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Preparation and x-ray pole-figure characterization of DC-sputtered Bi-2201, Bi-2212 and Bi-2223 thin films

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Abstract. Thin films of the three members of the superconducting series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, $n = 1, 2, 3$, were prepared by diode sputtering. X-ray characterization shows that all the films are single phase and c-axis oriented and in addition they are epitaxially grown. The latter is found by x-ray pole-figure measurements taken with a four-circle diffractometer. These are emphasized in this work. AC susceptibility measurements show that, while the 2201 films are not superconducting until 4 K, the transition temperatures of the 2212 films are 82 K–90 K and of the 2223 films 84 K–89 K.

1. Introduction

Since the discovery of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ superconductors [1] a lot of work has been devoted to their preparation and investigation. However, the preparation of these materials has proven to be a difficult task, because the multiple phases involved are hardly easy to isolate. Especially in the case of thin films, several other parameters are of importance, such as the oxygen stoichiometry, to which the critical temperature T_c is most sensitive, the microstructure of the films and the smoothness of the surface, which are crucial for potential applications.

In this work we report the preparation of thin films of the three members of the series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, $n = 1, 2, 3$, which will be hereafter referred to as 2201 ($n = 1$), 2212 ($n = 2$) and 2223 ($n = 3$). The films are prepared by DC sputtering and they are single phase, highly c-axis oriented and epitaxial, as determined by extensive x-ray measurements. The 2212 thin films exhibit high transition temperatures, the highest being 90 K, the 2223 thin films have transition temperatures as high as 89 K and the 2201 thin films are not superconducting until 4 K, as is determined by AC susceptibility measurements.

2. Preparation

Thin films of $Bi_2Sr_2CuO_{6+x}$ (2201), $Bi_2Sr_2CaCu_2O_{8+x}$ (2212) and $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ (2223), were prepared *in situ* by DC sputtering. DC sputtering, unlike magnetron sputtering, uses no magnets to support the discharge and thus it requires greater ambient pressures. This has proved to be beneficial to the phase formation, since it reduces the resputtering of species from the deposited film. The sputtering conditions and the *in situ* annealing procedures are described below.

2201 thin films. A 2 in diameter disk of nominal stoichiometry $Bi_2Sr_2CuO_6$ was used as target and a single crystal of $SrTiO_3(100)$ as substrate. The cathode voltage was 380 V, resulting in a discharge current of 150 mA. The substrate temperature was 790 °C during the deposition and the pressure inside the chamber was maintained at 2 mbar of pure oxygen. The deposition lasted for 2 h resulting in a film approximately 2000 Å thick. The deposited film was then annealed *in situ* at 790 °C under 6 mbars of pure oxygen for 30 min.

2212 thin films. A 2 in diameter disk of nominal stoichiometry $Bi_{2.05}Sr_2CaCu_2O_8$ was used as target and a single crystal of $SrTiO_3(100)$ as substrate. The cathode voltage was 340 V, resulting in a discharge current of 400 mA. The substrate temperature was 830 °C during the deposition and the pressure was maintained at 3 mbar of pure oxygen. The deposition lasted for 2 h, resulting in a film thickness of approximately 1500 Å. After the deposition an annealing procedure followed in two stages: 30 min at 830 °C in 3.2 mbar pure oxygen and 15 min at 500 °C in only 2×10^{-2} mbar pure oxygen. The first step is aimed at overdoping the sample with oxygen, while the second is believed to result in an optimum oxygen concentration.

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2223 thin films. A 2 in diameter disk of nominal stoichiometry $Bi_{2.05}Sr_2Ca_2Cu_{3.3}O_{10}$ was used as target and a single crystal of $SrTiO_3(100)$ as substrate. The Cu excess is introduced in the target to encourage the formation of the 2223 rather the 2212 phase and the Bi excess is intended to compensate for the Bi loss during deposition, Bi being known to be selectively resputtered [2]. The cathode voltage was 300 V and the discharge current was 300 mA. During the deposition the substrate temperature was 828 °C and the chamber pressure was 3 mbar pure oxygen. The deposition lasted for 2 h, resulting in a film thickness of approximately 1500 Å. An annealing procedure of 30 min at 828 °C in 6 mbar pure oxygen, followed by 90 min at 820 °C at 6 mbar pure oxygen, was used.

