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X-ray investigations of epitaxial $Bi_2Sr_2CaCu_2O_{8+x}$ thin films grown on $SrTiO_3$ substrates with MgO and CeO_2 buffer layers for the fabrication of biepitaxial Josephson junctions

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Abstract. X-ray diffraction methods have been used for investigation of epitaxial $Bi_2Sr_2CaCu_2O_{8+x}$ (BSCCO-2212) thin films grown by laser ablation on $SrTiO_3$ substrates buffered with MgO and CeO_2. The analysis showed that the films are nearly single crystalline. The deposition of a CeO_2 buffer layer improves the microstructure of the BSCCO-2212 film and leads to a light orthorhombic lattice distortion. For the film grown on a CeO_2/MgO ($\leq$ 10 nm) buffer layer system we observed 0° and 45° oriented domains. Using an original method, the lattice parameters *a* and *b* were measured. It was found that the critical current j_c is closely correlated with the structural quality of the films. First experiments were carried out to prepare biepitaxial Josephson junctions based on BSCCO-2212 material.

1. Introduction

The technology of fabrication of BSCCO-2212 thin films is well developed in many laboratories [1–3]. Interest in this area is stimulated by the possibilities of the film's utilization both in passive and active HTS devices. It is well known, however, that the parameters of the devices depend on the quality of the films. The existence of grain boundaries in polycrystalline thin films not only limits the value of their critical current but makes a noticeable contribution to the surface impedance. This provides extra noise and results in the formation of parasitic flux quantization loops in thin film SQUID magnetometers.

In this paper we demonstrate that the buffering of $SrTiO_3$ by thin CeO_2 and MgO layers (cubic lattices with lattice parameters of 5.41 Å and 4.21 Å respectively) opens a way for the fabrication of expitaxial *c*-axis oriented single-crystalline BSCCO-2212 thin films. The utilization of the MgO buffer results in the formation of domains with parallel orientation of the CeO_2 and $SrTiO_3$ substrate lattices as well as domains where these crystal lattices are misaligned with the [001] axis by 45°. We mainly focus below on detailed x-ray analyses of the fabricated heteroepitaxial structures. An elegant method for the determination of the lattice parameters of flat single crystals and thin films has been developed and used for the determination of the lattice constants and orthorhombic distortion of the lattice in the *a*–*b* plane. We also show that it is possible to create biepitaxial BSCCO-2212 Josephson junctions using the buffer layer system mentioned above.

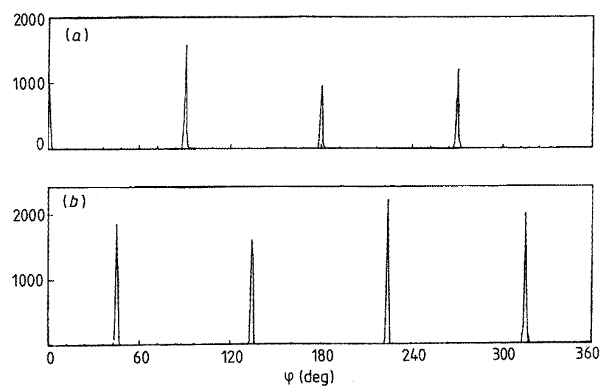

Figure 1. XRD φ-scans of (*a*) the $SrTiO_3$ (113) plane and (*b*) the BSCCO (119) plane in a BSCCO/$SrTiO_3$ system.

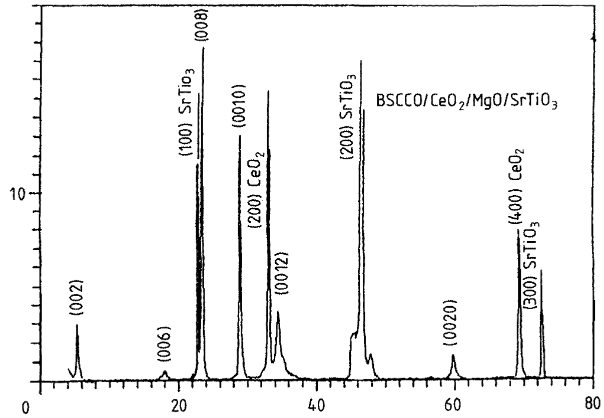

Figure 2. XRD θ–2θ scan of a BSCCO/CeO_2/MgO/$SrTiO_3$ multilayer system.

