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Research master thesis: Direct Visualization of Current Stimulated Oxygen bÿ Migration in YBa2Cu3O7-´Thin Films

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Faculté des Sciences | Département de Physiqe

Master Thesis

Direct Visualization of Current-Stimulated Oxygen Migration in $YBA_2Cu_3O_{7-\delta}$ Thin Films



to achieve the university degree of

Master of Science

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submitted to **Université de Liège**

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Abstract

During the last years we have witnessed colossal advancements in all-electrical doping control on cuprates. In the vast majority of cases, the tuning of charge carrier density has been achieved via electric field effect by means of either a ferroelectric polarization or by using a dielectric or electrolyte gating. Unfortunately, these approaches are constrained to rather thin superconducting layers and require large electric fields in order to ensure sizable carrier modulations [1, 2]. In this master thesis, we focus on the investigation of oxygen doping in an extended region through current-stimulated oxygen migration in $YBa_2Cu_3O_{7-\delta}$ superconducting bridges. The underlying methodology is rather simple and avoiding sophisticated overlay nanofabrication process steps and complex electronics. A patterned multiterminal transport bridge configuration allows us to electrically assess the directional counterflow of oxygen atoms and vacancies. Importantly, the emerging propagating front of current-dependent doping δ is probed *in situ* by polarized optical microscopy and scanning electron microscopy. The resulting imaging techniques, together with photo-induced conductivity and Raman scattering investigations reveal an inhomogeneous oxygen vacancy distribution with a controllable propagation speed permitting us to estimate the oxygen diffusivity. These findings provide direct evidence that the microscopic mechanism at play in electrical doping in cuprates involves diffusion of oxygen atoms with the applied current. The resulting fine control of the oxygen content in complex oxides paves the way towards a systematic study of complex phase diagrams and the design of electrically addressable devices.

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CHAPTER 1

Introduction

The physics of copper oxide superconductors continues to be one the most fascinating scientific topics since the discovery of their superconductivity in the late 80's [3]. This notoriety can be arguably attributed to a superconducting transition temperature greatly exceeding that of any known superconductor at ambient pressure, the plethora of unconventional electronic phases and the yet unsettled origin of the pairing mechanism [4]. It is not uncommon that slight changes in the stoichiometry of a material lead to large variations of its properties. The interplay and competition between various electronic orders can account for the reported sensitivity of these materials to parameters like composition, temperature, magnetic field, and pressure.

In particular, it has proven to be a colossal challenge to precisely control the oxygen stoichiometry and consequently to establish an accurate and consolidated phase diagram [5]. More specifically, it has been difficult to attain particular critical chemical compositions separating two distinct quantum ground states, which are important for the studies of quantum critical points in condensed matter. In addition, traditional methods consisting in synthesizing and characterizing samples one composition at a time may become an inefficient workload with questionable results when comparing different samples. Therefore, developing new technologies with high efficiency and accurate synthesis are becoming a first priority in material science [6].

In this work, we explore the possibility to tune the oxygen content in $YBa_2Cu_3O_{7-\delta}$ (YBCO) by mass-selective migration of oxygen atoms induced by large current densities. The material choice is primarily motivated by the fact that YBCO lies among the most investigated high- T_c superconductors and for which it is well documented that oxygen stoichiometry has a dramatic effect on its properties [7]. Indeed, the crystalline structure of YBCO changes from orthorhombic to tetragonal, while the *c*-axis lattice parameter increases by lowering the oxygen content. In the orthorhombic phase the critical temperature T_c , decreases as δ increases, exhibiting two plateaus, one near 90 K and another around 60 K.

The content of this thesis is divided in five chapters. **Ch. 2** offers a brief literature overview on the structural and superconducting properties of YBCO. The physical background, applications and models

of electromigration processes, that is current driven atomic migration, are covered in **Ch. 3**. All used samples and experimental procedures are described in **Ch. 4**, while the results and conclusions of the work are presented in **Ch. 5**. Finally, a summary of the achieved results is given in **Ch. 6**.

