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# Dopant rearrangement and superconductivity in $Bi_2Sr_{2-x}La_xCuO_6$ thin films under annealing

**C Cancellieri[1], P H Lin[1,2,3], D Ariosa[1] and D Pavuna[1]**

[1] EPFL, Institute of Physics of Complex Matter, LPRX, Lausanne, Switzerland
[2] Department of Engineering and System Science, National Tsing Hua University, Taiwan
[3] Academia Sinica, Institute of Physics, Taiwan

E-mail: claudia.cancellieri@epfl.ch

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**Abstract**

By combining x-ray diffraction (XRD), x-ray photoemission spectroscopy (XPS) and AC susceptibility measurements we investigate the evolution of structural and superconducting properties of La-doped Bi-2201 thin films grown by pulsed laser deposition (PLD) under different annealing conditions. We find that the main effect of oxygen annealing is to improve the crystal coherence by enabling La cation migration to the Sr sites. This activates the desired hole doping. Short-time Ar annealing removes the interstitial oxygen between the BiO layers, fine adjusting the effective hole doping. The superconducting critical temperature is consequently enhanced. However, longer annealings result in phase separation and segregation of the homologous compound Bi-1201. We attribute this effect to the loss of Bi during the annealing.

## 1. Introduction

The effect of hole doping [1] on the electronic properties of cuprates is one of the important lines of research for understanding the mechanism of high-temperature superconductivity. The first member of the homologous series of layered superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$) [2, 3], $Bi_2Sr_2CuO_6$ ($n = 1$, 2201), due to its structural simplicity, allows us to study the influence of dopants (hole content) on the superconducting behaviour. Oxygen content [4, 5] and cation substitution strongly affect the carrier concentration and, in the particular case of the Bi-2201, it is well known that La doping increases the critical temperature, $T_c$ [6, 7]. Understanding the main mechanisms involved in annealing procedures helps in finding the optimal path to obtain high-quality 2201 thin films. Here we present results obtained by measuring the structural and the superconducting properties of films treated under different annealing procedures. A series of films with La doping $x = 0.3$ was prepared by PLD and annealed repeatedly *in situ* and *ex situ* in argon and/or oxygen atmosphere. Structural and superconducting changes were monitored by x-ray diffraction (XRD) and AC susceptibility

  

measurements. We also performed complementary XPS studies of Bi and Sr core levels. The critical temperature, $T_c$, is strongly affected by the annealing: as-grown non-superconducting samples show superconductivity after the first annealing treatment, and the quality of the transition is improved by further annealing which can also induce phase separation for longer annealing exposures.

In section 2 we describe the experimental procedures employed to grow and anneal the samples. The effect of the annealing treatment is described in sections 3 and 4, in which we analyse the structural evolution by XRD and the $T_c$ changes by AC susceptibility. In section 5 we discuss the Bi oxidation state, by means of XPS on Bi 5d core levels. In section 6 we summarize the results and draw the conclusions of our work.

## 2. Sample preparation

$Bi_2Sr_{1.7}La_{0.3}CuO_6$ target for PLD is prepared by solid-state reaction method. Stoichiometric starting powders of $SrCO_3$, $La_2O_3$, CuO, and $Bi_2O_3$ are thoroughly mixed, then repeatedly calcined at 780 °C in a $Al_2O_3$ crucible. To enhance the homogeneity of the reaction, the powders are ground several times during the calcination. Subsequently, the product is ground and pressed into a pellet, then sintered at 810 °C for 24 h in air, followed by argon annealing at 600 °C for 6 h. Thin films of 30% La-doped Bi-2201 are grown by PLD on oriented (100) $SrTiO_3$ substrates. All of the films have a thickness of about 4000 Å. We use a pulsed YAG laser at 266 nm, 100 mJ pulses and 3 Hz repetition rate. The deposition is carried out under an oxygen pressure of 0.4 mbar and the substrate temperature is fixed at 640 °C. The as-grown samples (no post-annealing treatment) are not superconducting above 4 K. For this reason, several films are annealed *in situ* after the deposition in 1 atm of oxygen for 1 h at 700 °C. A second series of films is repeatedly annealed *ex situ* in dynamic flow of 1 atm of Ar or $O_2$ for 1 h periods at 700 °C. Following each step, the changes in the sample properties are monitored.