The annealing conditions that we described above were those, among several others tested, that resulted in films with highest T_c. The 2201 and 2223 films were prepared using the same sputtering chamber, while the 2212 films were made in a different chamber, so one cannot directly compare the experimental conditions for the 2212 films with the other ones. The substrate temperature was the temperature measured on the back side of a metallic heater that carried the film on its front side, and was kept strictly constant during the deposition, something which we found to be crucial for the phase formation. That was most important especially in the case of the 2223 films, where the temperature was close to the melting point so, if it were accidentally to rise even slightly, the deposited film would evaporate. This especially high deposition temperature was found necessary for the formation of the 2223 films. Lower values led to the co-appearance of the 2223 and 2212 phases.

3. Characterization

Conventional θ–2θ scans of the three phases are shown in figure 1. The presence of $(00l)$ reflections only proves that the films are single phase and c-axis oriented, i.e. their c-axis is normal to the film surface. This was expected because of the lattice match between the substrate and the film; $a(SrTiO_3) = 3.905$ Å [3], a(Bi-phases) $= 3.814$ Å [4]. From the peak positions we can estimate the c-axis length: $c(2201) = 24.6$ Å, $c(2212) = 30.9$ Å and $c(2223) = 37.5$ Å.

Rocking curves were obtained for certain peaks for all the films and exhibit the following full width at half-maximum (FWHM) values: FWHM(008) = 0.3°–0.4° for the 2201 thin films, FWHM(00 10) = 0.3°–0.5° for the 2212 thin films and FWHM(00 12) = 0.2°–0.6° for the 2223 thin films. The greater FWHM values of the 2223 films compared with the 2212 films are most probably due to oxygen inhomogeneity, something which explains also some other observations, which we will see below.

The superconducting properties of the films were tested by AC susceptibility, typical measurements of which are shown in figure 2. For films of the same phase the critical temperatures are found to differ slightly from one another, although the applied experimental conditions were the same. Since no other phases are detected

