

GROWTH AND ANALYSIS OF HIGHLY ORIENTED (11n) BCSCO FILMS FOR DEVICE RESEARCH

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ABSTRACT

Films of BCSCO superconductor of the type $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_x$ have been grown by liquid phase epitaxy method (LPE), using a partially closed growth chamber. The films were grown on (001) and (110) NdGaO_3 substrates by slow cooling process in an optimized temperature range below the peritectic melting point (880°C) of $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$. Optimization of parameters, such as seed rotation, soak of initial growth temperature and growth period results in the formation of 2122 phase BCSCO films. The films grown at rotation rates of less than 30 and more than 70 rpm are observed to be associated with the second phase of Sr-Ca-Cu-O system. Higher growth temperatures ($>860^\circ\text{C}$) also encourage to the formation of this phase. XRD measurements show that the films grown on (110) NdGaO_3 have a preferred (11n)-orientation. It is pertinent to mention here that in our earlier results [1] published elsewhere we obtained c-axis oriented $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ phase films on (001) NdGaO_3 substrate. Critical current density is found to be higher for the films grown on (110) than (001) NdGaO_3 substrate orientation. The best values of zero resistance (T_{co}) and critical current density obtained are 87 K and 10^5 A/cm^2 , respectively.

INTRODUCTION

Various growth techniques have been reported for Bi-Ca-Sr-Cu-O superconducting films. Most of these investigations deal with the growth of high quality c-axis oriented epitaxially grown films [1-5]. The intrinsic anisotropic properties of Bi-Ca-Sr-Cu-O superconducting system (i.e. the coherence length of about 2 °A along the c-axis and 24 °A in the a-b plane) leads to the growth kinetics resulting in the formation of (00n)-orientated films. However, a film with (00n)-orientation is unsuitable for the fabrication of Josephson tunneling junctions. It is because of the fact that coherence length along c-axis is too short to obtain a Josephson effect. For this reason it is important to grow (11n)-oriented high- T_c superconducting films. Furthermore, the epitaxial nature of these LPE grown films make them attractive for many other devices including IR photodetectors, microwave resonators and integrated structured devices.

Recently, (11n)-oriented superconducting BCSCO films have been grown by the MBE [6] and MOVCD [7-8] techniques. MgO [7] and SrTiO₃ [6,8] have been used to grow such films. However, there has been no attempt made to grow (11n)-oriented BCSCO films by the LPE method. Also there has been no report so far on the (11n)-oriented film of BCSCO using NdGaO₃ substrate although it has been used to grow (11n)-oriented YBCO (123) epitaxial films [9].

In this paper we report the growth of (11n)-oriented Bi₂CaSr₂Cu₂O₈ films on (110) NdGaO₃ substrate. Optimization of various growth conditions which lead to the formation of 2122 phase are described and discussed. Formation of the second phase observed during the process of optimization is also described.

EXPERIMENTAL

The experimental arrangement of the LPE apparatus consists of a resistively heated furnace having facility for translation and rotation of seed. A partially closed growth chamber in the form of a platinum crucible embedded in an alumina blanket and further placed in an alumina crucible is used for the growth of BCSCO films. The alumina crucible is covered at the top by an alumina plate with a central hole of about 1 cm. for passing through the seed rod. The details about charge preparation of BCSCO and the method of film preparation are same as reported by us [1].

Transport resistivity and critical current density measurements were made by standard four-probe method using gold electrodes. Electrodes were made by sputtering gold and silver epoxy was used to embed the silver wires on the samples. A 10 μV/mm electric field criterion was used to measure the critical current density.

RESULTS AND DISCUSSION

Table 1 illustrates the optimization of the growth conditions for single 2122 phase of BCSCO films. It is well known that on melting (885 °C) Bi₂CaSr₂Cu₂O₈ splits into sub-

Table 1. Growth parameters leading to single and mixed phase formation of 2122 BCSCO films.