## 3. X-ray diffraction

XRD analysis was carried out with a four-axis diffractometer using Cu K$\alpha$ radiation (1.5406 Å). The annealing in $O_2$ appears to improve the structural quality of the films, meaning that the disorder, present in the as-grown films, is reduced. The $\theta$–$2\theta$ analysis, shown in the figure 1, indicates a better crystal coherence along the $c$-axis: the 00$l$ peaks have not only higher intensity but also a better resolution of the Cu K$\alpha$ doublet. The rocking curve (RC) measures the in-plane correlation [8, 9], the full width at half maximum (FWHM) being inversely proportional to the in-plane crystal coherence length. We observe that the *ex situ* annealing in oxygen reduces the FWHM of the RC by 30%, meaning improved in-plane crystal coherence (figure 2). We believe that as-grown samples are structurally disordered, i.e. $La^{+3}$ cations are not in the appropriate positions. However, the extended repetition of this annealing procedure is detrimental to the quality of the films: after the third annealing we observe a decrease in the peak intensities and the nucleation of a new phase. This behaviour is drastically enhanced by Ar annealing: films annealed in Ar atmosphere show phase separation already after the first annealing. The amount of extra phase is strongly increased after the second annealing (figure 3).

In order to identify the impurity phases revealed by the presence of the six extra peaks marked by arrows in figure 4, we first tried to index those peaks using the tabulated XRD patterns of all possible compounds containing Bi, Sr, La, Cu and O. No matching was found for any of them or their mixtures. Furthermore, we noticed that these extra peaks can all be indexed as successive diffraction orders of a single lattice distance (9.5 Å). The latter implies a single