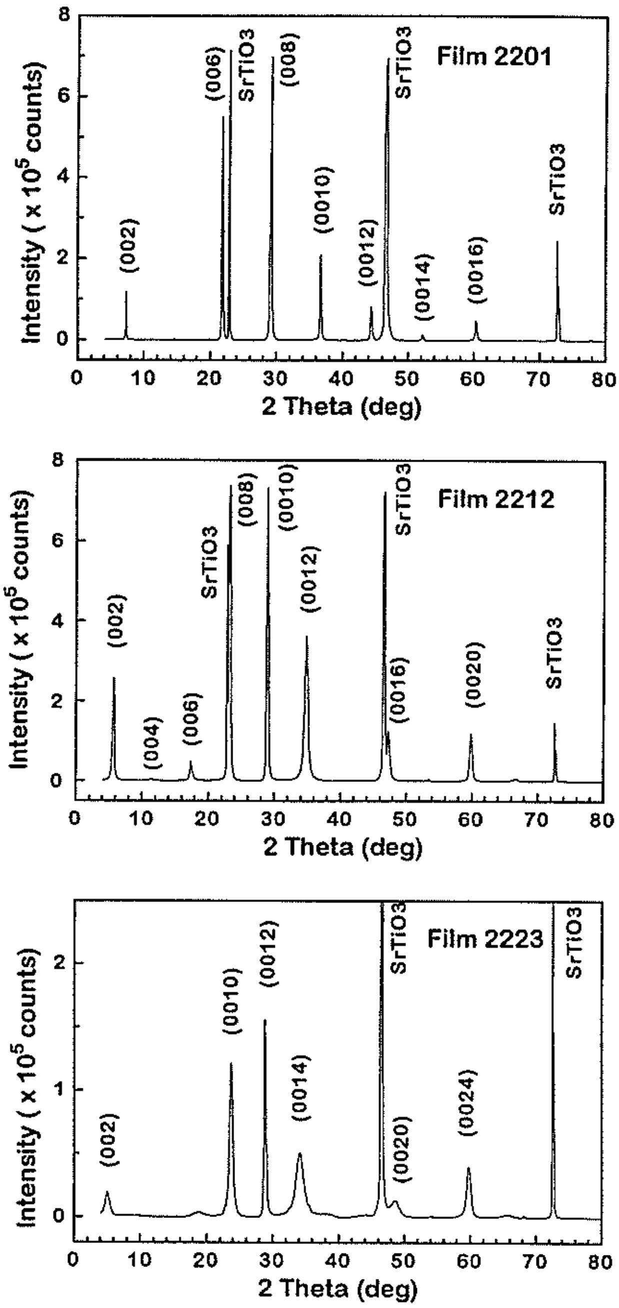

Figure 1. X-ray diagrams of Bi-2201, Bi-2212 and Bi-2223 thin films.

from x-rays and all the films are epitaxial, we ascribe this to different oxygenation states, i.e. different oxygen concentration as a whole and oxygen inhomogeneity. Indeed, films with higher T_c show smaller transition widths and smaller FWHM values. The 2212 films have critical temperatures $T_c^{onset}(90\%) = 82$ K–91 K and transition widths $\Delta T_c = 2$ K–7 K. Correspondingly, the 2223 films have $T_c^{onset}(90\%) = 84$ K–89 K and $\Delta T_c(90\%–10\%) = 2$ K–5 K, while the 2201 films are not superconducting, at least not until 4 K. The low T_c of the 2223 thin films compared with the 2212 thin films and also with the known bulk value of $T_c = 110$ K is ascribed again to the non-ideal oxygenation (for example, an imperfect filling of the Cu–O layers).

Table 1. Full width at half-maximum values in χ- and φ-axes of several x-ray poles, obtained with a four-circle diffractometer, from four different thin films.

Film phase	Peak	FWHM (deg) (in χ-axis)	FWHM (deg) (in φ-axis)
$Bi_2Sr_2CuO_6$	$SrTiO_3$ (011)	1.9	0.6
	$Bi_2Sr_2CuO_6$ (115)	2.3	1.0
	$Bi_2Sr_2CuO_6$ (113)	2.5	0.8
	$Bi_2Sr_2CuO_6$ (028)	1.4	0.7
$Bi_2Sr_2CaCu_2O_8$ (film A)	$SrTiO_3$ (011)	2.5	0.4
	$Bi_2Sr_2CaCu_2O_8$ (015)	2.6	0.6
	$Bi_2Sr_2CaCu_2O_8$ (013)	2.8	0.6
	$Bi_2Sr_2CaCu_2O_8$ (11 10)	1.8	0.6
$Bi_2Sr_2CaCu_2O_8$ (film B)	$SrTiO_3$ (011)	1.5	0.4
	$Bi_2Sr_2CaCu_2O_8$ (015)	2.6	0.6
	$Bi_2Sr_2CaCu_2O_8$ (013)	2.7	0.5
	$Bi_2Sr_2CaCu_2O_8$ (11 10)	1.7	0.6
$Bi_2Sr_2Ca_2Cu_3O_{10}$	$SrTiO_3$ (011)	2.5	0.6
	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (015)	4.5	1.0
	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (019)	4.2	0.9
	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (11 12)	1.7	0.8

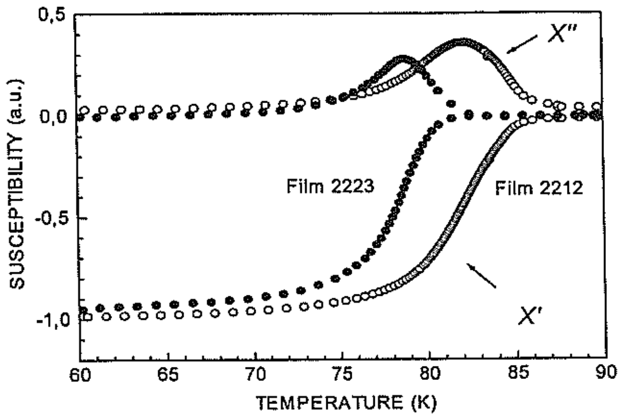

Figure 2. AC susceptibility (real part χ' and imaginary part χ'') of the Bi-2212 and Bi-2223 thin films.