Growth parameters	1st soak		2nd soak		Seed rotation rpm	Growth temp °C	Charge preparation of BCSCO	Remarks
	Time hrs	Temp °C	Time hrs	Temp °C				
Optimized growth parameters for 2122 phase formation	12	925	4-5	855-860	50-70	855-835	900 °C for 1 hr	DF(5) [*] CF(15) ^{**}

*DF(5) = Discontinuous film for the growth time of 5 hours

**CF(15) = Continuous film for the growth time of 15 hours

phases. Therefore, in order to form a single phase 2122-BCSCO and to avoid intergrowth of sub-phases various growth parameters as described in table 1 have to be optimized. It is observed that seed rotation of more than 70 and less than 30 rpm encourage the formation of secondary phases in the film. Similarly, the second soak of about 4-5 hours is necessary to allow maximum reformation of 2122 phase in the molten solution. It is important that the second soak be carried out below the peritectic melting point of $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ phase. Charge preparation of BCSCO also plays a crucial role in the formation of 2122 phase films. Fig. 1 shows resistivity versus temperature relationship of films grown from different charge preparations. Judging by the T_{co} at 85 K, it is observed that the charge preparation at 900 °C for one hour is conducive for the growth of 2122 films. The best supersaturation conditions leading to the formation of 2122 phase and elimination of second phase are found in the temperature range of 855-835 °C. This fact is demonstrated in graph of resistivity versus temperature shown in Fig. 2. The T_{co} for the film grown under supersaturated conditions is 87 K; whereas for the one grown in undersaturated conditions it is about 70 K. The same inference is derived from the Fig. 3 (J_c versus temperature) where J_c is observed to be almost 3 times higher for the film grown under supersaturated conditions than the film grown in undersaturated conditions.

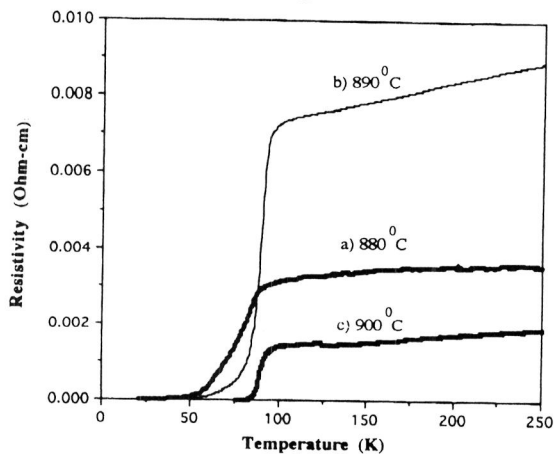


Fig. 1. Resistivity versus temperature of BCSCO films under different charge preparation conditions.

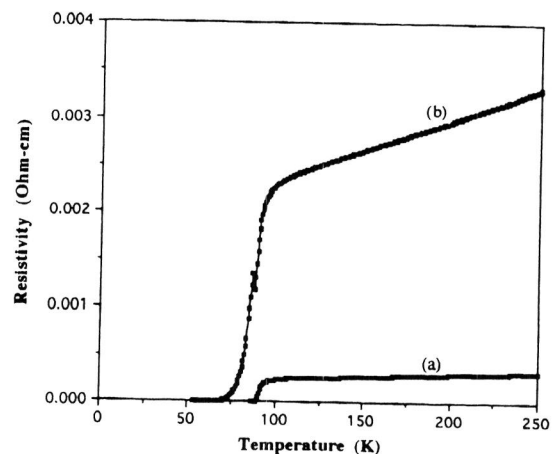


Fig. 2. Resistivity versus temperature of BCSCO films grown between a) 855-835 °C and b) 845-825 °C for 15 hours growth period.

