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BiSrCaCuO thin films with deficit of bismuth synthesized by Molecular Beam Epitaxy

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BiSrCaCuO thin films were grown on (100) SrTiO3 substrates by molecular beam epitaxy (MBE) with variation of the Bi deposition time. A new 2x212 family with x varied between 1 and 0 was grown. The X-ray study, the Rutherford back scattering (RBS), reflection high energy electron diffraction (RHEED) and Atomic force microscopy (AFM) were used to characterize the films. It was shown that the growth method used leads to intergrowth nanostructures. The transport measurements of BiSrCaCuO thin films were performed. The results analysed using the theory of percolation show a 2D character of conductivity in the films studied.

Keywords: Molecular Beam Epitaxy, Thin films, Superconductors, BiSrCaCuO.

1.INTRODUCTION

The superconductivity at high critical temperature in cuprates is closely related to their strongly anisotropic and lamellar structure. Among the different families, the critical temperature increases with the number n of CuO_2 planes up to n=3 and decreases slightly for n larger than 3[1,2]. The Charge Reservoir block layer includes, in general, two different cations A and B with a rock-salt oxide structure. The charge transfer decreases with the distance between the reservoir and the CuO_2 planes[3]. The optimum doping seems to be intrinsically limited to the two first CuO_2 planes, neighbouring the charge reservoir layer. We try to increase the charge reservoir efficiency by nanostructuration. We imagine that if the reservoir blocks have a finite nanoscale size, the local number of CuO_2 planes with optimum doping can be larger. This should play a positive role on the superconducting properties. In order to test this hypothesis, BiSrCaCuO "nanostructured" thin films were prepared by sequential molecular beam epitaxy (MBE). We present here the structure and the transport properties of these samples

2. EXPERIMENTAL

BiSrCaCuO films were grown on (100) $SrTiO_3$ substrates by using a Riber Eva 32 MBE system with Oxygen Plasma Source. The deposition equipment and conditions were already described elsewhere[4]. The deposition sequence used is the same as for the growth of Bi-2212 films but the bismuth deposition time is reduced in a wide range. The total thickness of the films is around 30 nm. X-ray diffraction measurements were done on a classic $\theta/2\theta$ diffractometer with CuK_α radiation and on a four-circle diffractometer using synchrotron facilities at LURE. The cationic composition of the films is determined by Rutherford Backscattering Spectroscopy measurements. The roughness was determined from classical AFM measurements. A standard four points procedure with silver paint contacts was used for the transport measurements on the films. The distance between the voltage contact area is around 0.6mm. During the cooling the samples are kept in helium gas atmosphere.

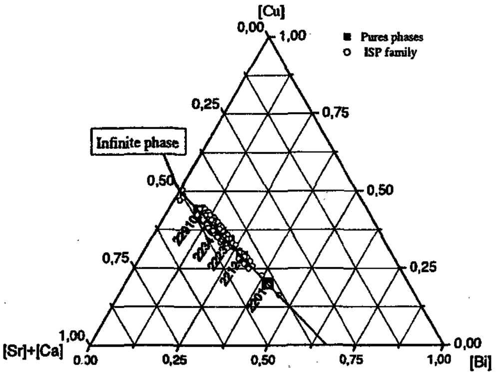

Figure 1Cationic composition of the samples (open circles).

3. RESULTS

The cationic composition of the films is indicated on the ternary diagram of the **Figure 1** as open circles. (The strontium is added with the calcium to take into account the possible substitutions between these two cations). The positions of the stoechiometric 22(n-1)n phases and of the infinite layer are indicated as references, along a line. The films are found in between the pure phases, on the line, with various Bi rate. The RHEED diagram keep 2D lines during the growth. And the films roughness is quite low, in the range of 1 nm. Despite the consequent reduction of the bismuth overall concentration, HRTEM micrographs[4] show that the bismuth atoms are still organised in $(BiO)_2$ bilayers, and that the bilayers are discontinuous.