The 2223 films were prepared in especially extreme conditions, in order to prevent the appearance of the other Bi phases in them. The high substrate temperatures during the deposition and the annealing may have prevented full oxygenation of the 2223 films. Also, their broader lines compared with the 2212 and 2201 films, as can be seen in the θ–2θ scan of figure 1, may be the result of the presence of stacking faults. Stacking faults have often been observed in the Bi-2223 system [5] and they hamper the diffusion of oxygen into the films, so they may be the cause of oxygen inhomogeneity.

4. Pole-figure results and discussion

X-ray measurements performed with a four-circle diffractometer prove that all the films are epitaxial, i.e. on all parts of the film, the axes *a* and *b* have the same direction in space. The method of obtaining the so-called pole figures is briefly described below. The experimental set-up is shown in figure 3.

The sample is placed on the Euler circle, where the four angles 2θ, ω, χ, φ can be varied independently (see

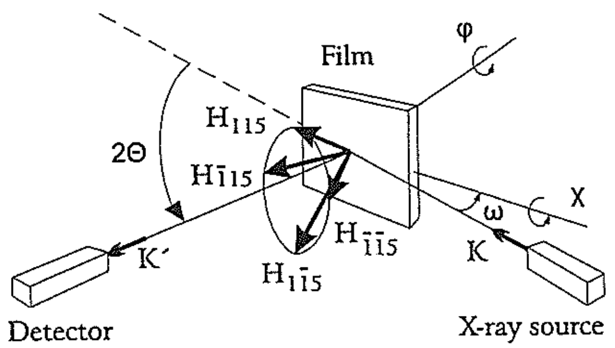

Figure 3. Schematic diagram of the experimental set-up in the pole-figure measurements.

figure 3). Thus, any reflection (hkl) can be obtained. In order to obtain a diffraction from a specific reflection (hkl), we must make the corresponding reciprocal lattice vector H_{hkl} satisfy the well-known Bragg law $k' - k = H_{hkl}$ (stated otherwise, $2d \sin\theta = \lambda$), where k, k' are the wavevectors of the incident and diffracted x-ray beam respectively, with amplitudes $|k| = |k'| = 1/\lambda$ (λ the wavelength of the x-ray beam) and H_{hkl} is normal to the set of planes (hkl) and has magnitude $|H_{hkl}| = 1/d$, i.e. equal to the inverse distance between the planes. The above imply that two conditions must be fulfilled. First, H_{hkl} must coincide with the bisector of the angle which is formed by the source, the sample and the detector, i.e. the angle formed between k and k'. This can be fulfilled for certain values of the angles χ and φ, only. Second, the angle formed by the source, the sample and the detector must have such a value that the amplitude $|k - k'|$ exactly equals the amplitude $|H_{hkl}|$. This can be done by adjustment of the angles 2θ, ω.

The experimental procedure is as follows. First we enforce a θ–2θ geometry. This is done by placing the detector at an angle 2θ satisfying the Bragg law $2d \sin\theta = \lambda$ for the wavelength λ of our x-ray source and the plane distance d of the chosen (hkl) reflection, while setting $\omega = 2\theta$. Next, we rotate the film by an angle χ equal