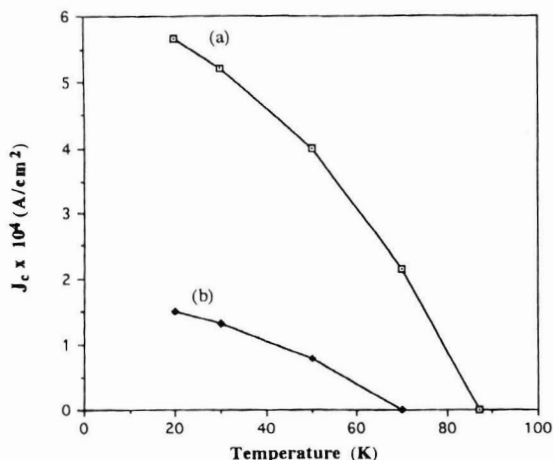


Fig.3. J_c versus temperature relationship of 2122 film grown between a) 855-835 °C and b) 845-825 °C for 15 hours growth period.

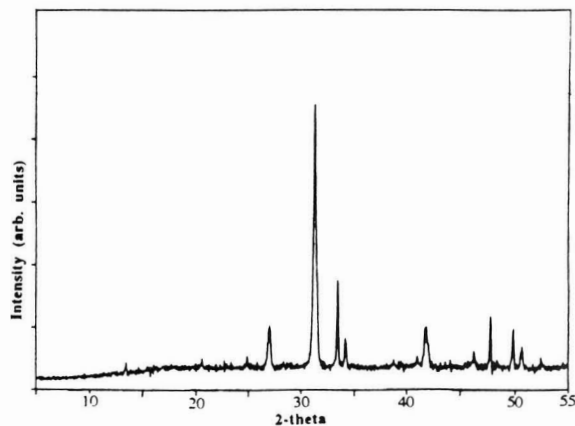


Fig.4. XRD pattern of the needle crystals belonging to the family of $(Ca_{1-y}Sr_y)_{1-x}CuO_{2-z}$ system.

As mentioned above the second phase of BCSCO is formed under certain growth conditions. Fig.4 shows an XRD graph of such a phase. This phase is observed to be associated with $(Ca_{1-y}Sr_y)_{1-x}CuO_{2-z}$ [10] family of infinite layer superconductors which exhibit superconductivity only under high pressure and for a specific composition. The EDAX analysis of this phase confirms the presence of Ca, Sr, Cu and O elements. This phase grows on the $NdGaO_3$ substrate as well as along the walls of the platinum crucible with different morphologies. Fig.5 shows a scanning electron micrograph of this phase grown in the form of needle crystals. The resistivity of one of these needles shows a semiconducting behavior which is in agreement with the reported literature[11]. The resistivity of these needles below 50 K almost becomes insulating in nature. These needles have a thickness between 10-50 micron and get cleaved easily. Fig.6 illustrates the same phase grown on (110) $NdGaO_3$ substrate. Here the morphology is in the form of clusters. The difference in the morphology can be understood by the fact that the nucleation takes place at two different surfaces i.e. platinum wall for needle shape crystals and a smooth surface of substrate for cluster type formation.

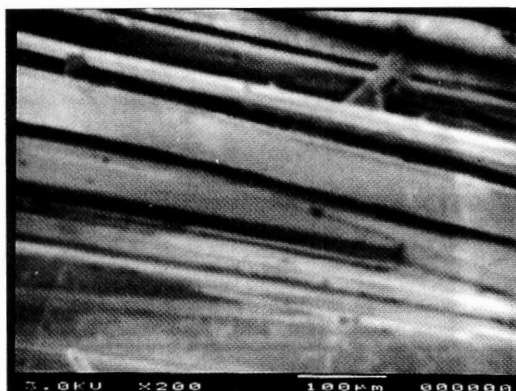


Fig.5. SEM showing the needle morphology of the crystals of $(Ca_{1-y}Sr_y)_{1-x}CuO_{2-z}$ system.