3.1 STRUCTURE

The x-rays diffraction spectra, in Bragg-Brentano geometry, of all the samples have similar shapes. An example, corresponding to a $Bi_{0.17}(SrCa)_{0.46}Cu_{0.37}$ film, is presented on the **Figure 2**. The stars indicate the $SrTiO_3$ substrate diffraction lines position (the very fine lines correspond to CuK_β diffraction). The film (00l) lines are very broad. The films are obviously the result of the intergrowth of several phases. We used an interstratification model[5] to try to reproduce the spectra. For example, the simulation presented on the **Figure 2** correspond to a randomly intercalation of 2212 (40%) with $CaCuO_2$ layers (60%). This gives the possibility to generate 2223, 2234, 2245 ... 22(n-1)n phases (but with lower and lower probability). The average composition of this simulated intergrowth is $Bi_{0.16}(SrCa)_{0.48}Cu_{0.35}$, close to the experimental composition. This model cannot take into account the nanostructuration of the charge reservoir layers.

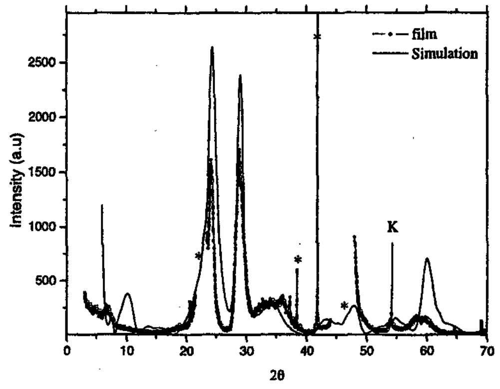

Figure 2Bragg-Brentano X-ray diffraction spectrum for $Bi_{0.17}(SrCa)_{0.46}Cu_{0.37}$ film and result of the simulation.

In order to get information about the (a,b) plane we used the synchrotron radiation (LURE) to map the reciprocal space and get "Q-scans". A typical example of a (h, k, at l fixed) Q-scan is presented on **Figure 3** This scan was obtained with a value of l corresponding to c = 0.3176 nm; the substrate is used as a reference to fix the h and k values. On **Figure 3**, the peaks of the film are in the positions (0,0,L) and (1,1,L). Traces of the substrate diffraction appear at (0,1,L) and (1,0,L) positions. Such Q-scans with a square symmetry were observed, for different values of l, on many samples.

On the Q-scans, the diffraction peaks are sharp and correspond to the values a = b = 0.387nm, in agreement with the values obtained in Bi-2212 compounds[6]. No trace of orthorhombicity was observed on this type of samples. This result confirms the quality of the epitaxy, in spite of the complexity of the stacking along the c axis.

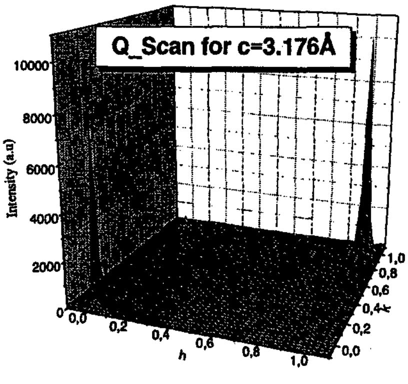

Figure 3 Q-scan at l fixed (here c=0.3176nm).

For a better understanding of the origin of the (00l) lines of diffraction, anomalous diffusion measurements in the vicinity of the bismuth threshold were carried out.

The results are presented on the **Figure 4** The same symbol is used to draw a specific (00l) diffraction of an incidental beam energy E=13.80 keV, below the of bismuth absorption threshold, and for E=13.43 keV just after the threshold.

The intensity of all the peaks decreases for E = 13.43keV except for those indicated by "K" (**Figure 2** and **Figure 4**). This result highlights that the element bismuth does not play a rule in the expression of the structure factor of this line of diffraction. We can conclude that the phase associated with the peak K is of the type "infinite layer", without bismuth charge reservoir.