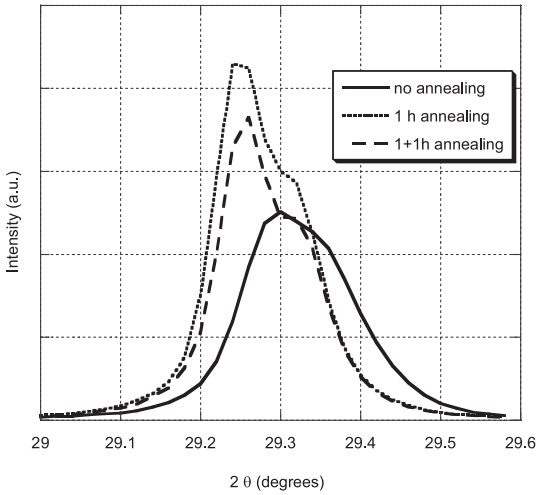


**Figure 1.** Evolution of the (008) Bragg reflection of a Bi-2201 films under annealing in oxygen.

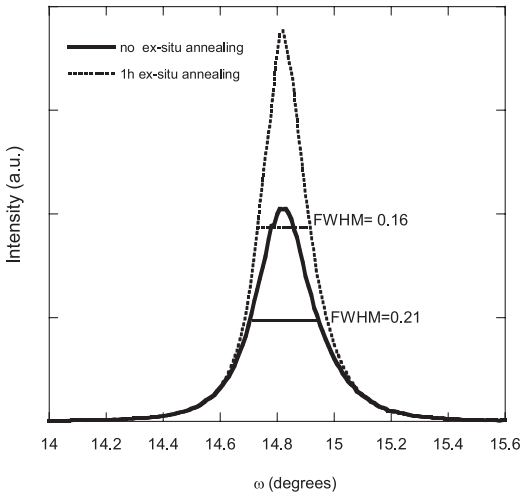


**Figure 2.** X-ray RC evolution with $O_2$ annealing. The values of FWHM were obtained using a Lorentzian fit.

orientation for the impurity, presumably due to the epitaxial growth within the Bi-2201 matrix. This epitaxial impurity must have a small in-plane lattice mismatch with respect to the matrix, and present a weak deviation from the global composition. On the other hand, the closest structures found in the literature with a *c*-axis of 9.5 Å are $HgBa_2CuO_{4+\delta}$ and $TlBa_2CuO_{5-\delta}$, i.e. the Hg-1201 and Tl-1201 structures [2, 10]. By analogy we assumed that the impurity phase was $Bi(Sr, La)_2CuO_5$ (Bi-1201) [11]. High volatility of Bi is well known [12]: annealing at high temperature causes Bi deficiency and induces the formation of the impurity phase. Additionally, the atomic ratios of as-grown films were measured by Rutherford backscattering (RBS), and the results showed that the stoichiometry ratio of the target (2:2:0:1) is conserved on films. In order to confirm the hypothesis of the presence of the 1201 phase, we computed the intensity pattern of an oriented $BiSr_2CuO_5$ crystal using standard x-ray diffraction theory

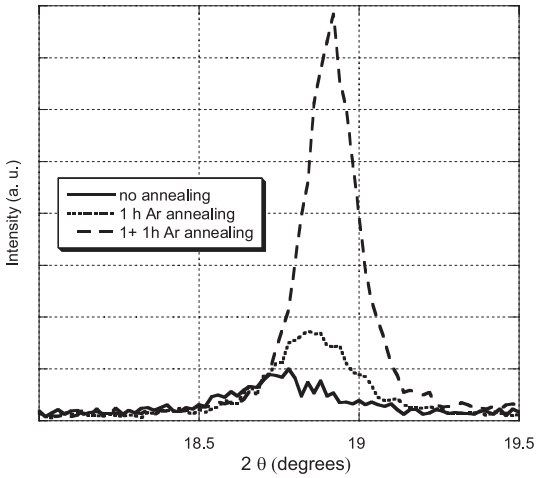


**Figure 3.** Variation of the peak of the 1201 phase with Ar annealing exposure.

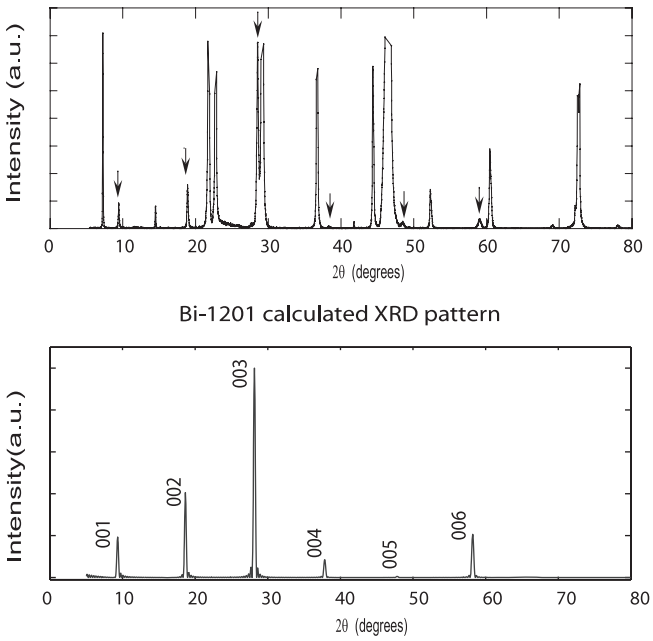


**Figure 4.** Comparison of the $\theta$–$2\theta$ diffractograms (1201 peaks are indicated by arrows) and the calculated pattern for Bi-1201.

and, by refining the *c*-axis structure, we were able to reproduce the experimental pattern of figure 4 reasonably well. The relative intensities of the experimental measurement are in good agreement with the computed pattern. The resulting fractional coordinates are listed in table 1. Surprisingly, it turns out that in the segregated 1201 phase 90% of the Sr sites are occupied by La atoms.