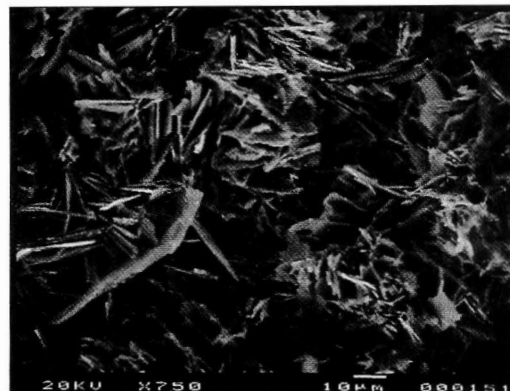


Fig.6. SEM showing cluster type morphology of the Bi-Ca-Sr-Cu-O sub-phase grown on (110) $NdGaO_3$.

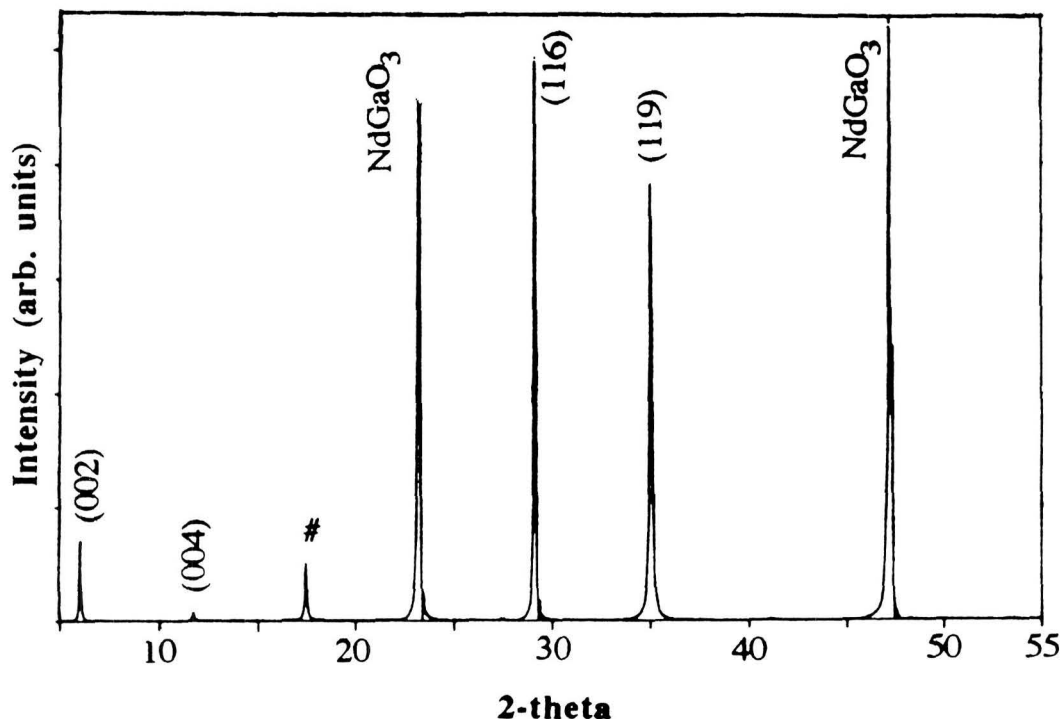


Fig.7. X-ray powder diffraction graph of 2122 phase BCSCO film grown on (110) NdGaO₃ substrate. The symbol # stands for unidentified.