CHAPTER 2

YBCO

By 1986 the highest superconducting critical temperature T_c known was that of Nb_3Ge - 23.2 K, discovered in 1965 [8]. This seemed to confirm a theoretical upper temperature limit for superconductivity of 30 K [9]. This changed with the discovery of superconductivity in a lanthanum-barium cuprate (LBCO) system by J. G. Bednorz and K. A. Müller [3]. Some of their samples showed an onset of the metal-tosuperconductor transition at temperatures as high as 35 K. Importantly, the researchers challenged the conception that a superconductor needs to be a good conductor above T_c . Instead of looking into elemental metals and alloys, as done throughout the twentieth century, they started systematically working on complex metal oxides, notably cuprates and nickelates whose conductivity and structure could be tuned by controlling the nature and ratios of the cations in the structure. These materials are natively insulating ceramics, and were until that point not expected to exhibit superconductive properties. Bednorz and Müller shared the Nobel prize of Physics the following year, for showing that structural interactions in complex crystals can give rise to superconductivity at higher-than-expected temperatures and for inspiring a surge in functional material discovery. Soon after their initial report, it will be shown that T_c's above 40 K are very much possible [10] in the LBCO system and only seven months later, an astounding critical temperature of 93 K (a whole 16 K above the boiling point of N_2) was reported for a similar phase-mixed ceramic sample in the yttrium-barium cuprate (YBCO) system [11]. The stoichiometry in the YBCO system was shown to be $YBa_2Cu_3O_{7-\delta}^{-1}$, with $0 < \delta < 1$ by C. W. Chu's group [12], and confirmed quickly by others [13].

Chu *et al.* [12] have also compared a number of $ABa_2Cu_3O_{7-\delta}$ compounds where *A* is a rare earth and have shown a considerable indifference of the T_c to the radius of the atom, providing indication that the origin of the electronic coupling is confined to the planar CuO_2 arrangements characteristic of the system. Despite these early clues, the complex nature of the interactions that lead to the emergence of superconductivity in cuprate superconductors [4] is still being debated.

Various similar, high-temperature superconductors have been discovered in the last 30 years, and continue providing motivation for further study. Nevertheless, YBCO (also referred to as Y123) has made

¹Chu *et al.* used $YBa_2Cu_3O_{6+x}$ in their paper, whereas Cava *et al.* described the phase as $YBa_2Cu_3O_{9-\delta}$ with $\delta = 2.1$.

a lasting presence in the community as the benchmark for cuprate superconductors. In this chapter we will take a look at the structure, properties and preparation of YBCO.

2.1 Structure and Chemistry

 $YBa_2Cu_3O_{7-\delta}$ is an oxygen deficient complex oxide presenting an interlacing perovskite-rock saltperovskite structure, further discussed below in Sec. 2.1.1 and first identified by Capponi *et al.* [14]. Oxygen deprived YBCO (with high δ values) is thermodynamically favored with the material losing oxygen at temperatures well below melting and phase separation of the compound. However, highly doped materials are readily prepared [15]. If properly doped ($\delta \le 0.5$), YBCO behaves as a poor metal but when underdoped it becomes an insulator [4]. Melting of the material is dependent on O_2 partial pressure, δ and phase purity and happens over a temperature range above 1000 °C [16] at ambient pressure.



Figure 2.1. Left: Calculated liquidus projection of the Y_2O_3 –BaO– CuO_x ternary phase diagram at atmospheric oxygen partial pressure. 200, 211, 202, 123 and 001 are two-phase equilibrium regions for liquid and Y_2O_3 , Y_2BaCuO_5 , $Y_2Cu_2O_5$, $YBa_2Cu_3O_{7-\delta}$ and CuO respectively. Right: Calculated isothermal section of the Y_2O_3 –BaO– CuO_x ternary phase diagram at 1223 K and atmospheric oxygen partial pressure. Taken from [17].