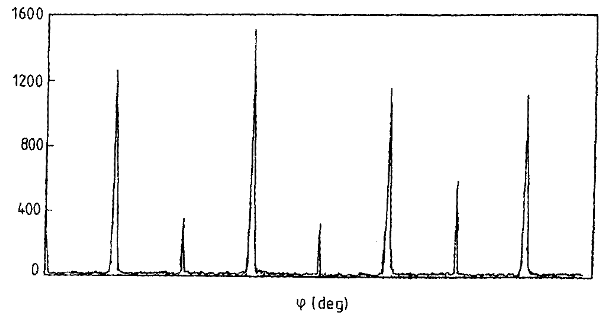

Figure 3. XRD φ-scan of the BSCCO (119) plane in a BSCCO/CeO_2/MgO/$SrTiO_3$ multilayer system.

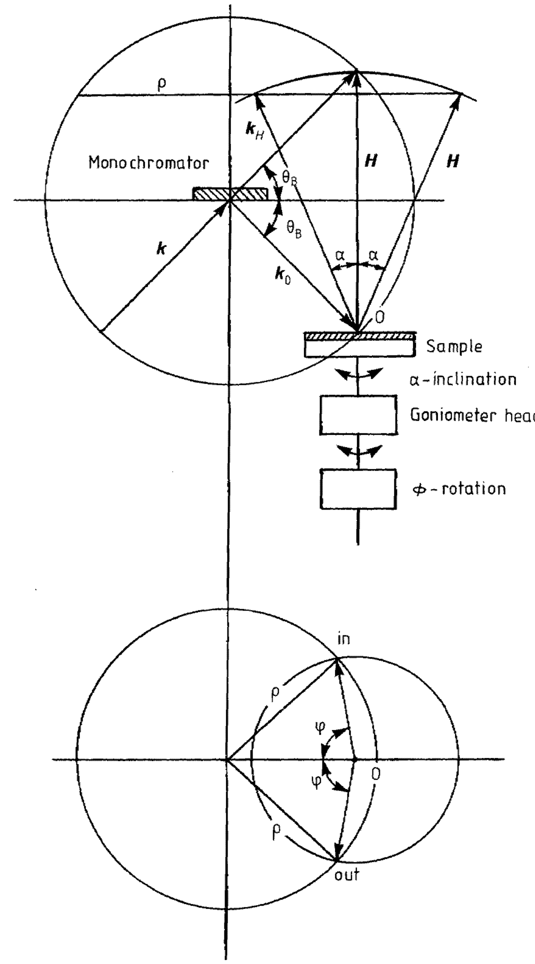

Figure 4. Optical scheme for the determination of the lattice constants for BSCCO films.

2. Sample preparation

Three series of partly multilayered epitaxial structures BSCCO/$SrTiO_3$, BSCCO/CeO_2/$SrTiO_3$ and BSCCO/CeO_2/MgO/$SrTiO_3$ have been fabricated *in situ* by a laser ablation technique. The typical thicknesses of the BSCCO-2212, CeO_2 and MgO layers were 100 nm, 170 nm and 10 nm respectively. For electrical measurements some of the samples were patterned by laser writing of bridges with a width of 50 μm [4]. The details of the deposition process as well as the methods of T_c and j_c measurement have been described elsewhere [5, 6].

3. Results of x-ray analysis, and discussion

Phase composition, crystal orientation and film structure parameters were determined by θ–2θ scans and high-resolution double- and triple-crystal diffractometry. In BSCCO-2212 films the following symmetrical and asymmetrical reflection peaks have been observed: (0, 0, 2), (0, 0, 6), (0, 0, 8), (0, 0, 10), (0, 0, 12), (0, 0, 20), (1, 1, 9), (0, 2, 10). The existence of asymmetric reflection peaks (1, 1, 9) and (0, 2, 10) shows that the films are practically single crystalline.

The structure of the CeO_2 buffer layers is also close to the single-crystalline one since the asymmetric (1, 1, 1) reflections are clearly observed.