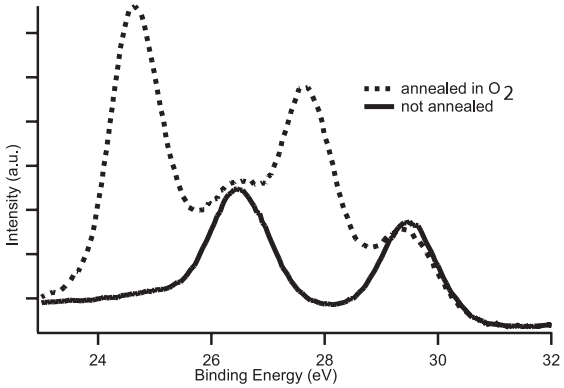


**Figure 5.** Bi 5d core levels acquired at $h\nu = 60$ eV.

**Table 1.** Fractional coordinates of Bi-1201 from XRD refinement.

| Fractional coordinates of Bi-1201 | | | |
|---|---|---|---|
| | *x* | *y* | *z* |
| Bi | 0 | 0 | 0 |
| Sr(10%)–La(90%) | 0.5 | 0.5 | 0.33 |
| Cu | 0 | 0 | 0.5 |
| O(1) | 0 | 0.5 | 0.5 |
| O(2) | 0 | 0 | 0.17 |
| O(3) | 0.5 | 0.5 | 0 |

## 4. Photoemission: core levels

We performed photoemission core level spectroscopy measurements at the Synchrotron Radiation Center in Madison, Wisconsin, on the 6 m toroidal grating monochromator beamline. The photoelectrons were collected and analysed by a cylindrical mirror analyser (CMA). The photon energy range was 8–200 eV and the energy resolution was typically 50 meV. The axis of the analyser was at 45° with respect to the sample normal. We measured the Bi 5d doublet at a photon energy of 60 eV. This doublet seems the most affected by the annealing treatment. The other core level measured in this energy range was Sr 3d, which showed no variation upon annealing. We analysed two series of films: one was annealed *in situ* in oxygen atmosphere for 1 h at 700 °C and the other was prepared without post-annealing treatment. Our results, represented in figure 5, clearly show a splitting of the doublet with a new stronger component appearing at lower binding energies. The presence of the second doublet is observed only in oxygen-annealed films. Films not annealed may present a small surface component at lower oxidation state which disappears at normal emission angle (bulk contribution). The new doublet at 25.2 and 28.2 eV is in good agreement with the values reported in the literature [13] for the 2212 phase, while the doublet position for the as-grown sample indicates a higher Bi oxidation state. In general, annealing in oxygen conserves the excess oxygen in the sample. Therefore, the effective reduction of Bi under oxygen treatment implies an internal atomic rearrangement. The $La^{+3}$ cations, present in the structure, can be responsible for the reduction of Bi. If $La^{+3}$ cations, initially trapped in interstitial sites [14], migrate to the Sr sites during the annealing; they will add extra electrons in the Bi layer environment. This picture is in agreement with the increase of crystalline order discussed in section 3. In this case, since La has smaller

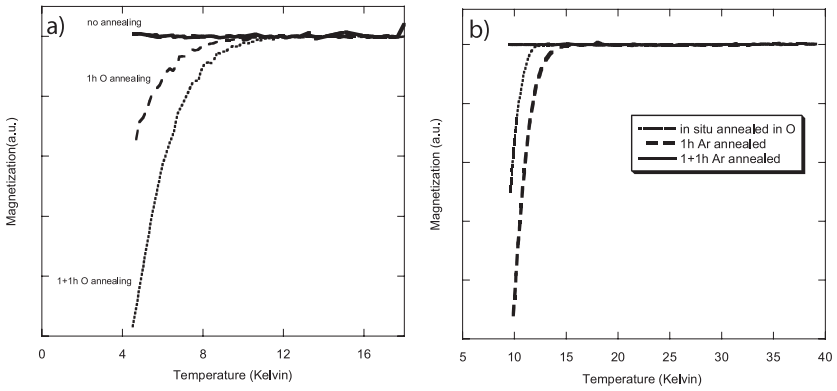


**Figure 6.** Real part of the magnetization of (a) samples repeatedly annealed in $O_2$ and (b) sample annealed in Ar.

electronegativity than Bi, Bi will be reduced and La oxidized. Unfortunately we could not measure the $O_2$ content in the films; it changes with annealing and could affect the doping ($T_c$). XPS measurements show how the Bi is the most affected by the oxygen content. The presence of extra oxygen in BiO planes is confirmed by the higher oxidation state of as-grown samples.