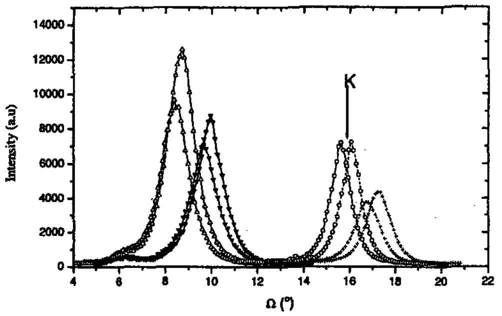

Figure 4Anomalous diffusion of the lines (00l) at the bismuth absorption threshold (E=13.43keV and E = 13.80keV).

The inter-reticular distance associated to the K line is d=0.17nm and could correspond to the distance between CuO_2 planes in the strontium infinite layer phase.

3.2 INFLUENCE OF THE Bi RATIO

This peak K tends to disappear when the bismuth concentration in the film increases (see **Figure 5**). Simultaneously the peak associated to d=0.31nm becomes more intense (see **Figure 6**).

The position of this peak correspond to the position of (0 0 10) diffraction of the Bi-2212 phase. We attribute this behaviour to the percolation of 2212 domains. In this family of samples small islands of 2212 phase remains. According to the bismuth concentration, their size and their quantity vary. These small islands will remain disconnected or will join and percolate.

We note $N_S(Bi)$ the limiting value of the "average" number of bismuth planes per cell which definite a "2D percolation threshold ".If $N_C(Bi) < N_S(Bi)$, one is below the 2D percolation threshold of the 2212 domains. If $N_C(Bi) > N_S(Bi)$, one is above the 2D percolation threshold and the 2212 blocks become larger and larger and percolate. Simultaneously the K peak and the "infinite layer" domains disappear.

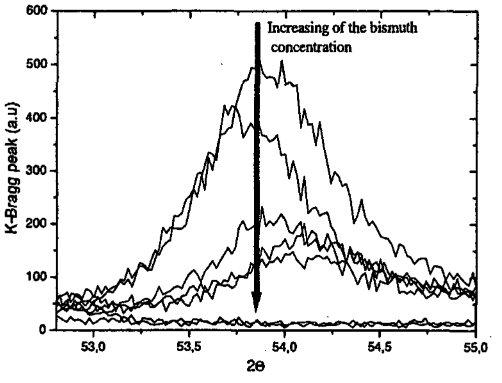

Figure 5 Evolution of the diffraction peak "K" (d□0.17nm) with the bismuth concentration.

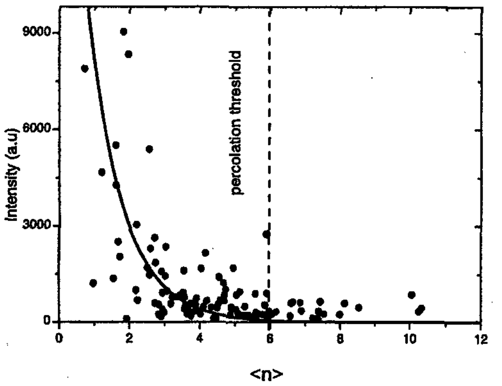

Figure 6 Intensity of (001) diffraction peak corresponding to d□0.31nm in function of the average number of CuO_2 planes by cell.

3.3 TRANSPORT PROPERTIES

The films show superconductive transitions until Nc(Bi) <0.5. The maximum T_{coff} value measured is 50K. The transitions are very broad and broaden out with the Bi ratio (see **Figure 7**). So the paraconductivity cannot be interpreted directly within the Gaussian fluctuations by the Azlamasov-Larkin model. These films are heterogeneous materials. We must have a spatial distribution of the critical temperatures in the films, due to the local variations of cationic composition and probably also to the oxygen distribution. It is thus more realistic to think that there are granular effects due to the presence of domains with different resistivity values.

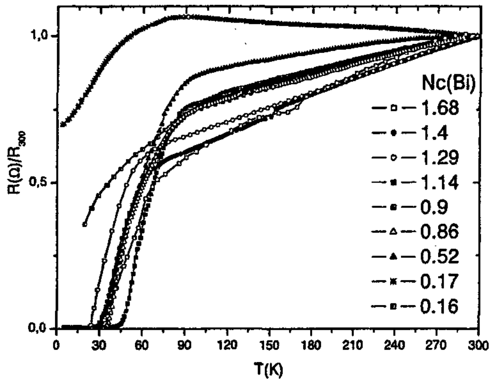

Figure 7Normalized R(T) curves for 9 samples with various values of Nc(Bi).