There are no reflection peaks from MgO buffer layers on the diffraction patterns. The reason is not only the small thickness of the MgO buffer but also the peculiarities of its grown on $SrTiO_2$ substrates [7].

The mutual orientations of the crystal lattices of the individual films in multilayered structures are determined from the analysis of the φ-scans of asymmetric Bragg reflection peaks. For this purpose we used the (1, 1, 3) $SrTiO_3$ and the (1, 1, 1) CeO_2 peaks in coplanar diffraction geometry and the (1, 1, 9) BSCCO-2212 peak in configuration with the χ-inclination of the samples. The quality of the films and the degree of structural perfection were characterized from the full width at half maximum (FWHM) of the diffraction patterns.

3.1. BSCCO/$SrTiO_3$ system

The strong (1, 1, 9) reflection was used for the determination of the space orientation of the film's lattice. The projection of the reciprocal vector corresponding to this reflection on the *a*–*b* plane is oriented along [110] axis. Figure 1 shows x-ray diffraction (XRD) φ-scan measurements of the BSCCO (1, 1, 9) and $SrTiO_3$ (1, 1, 3) crystal plane. It is clear that the lattice of the films is rotated about 45°

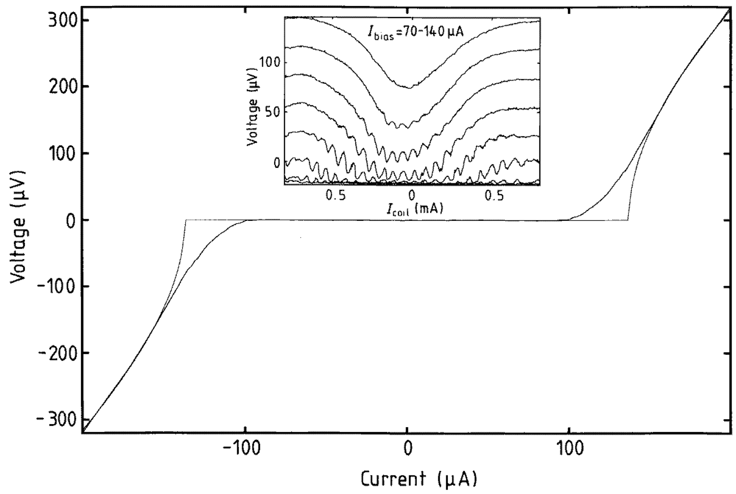

Figure 5. Current–voltage characteristic and magnetic flux-voltage modulation of a BSCCO-2212 SQUID formed by biepitaxial Josephson junctions at a temperature of 25 K. The thin curve represents a RSJ fit; parameters are given in the text.

relative to the substrate. This corresponds to the epitaxial relation

$$BSCCO(001) \parallel SrTiO_3(001)$$

$$BSCCO[110] \parallel SrTiO_3[100].$$

The last configuration is more favourable from the energetic point of view than the direct epitaxy $[100]BSCCO \parallel [100]SrTiO_3$. The discrepancy of the lattice parameters in the $[100] \parallel [100]$ configuration should result in significant compressive stress of the BSCCO film lattice while in $[110] \parallel [100]$ geometry only a small (2.4%) tensile stress occurs. The absolute values of the full width at half maximum of the φ-scan for $(0, 0, 20)$ and $(0, 2, 10)$ reflections are equal to 0.45° and 0.53°, respectively.

3.2. BSCCO/CeO_2/$SrTiO_3$ system

The XRD φ-scans of the CeO_2 $(1, 1, 1)$ and BSCCO $(1, 1, 9)$ reflections were used for the determination of the self-oriented film and substrate lattices. The analysis showed that there are no changes in the self-orientation relationship due to the buffer. The following epitaxy rules take place:

$$BSCCO(001) \parallel CeO_2(001) \parallel SrTiO_3(001)$$

$$BSCCO[110] \parallel CeO_2[110] \parallel SrTiO_3[100].$$

It is necessary to note that slight differences in the lattice constants of BSCCO-2212 ($a = 5.39$ Å) and CeO_2 ($a = 5.41$ Å) films should result in smaller relative deformations of the film lattice (2%) at the substrate–buffer layer interface. This immediately leads to a considerable decrease of the half-width of the curves on diffraction patterns: $FWHM_{(0,0,20)} = 0.23°$ and $FWHM_{(0,2,10)} = 0.34°$.

