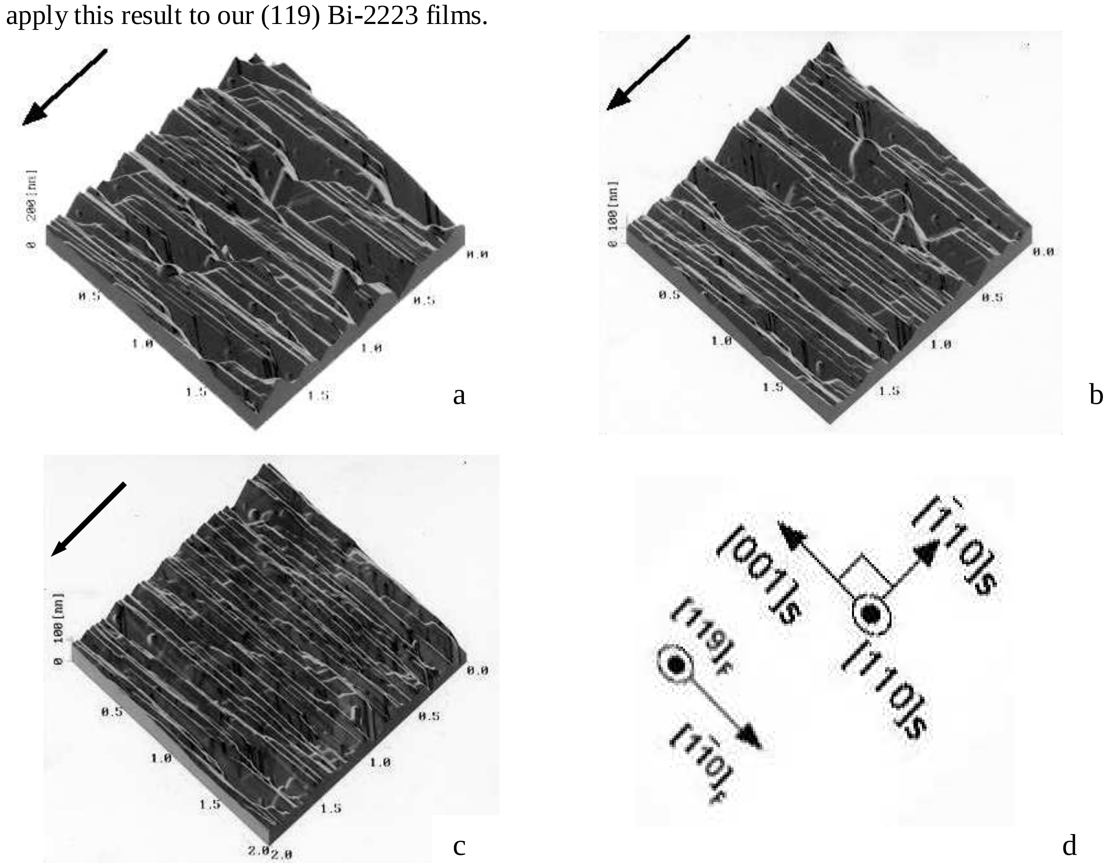


Fig. 3. AFM images (2μm x 2μm) for the (119) Bi-2223 films grown at 610 °C on vicinal STO with different off - angles a) 10 °, b) 15 ° and c) 20 ° (samples V1, V3, V5 from Table1). d) the main crystallographic axis Big arrow indicates the direction of the substrate's off-angle.

In Fig. 3 are shown the AFM images for the films grown on substrates with different off-angles along $[001]_s$ azimuth for 610 °C growth temperature. The higher the off-angle is, the more uniform, continuous, lower roughness and thinner steps are formed. The surface morphology is very different from the previous one. These results suggest that in the case of vicinal substrate, with the increase of the off-angle the growth mechanism is changing to a step-flow type (similar as for c-axis Bi-2223 films). The first obvious advantage is the decrease in surface roughness of the film. Second, and maybe the most interesting is that germination occurs preferentially, at the points with the lowest free energy of the substrate's vicinal steps. The tilted domains will grow parallel, following only one direction and not two-directions as for the films grown on flat substrates. The growth direction is the same c-axis direction, but for the vicinal substrate the angle between this direction and substrate's surface will be α - (off-angle), where α is the angle introduced in the previous paragraph. There will be no "twinned" mountain-range grains. We have estimated the angle between the surface of the substrate and the lateral surface of the steps, considering that the steps are symmetric as resulted from the AFM profile of the steps in the cross-section taken perpendicular to $[001]_s$ azimuth. The obtained value of 30°, for the 20° vicinal STO, is in excellent agreement with the theoretical value calculated for the (119) Bi-2223 phase (α - (off-angle)=27.3°). Considering this result, even if indirectly, we believe that our films grown on vicinal substrates are single-phase (119) Bi-2223. Local (EDS) and overall (ICP) compositions of the films are supporting this observation (see 2, experimental). XRD could not been performed for the films on vicinal substrates. The third advantage resulting from the second one is that for the films grown on vicinal substrate transport properties should be better. This assumption is based on the observation that, when using vicinal substrate, in the $\perp$ direction to $[001]_s$ azimuth there are no "twin" boundaries as for the mountain-range morphology and in the // direction steps are continuous, uniform and without grains due to secondary germination. For the "one-" and "two-temperatures routes (Table 1, Fig. 4), the critical temperatures have been increased for the optimum synthesis conditions and 20° substrate off-angle to $T_{c0//}$=68K/$T_{c0\perp}$=67.2K and to $T_{c0//}$=74.5K/$T_{c0\perp}$=74K, respectively.