Fig.7 shows an XRD pattern of a BCSCO film grown on (110) NdGaO₃ substrate. The figure shows the strong presence of (116) and (119) plane orientations. Assuming the well established values of lattice constants i.e. $a=5.40$, $b=5.42$ and $c=30.81$, the theoretical value of (119) orientation comes out to be 2.551 ('d' value) which is very close to the experimental value of 2.558. Similarly, the theoretical and experimental values for (116) orientation are 3.067 and 3.065, respectively. There is the possibility that (116) plane may be mistaken due to its proximity to (0010) orientation. But analyzing on the basis of authentic lattice constants reported in the literature, the closest possible match in terms of 'd' spacing is in favor of (116) orientation only. Moreover, by comparing with our earlier results [1] of c-axis oriented LPE films of BCSCO, it is clear that the major peaks in the Fig.7 can be attributed to (116) and (119) orientations. So far, (110) [7], (117), (118) and (119) [6,8,12] orientations have been reported in the literature for 2122 phase of BCSCO superconducting films using MgO and SrTiO₃, respectively. As indicated in Fig.7 there are two major peaks due to NdGaO₃ substrate. Two smaller peaks of (002) and (004) are also present. While the (11n)-orientations are influenced by epitaxy of (110) NdGaO₃ substrate, the (00n) planes result due to the anisotropic growth kinetics of the Bi-oxide superconducting system. Fig.8 is a backscattered SEM of (11n)-oriented grown 2122 phase film of BCSCO. The texture of the film is observed to be smooth. The particles in the figure are those of KCl flux. Fig.9 shows the relationship between critical current density (J_c) and temperature for the films grown on (001) and (110) orientations of the NdGaO₃ substrates. The value of J_c at 20 K for the film grown on (110) substrate orientation is about 1.5 times of the film grown on (001) substrate. The higher value of J_c for the film having (11n) preferred orientation may be because of the depairing mechanism (of J_c) where shorter coherence length of the c-axis contributes to higher critical current



Fig.8. Backscattered SEM picture of a smooth 2122 phase film grown on (110) NdGaO₃ substrate.

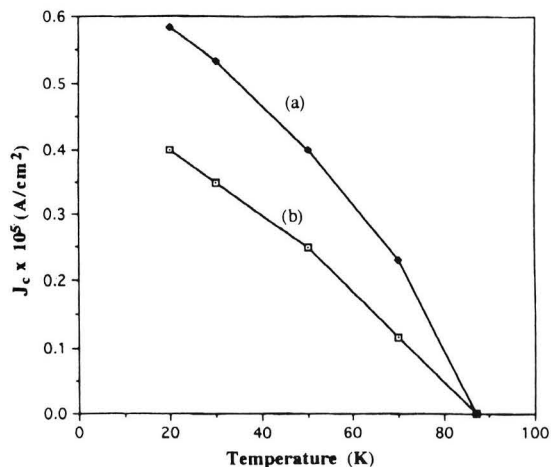


Fig.9. J_c versus temperature relationship of 2122 films grown on a) (110) and b) (001) NdGaO₃ substrate in the temperature range of 855-835 °C.

density. The critical current density reported here should be around 10^5 A/cm² at 4.2 K, although we were unable to measure it due to temperature limitation in our cryogenic system. This value is less than the values that have been reported for laser ablated, MOCVD and MBE grown epitaxial films of BCSCO. This may be because of the limitations of the LPE grown films where at higher temperatures, a slight misorientation of the seed and lattice and thermal expansion coefficient mismatch (between substrate and the grown material) can result in the introduction of dislocations. These dislocations (low angle grain boundaries) can become the source of weak-links which are known to reduce the current density of the superconducting materials. The other limitation associated in our films is the presence of microcracks which might be formed due to fast cooling of the NdGaO₃ substrate. The fast cooling of the substrate is, however, necessary to prevent the diffusion of Ga from NdGaO₃ substrate into the film.

CONCLUSIONS

In conclusion, a preferential orientation of (11n) of the Bi₂CaSr₂Cu₂O₈-phase deposited on (110) NdGaO₃, has been obtained by the LPE method. Besides (11n) orientation, smaller peaks in XRD pattern (Fig.7) attributed to (00n) planes are also observed. Presence of these (00n) orientations is due to the high anisotropic properties of BCSCO superconducting system. Under certain growth conditions a phase belonging to the family of (Ca_{1-y}Sr_y)_{1-x}CuO_{2-z} infinite layered superconductor is observed. Critical current is observed to be higher for the films grown on (110) than on (001) orientation of NdGaO₃ substrate. The highest critical current density and the zero resistance temperature (T_{c0}) obtained are 10^5 A/cm² and 87 K, respectively. The films can be grown on both vertical as well as horizontally mounted substrates.

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