3.3. BSCCO/CeO_2/MgO/$SrTiO_3$ system

Figure 2 shows a typical θ–2θ x-ray diffraction pattern of the BSCCO/CeO_2/MgO/$SrTiO_3$ multilayer. From the data it follows that the BSCCO films are highly c-axis oriented and do not contain additional phases. The diffraction pattern of the φ-scan $(1, 1, 9)$ reflection is drastically changed when the buffer layer system with a thin ($<$ 10 nm) MgO film has been used. From the XRD φ-scan of the $(1, 1, 9)$ reflection of the BSCCO film it follows that in addition to the reflections corresponding to the previous epitaxy relation

$$BSCCO(001) \parallel CeO_2(001) \parallel SrTiO_3(001)$$

$$BSCCO[110] \parallel CeO_2[110] \parallel SrTiO_3[100]$$

there are lines confirming the existence of another epitaxy rule:

$$BSCCO(001) \parallel CeO_2(001) \parallel SrTiO_3(001)$$

$$BSCCO[100] \parallel CeO_2[110] \parallel SrTiO_3[100].$$

Figure 3 shows the result of the φ-scan measurement of the multilayer. The existence of domains with 45° and 0° orientations in the BSCCO films results from the peculiarities of the epitaxial growth of thin MgO films on $SrTiO_3$ substrates. It has been found that in CeO_2/MgO/$SrTiO_3$ multilayers with a MgO thickness $<$ 10 nm there are domains in the CeO_2 layer oriented both $[110] \parallel [100]$ and $[100] \parallel [100]$ compared with the substrate lattice [7]. The BSCCO film deposited on the CeO_2 buffer simply reproduces this configuration. Increasing the thickness of MgO buffer ($>$ 10 nm) tends to suppress the formation of the $[110] \parallel [100]$ domains. The half-widths of the $(0, 2, 10)$ reflexes for 45° and 0° domains are equal to 0.170° and 0.470° respectively. Our results concerning the appearance of two domains are in agreement with the observation of 45° tilted domains during the growth of BSCCO-2212 on MgO substrates published by other

Table 1. Comparison of structural and electrical data of the analysed heterostructures.

	BSCCO	BSCCO/CeO_2	BSCCO/CeO_2/MgO
T_{c0} (K)	79	76	75
j_c (77 K) (A cm^{-2})	8×10^4	—	—
j_c (60 K) (A cm^{-2})	1.7×10^6	2.6×10^5	6×10^5
j_c (40 K) (A cm^{-2})	$> 2 \times 10^6$	1.1×10^6	1.8×10^6
a (Å)	5.520	5.490	5.451
b (Å)	5.536	5.510	5.476
c (Å)	30.80	30.89	30.89
FWHM $_{(0,2,10)}$ (45°) (deg)	0.53	0.34	0.17
FWHM $_{(0,2,10)}$ (0°) (deg)	—	—	0.47

authors [8], but the tendency to suppress the formation of the [110]‖[100] domains for higher MgO film thicknesses is still unclear.

The high quality of fabricated BSCCO films provides the possibility for the determination of the unit cell parameters a and b. For this reason an elegant method has been developed and used. It is based on the φ-scan technique performed on a six-circle x-ray diffractometer and essentially uses the χ-inclination geometry and two-wave approximation on the x-ray diffraction. The optical scheme of the method is shown in figure 4. The coherent x-ray radiation with wavelength λ ($k = 1/\lambda$) diffracts on the reciprocal vector $\boldsymbol{H}$ of the single crystal in the $\boldsymbol{k}_H$ direction. The diffraction angle θ_B is definitively related to the vector $\boldsymbol{H}$ by Bragg's equation $\boldsymbol{k}_0 \cdot \boldsymbol{H} = \frac{1}{2}|\boldsymbol{H}|^2$. The following procedure is suggested for its determination. The vector $\boldsymbol{H}$ is rotated step by step through an angle α and each time one measures the angle ϕ between the point of its intersection with the Ewald's sphere under rotation of the sample around the ϕ-axis. The substitution of these angles into the simple geometrical relationship $\cos\phi = \tan\theta_B(1 - \cos\alpha/\sin\alpha)$ allows the determination of θ_B and consequently the interplane distances $d_{h,k,l} = 1/|\boldsymbol{H}|$. Precision measurements of the Bragg angles of the $(2, 0, 10)$ and $(0, 2, 10)$ reflections were performed. The accuracy of the determination of the distances between the crystallographic planes $d_{h,k,l}$ in this method was limited mainly by the width of the rocking curves and was close to $\Delta d/d = 0.002$.