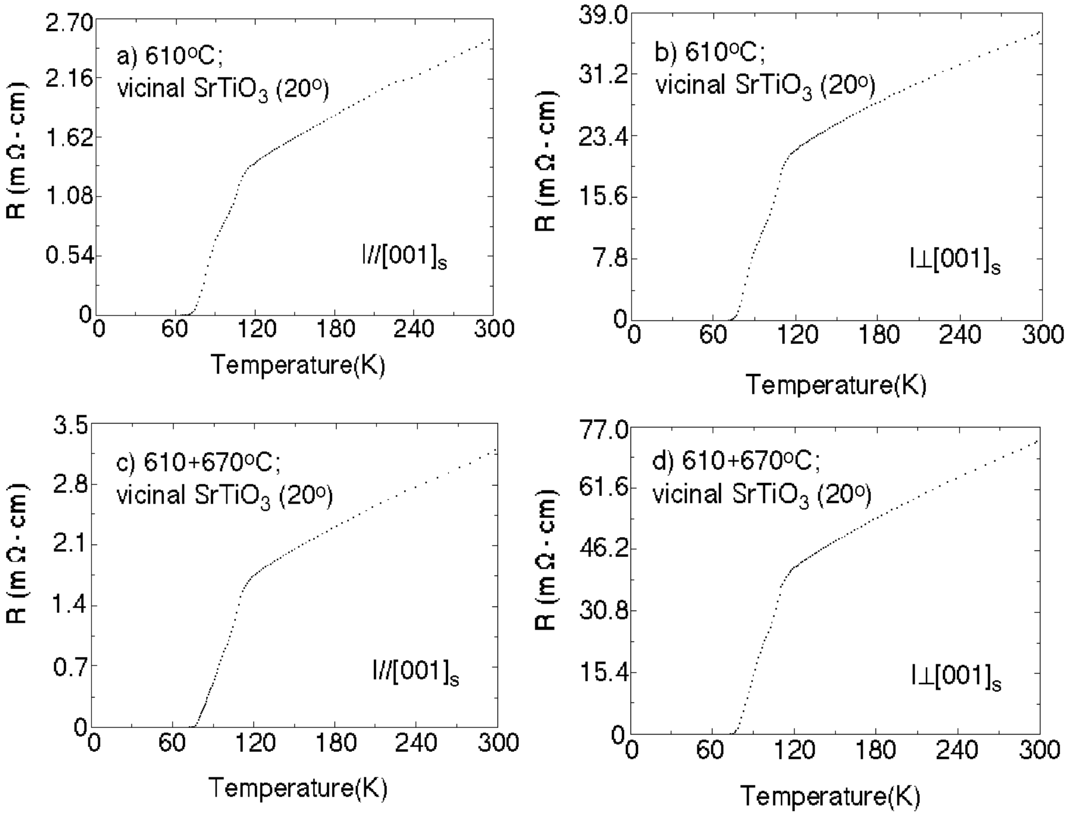


Fig. 4. Resistivity curves versus temperature measured with the applied current (I) parallel and perpendicular to the [001] substrate's azimuth for the films grown on vicinal (20 °) STO by single temperature (a and b) (sample V5 from Table 1) and two-temperature methods (c and d) (sample V11 from Table 1).

4. Conclusions

Growth control through the optimization of the growth technological parameters and by using vicinal substrates, for (119) Bi-2223 films produced by MOCVD have been presented and discussed. Thin films with improved superconducting properties are obtained when "two-temperature" growth route is applied and/or is combined with step-flow growth mechanism (step-like morphology), induced by the vicinal substrate. Generally, higher of-angles of the vicinal substrates are resulting in films of higher quality. Our films are bi-axially in-plane aligned and have the maximum T_{c0} of 74K for an off-angle equal to 20 °. The films with maximum T_{c0} have the lowest roughness.

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