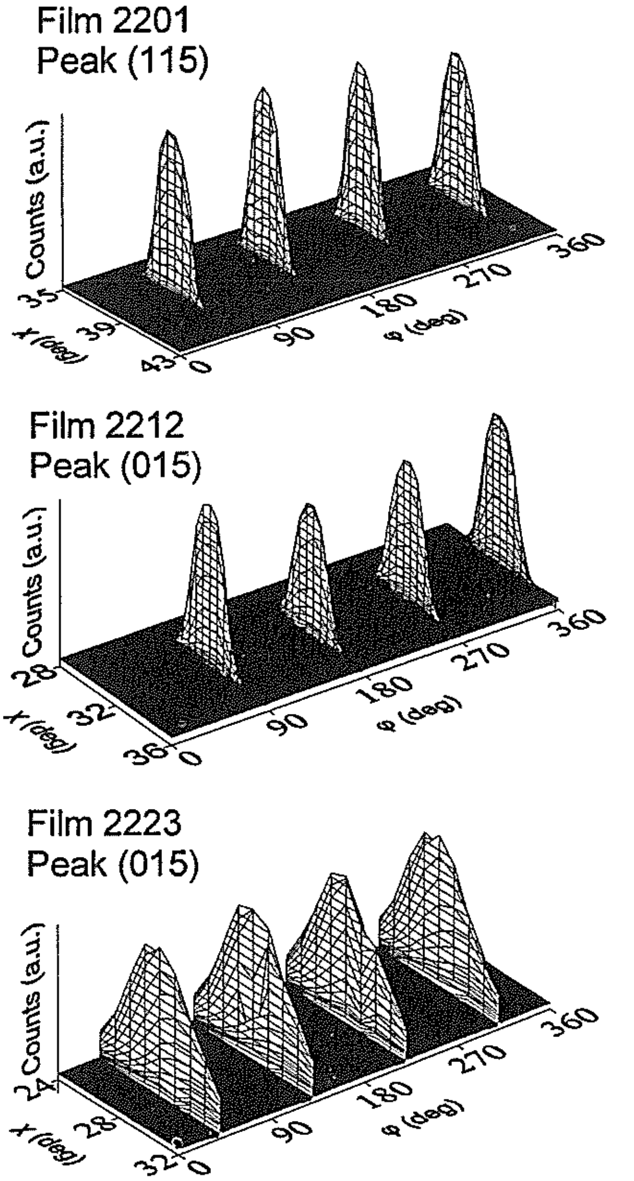

Figure 4. Pole figures of the Bi-2201, Bi-2212 and Bi-2223 thin films.

to the angle that $\boldsymbol{H}_{hkl}$ forms with the c^*-axis. The latter is calculated easily from vector analysis considering that $\boldsymbol{H}_{hkl} = ha^* + kb^* + lc^*$ where a^*, b^*, c^* are the reciprocal lattice vectors ($c^* \parallel c$ in our case of the tetragonal unit cell). Notice that $\boldsymbol{H}_{hkl}$ together with three other vectors form a right cone, since they all have the same amplitude $(1/d)$ and they all form the same angle χ with the c-axis. On setting the angle χ as we said above, the cone in figure 3 becomes tangential to the bisector of the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$. The XRD data are then collected while we rotate the sample from 0° to 360° (angle φ). The same is done for several values of χ near the value which was set initially, where a maximum ought to be expected.

Following the procedure described above, we obtain pole figures from films of the three phases, for several choices of $\boldsymbol{H}_{hkl}$. Cu Kα_1 radiation is used with λ = 1.5405 Å. In figure 4 we show the pole figures of the reflections $\boldsymbol{H}_{115}$, $\boldsymbol{H}_{015}$ and $\boldsymbol{H}_{015}$ for the films 2201, 2212 and 2223 respectively. Notice that, on rotating the sample

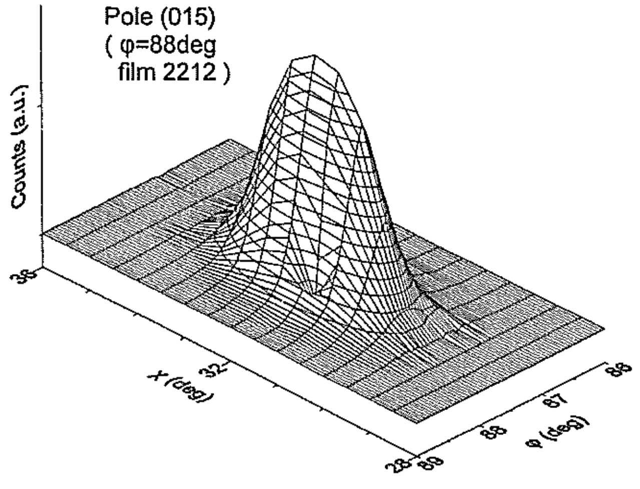

Figure 5. Pole at $\varphi = 88°$ of the (015) reflection of film 2212 of figure 4 enlarged.