It was found that the BSCCO-2212 film on the $SrTiO_3$ substrate has a tetragonal crystal lattice while in BSCCO/CeO_2/MgO/$SrTiO_3$ (45° domains) and BSCCO/CeO_2/$SrTiO_3$ heterostructures a weak orthorhombic lattice distortion takes place with the ratio $b/a = 1.0046$ and 1.0036 respectively. For single crystals this ratio is close to 1.009 [9]. The average value of the lattice constant in the c-direction was calculated from the angle position of $(0, 0, 21)$ reflection on θ–2θ scans. Table 1 summarizes the determined values of the lattice parameters a, b and c, the values of the half-width of the rocking curves, and T_c and j_c of the films. It is clearly visible that the utilization of the buffer layers improve the microstructure of the BSCCO films. The half-width of the $(0, 2, 10)$ reflect of BSCCO films in BSCCO/CeO_2/MgO/$SrTiO_3$ and BSCCO/CeO_2/$SrTiO_3$ multilayers is correspondingly three and two times smaller than the one for the directly deposited BSCCO/$SrTiO_3$ films. This correlates with the transport properties of the films. The narrower the half-width of the reflections and the closer the ratio b/a to that of single crystals, too, the larger the critical current density for the same T/T_c ratio. It is interesting to note that the larger T_c corresponds to a smaller value of the lattice constant c.

4. Biepitaxial Josephson junctions

We prepared biepitaxial BSCCO-2212 Josephson junctions on $SrTiO_3$ substrates by laser ablation of 20 nm thick MgO seed layers and of 100 nm thick BSCCO-2212 superconducting layers. After MgO deposition and covering with a photoresist mask, parts of the MgO layer were removed by wet chemical etching. 45° in-plane grain boundaries in the BSCCO films were created at the border of the MgO covered parts because of the 45° lattice rotation of BSCCO-2212 on the MgO-cleaned $SrTiO_3$ surface and the undislocated growth of BSCCO-2212 on the MgO seed layer. Microbridges and SQUIDs with linewidths of 3 to 7 μm were patterned by common photolithography and Ar^+ ion milling. By the four-probe techniques we could measure current–voltage characteristics (IVC) which can be described by the resistively shunted junction (RSJ) model. In figure 5 we show an IVC of a SQUID with 2×6 μm wide junctions at a temperature of 25 K and a RSJ fit with the parameters $I_c = 137$ μA and $R_N = 2.2$ Ω. For this fit we did not consider the influence of the noise on the IVC. In particular cases we found hysteretic IVCs at low temperatures. The junctions were superconducting up to temperatures of about 60 K. We measured the voltage modulation due to an external magnetic field, as shown for a d.c. SQUID in the inset of figure 5. Flux modulation voltages of the junctions and of d.c. SQUID structures were obtained up to temperatures of approximately 50 K. We observed Shapiro steps due to microwave radiation in the IVCs of the junctions. First noise measurements of our d.c. SQUID structures showed a field sensitivity of 2×10^{-4} ϕ_0 $Hz^{-1/2}$ for frequencies higher than 100 Hz. Further measurements are in progress and will be published elsewhere [10].

5. Summary

The x-ray analysis of multilayer heterostructures confirmed that the utilization of a MgO/CeO_2 buffer layer system provides the possibility of fabricating high-quality epitaxial BSCCO films. By variation of the thickness of the MgO layer on the $SrTiO_3$ substrate it is possible to prepare biepitaxial BSCCO-2212-based Josephson junctions. Previously such a possibility has been demonstrated only for BSCCO-based junctions with BSCCO-2223 superconducting electrodes [3].

Acknowledgments

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