## 5. AC susceptibility

We studied the evolution of the $T_c$ with the annealing treatment by measuring the film magnetization versus temperature in an AC susceptometer. The as-grown samples are not superconducting. However, a short *in situ* annealing of 30 min in 1 atm of $O_2$ and at 700 °C is enough to induce superconductivity, which can be further improved by *ex situ* annealing. In figure 6(a) we plot the real part of the magnetization as a function of the temperature. We observe an increase in both the critical temperature and the intensity of the diamagnetic signal after double annealing in oxygen. However, further annealing in oxygen deteriorates the superconductivity, in accordance with the observed structural evolution. In the case of Ar annealing of as-grown samples, we can induce superconductivity as in the case of $O_2$, but the superconductivity is lost after the second annealing. Nevertheless, superconductivity is fully restored by subsequent annealing in oxygen. Finally, regarding superconductivity, the best results are obtained by combining both types of annealing as follows: a post-annealing in oxygen followed by argon annealing (see figure 6(b)). The $T_c$ values of our films, measured by AC susceptibility, are significantly lower than the values published for equally doped thin films [6] and single crystals [15, 16] measured by the resistivity technique. Resistivity measurements show systematically higher $T_c$ values than AC susceptibility due to the sample inhomogeneity, especially in thin films. Indeed, we also have performed resistivity measurements on films which show the best susceptibility transition and we found large transitions typical of inhomogeneous samples with $T_{c\ \mathrm{onset}} = 25$–$28$ K in good agreement with the value found in the literature for analogous films. Figure 7 shows the normalized resistance measurements of an $O_2$-annealed film and of the same film annealed in Ar for 1 h.

## 6. Conclusion

The picture emerging from the aforementioned results is that annealing in $O_2$ favours La ordering within the structure, while Ar annealing removes the excess oxygen by bringing the sample to the desired hole-doping region: $T_c$ is consequently enhanced. Further Ar

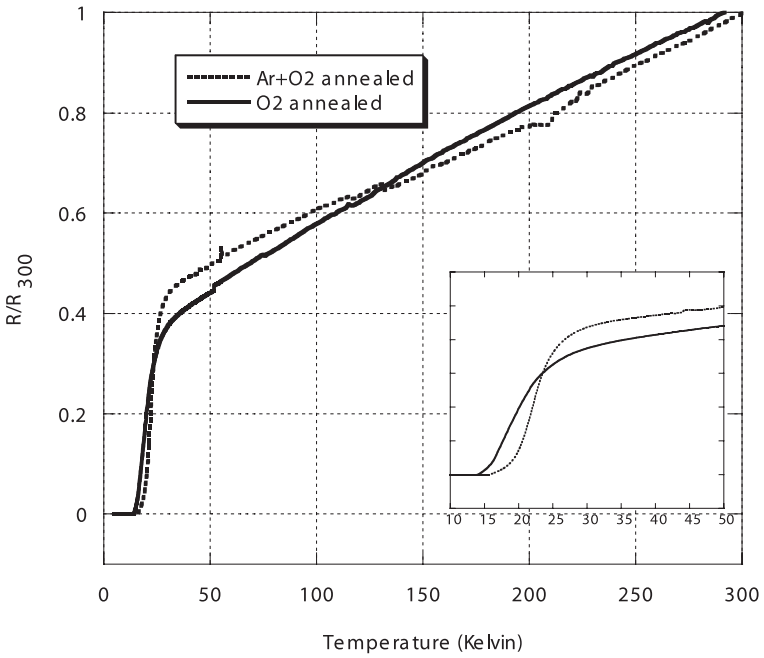


**Figure 7.** Normalized resistance versus temperature of a film annealed in $O_2$ before and after Ar annealing.

annealing removes additional oxygen, making the sample unstable again with respect to La–Sr substitution. Remarkably, this effect is reversible, since a new annealing in oxygen restores the superconductivity. The charge redistribution associated with the first $O_2$ annealing is revealed in XPS measurements as an effective reduction of the Bi, pointing out the role of competing La and Bi electronegativities. Another effect of further Ar annealing is to induce phase separation of the Bi-deficient homologous compound 1201, presumably due to the high Bi volatility.

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