by φ, four reciprocal lattice vectors diffract successively; these are for example $\boldsymbol{H}_{115}$, $\boldsymbol{H}_{\bar{1}15}$, $\boldsymbol{H}_{1\bar{1}5}$ and $\boldsymbol{H}_{\bar{1}\bar{1}5}$ for the film 2201. The films are epitaxial since only four distinct peaks appear. The orientation of the film's axes a and b coincides with that of the substrate's axes a and b, since peaks (hkl) of the substrate and the film having the same h, k values were observed at exactly the same values of angle φ. In figure 5 we show one of the poles of figure 4 enlarged; the (015) pole of the 2212 thin film of $\varphi = 88°$. In table 1 we present FWHM values in χ- and φ-axes for one 2201 thin film, two 2212 thin films and one 2223 thin film. We present also the FWHM values of the substrates. As can be seen, in all cases the width of the peaks in the φ-axis is small. Since φ represents rotations about the normal to the film surface and is thus related to the orientation of the a–b plane, small φ-axis widths suggest a high degree of epitaxy. On the other hand, χ represents rotations about a tangent to the film surface and it is related to the orientation of the c-axis as well as to the value of the plane distances d. The observed widths of the peaks in the χ-axis are larger than in the φ-axis, but they are actually limited by the quality of the substrates, the corresponding widths of which are also large. This proves the high order of orientation of the c-axis in all the films, particularly the 2201 films. The larger χ-axis widths of the 2223 films compared with the others may be due to a dispersion in the values of d, resulting from a possible presence of stacking faults.

From the above, it is deduced that all the films are epitaxial, the degree of epitaxy being highest for the 2201 films. Most crucial for achieving epitaxy has been the fact that the films were prepared *in situ*. Films prepared as such are also free of grain boundaries and so are most appropriate for investigations of the intrinsic properties of the Bi system. Several papers have already been published investigating the magnetic phase diagram, which contains several regimes of different behaviour [5, 6], the electronic structure [7], which is crucial for the understanding of superconductivity, or the effect of pinning on the critical current, which is of great importance from the point of view of applications [8]. Investigation of the magnetic properties of the Bi system directly through magnetization measurements is in progress.

5. Conclusion

We have reported the preparation of the three phases of the superconducting series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, $n = 1,2,3$, in the form of thin films made by DC sputtering. The films are single phase, highly oriented with c-axis normal to the substrate and epitaxial, as we confirm by extensive x-ray measurements with a four-circle diffractometer. The 2212 films have high transition temperatures of 82 K–91 K and the 2223 films have transition temperatures of 84 K–89 K. The high quality of the films makes them appropriate for investigations of the intrinsic properties of the Bi system, which are now in progress.

References

[1] Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Japan. J. Appl. Phys.* **27** 209

[2] Kampwirth R T, Anderson P H, McDonald D B, Miller D J, Gray K E, Sungaila Z F, Balachadran B and Wagner A 1989 *Appl. Phys. Lett.* **55** 2135

[3] Swanson and Fuyat 1953 *NBS Circular 539* vol III

[4] Torardi C C, Subramanian M A, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flemming R B, Choedhry U and Sleight A W 1988 *Science* **240** 631

[5] Wagner P, Frey U, Hillmer F and Adrian H 1995 *Phys. Rev.* B **51** 1206

[6] Miu L, Wagner P, Hadish A, Hilmer F and Adrian H 1994 *Physica* C **234** 249

[7] Hatterer C J *et al* 1996 *Physica* C **261** 153

[8] Frank H, Lethen J, Buschmann L, Decker B, Wiesener J, Wirth G, Wagner P, Adrian H, Lemmens P and Guntherodt G 1996 *Physica* C **259** 142