3.4 DISCUSSION

We propose a model of percolation to interpret the results. The nucleation of double-layered BiO_2 follows a random process. We can thus define a variable of percolation by the probability p of nucleation of double-layered BiO_2 and the defect generated by the discontinuity of BiO_2 by the probability (1-p).

The probability P_k when k is double-layered missing, is given by the following relation:

$$P_k = kp^k(1-p)^{k-1} \tag{1}$$

In this case the average number of copper planes counted is:

$$\langle n\rangle = \langle 2+4k\rangle = \sum_{k=1} p_k(2+4k) \tag{2}$$

We thus deduce the expression for the percolation parameter:

$$p = \frac{8}{\langle n\rangle + 6} \tag{3}$$

The <n> value can be determined experimentally from the RBS measurements by the relation.

$$\langle n\rangle = \frac{Nc(Sr)+Nc(Ca)+Nc(Cu)}{Nc(Bi)} - \frac{1}{2} \tag{4}$$

when Nc(X) correspond to the average number of planes of the element X by cell. The increase of bismuth ratio favours the percolation of 2212 domains. Thus it must exist a 2D percolation threshold, noted p_c, from which bonds are established between the BiO_2 domains. This threshold is determined graphically from the **Figure 6**.

We notice that the intensity of peak 2212 starts to increase for $<n_c>$ ˜ 6. Equation (3) give the corresponding value of p:

$$p_c = 0.66 \tag{5}$$

An analysis based on the model of resistance network; show that conductivity follows an exponential law of the type:

$$R \propto (p-p_c)^{-t} \tag{6}$$

This is the result of a problem of percolation in a random binary mixture of static and active media. Broadbend and Hammersley9 showed that the flow of a fluid (in our case the fluid can be compared to a fluid of electrons), through a random static medium, can occur only if the concentration of the active medium is below a certain value threshold known as the "percolation threshold".

The value of t is given by the expression[7,8]:

$$t = (d-2)\nu + 1 \qquad (7)$$

We point out that ν is an universal parameter: its value depends on the dimension (d) of the system. In the three-dimensional case: $d = 3$, $\nu = 0.88$ then $t = 1.88$.

While in the two-dimensional case $d = 2$, $\nu = 1.33$ and $t = 1$.

By analogy, we can compare our samples to a binary mixture of two media, a static one and another active. The active medium is represented by the 2212 phase, considered to be optimum doped. The static medium is form by the other areas, less or not doped.

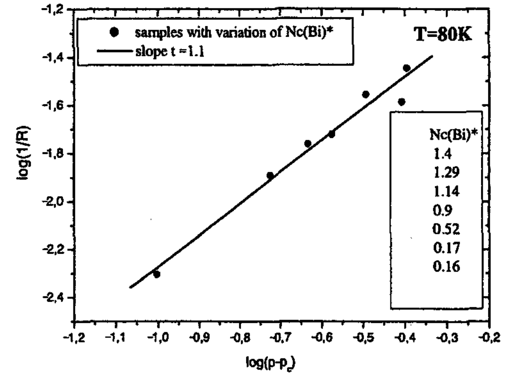

Figure 8 log(1/R) in function of log (p-p_c).

To determine the value of t, we have plotted (see **Figure 8**) the logarithm of the conductance, in normal state at 80K, of seven different samples in function of log (p-p_c), with $p_c = 0.66$. The dots are aligned on a line with a $t = 1.1$ slope. This value of t is close to the theoretic value 1.33 and indicates that the conductivity remains 2D in this family of films.

4.CONCLUSION

A new Bi-2x212 family with x varied between 1 and 0 was grown as thin films by MBE. Discontinuities in the $(BiO)_2$ bilayers were observed. But these "nanostructuration" does not increase the value of T_c. A model of percolation shows that the two-dimensional character of the conductivity remains preserved: The intergrowth phenomenon does not seem to affect the continuity of the cuprates planes.

5. AKNOWLDGMENTS

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