Figure 2.1 shows the liquidus projection of the copper-rich corner of Y_2O_3 –BaO– CuO_x ternary phase diagram at ambient oxygen partial pressure (left panel) and an isothermal cut of the whole diagram at 1223 K elaborated from experimental data by thermodynamical modeling (right panel) by Lee *et al.* [17]. Note how several *Y* rich compounds form easily from the Y123 phase even though the compound is in the barium rich corner of the diagram. The chemical neighborhood of $YBa_2Cu_3O_{7-\delta}$ becomes very crowded as the temperature increases above 1000 K, with two peritectic and three eutectic points falling in a small section of the diagram² within a temperature range of 300 K. The authors discuss similar cuts at higher temperatures and conclude that the recession of the Y123-liquid two-phase region is most strongly correlated to the increasing stability of Y_2BaCuO_5 even in *Y* deficient regions. They also show

²The liquidus projection shows the peritectic points for $YBaCuO_5$, $YBa_2Cu_3O_{7-\delta}$ and $Y_2Cu_2O_5$ are 1503, 1275 and 1402 K respectively, and identifies two eutectic temperatures, one ternary for $YBa_2Cu_3O_{7-\delta}/BaCuO_2/CuO$ -liquid at 1179 K and one binary for $Y_2Cu_2O_5/Cu_2O$ -liquid at 1330 K.

that decreasing oxygen partial pressure significantly increases the liquid-phase region in the ternary diagram.

Due to the sensitive preparation which involves the stoichiometry of four elements, the strong crystallographic correlations and the mobility of the oxygen atoms, individual sample properties are heavily dependent on sample history [18]. Notably, granularity is detrimental to the critical current density [19] of devices and YBCO, being a brittle ceramic [20], requires refined fabrication techniques to be applied in devices.

Importantly, the material contains the layer order $[-Y - CuO_2 - BaO - CuO_{1-\delta} - BaO - CuO_2 -]$ with clearly defined base-pyramidal CuO_2 planes, which are essential components of all related cuprate superconductors. In fact, all four generalizations of R. J. Cava [21] for superconductivity in cuprates apply to YBCO: (i) superconductivity is contained in the quasi-2D CuO_2 planes [22], (ii) the CuO quasi-1D chains serve as the charge reservoir layers [23], (iii) the $Cu \, 3d$ and $O \, 2p$ orbitals have similar energies and give rise to highly hybridized bands [24] and (iv) the superconductivity coincides with the metal-to-insulator transition when sufficient hole doping is achieved in the CuO_2 planes [7].

Yttrium is a trivalent cation [25] and barium is a large earth alkaline comfortably fitting in the *A* position in the tripled perovskite (*ABO*₃) structure. The oxidation states in $YBa_2Cu_3O_{7-\delta}$ are therefore dictated by the interactions between the oxygen and the copper atoms, giving rise to the formal valence distribution [22]:

$$YBa_{2}Cu_{3}O_{7-\delta}^{-2}$$
(2.1)

The formal valence of Cu is a special function of δ , close to +1 in the chains and a bit above +2 in the planes [24] for highly doped materials, whereas it is close to +2 in both at locations where $\delta \approx 0.5$ [26]. Furthermore, the formal valence on all copper atoms is a function of the oxygen deficiency δ and the material remains a non-stoichiometric compound to conserve electroneutrality. An ideal tripled perovskite cell would require two more oxygen atoms to have all the copper in BO_3 octahedra but does not exist in the Y_2O_3 –BaO– $CuO_{1-\delta}$ system [17], probably due to the sizes of the involved cations. Instead, YBCO is a distorted, non-stoichiometric crystal only partially resembling a perovskite. This distorted charge picture is key to the interesting properties of YBCO.

Well doped YBCO is a black or dark grey ceramic, whose main downsides in its handling are mechanical, due to the brittleness (Young modulus is E = 180 GPa at full theoretical density³, but significantly lower in real materials [20]). Chemically, it is stable enough to be stored in ambient and to be used in commercial devices, both as superconducting wires and integrated electronics. Yttrium atom substitutions are possible as a lot of properly sized rare-earth cations (e.g. *Sm* and *Gd*) can take the sandwiched position of the *Y* atom in the structure. YBCO samples are stable at ambient conditions⁴ for very long periods of time, but are susceptible to carbonate and hydroxide layer formations [27]. Oxygen exchange with other metal oxides is known to occur at interfaces [28].

³Density as mass of all atoms in the volume of the unit cell for $\delta = 0$ and all *CuO* chains filled.

⁴Atmospheric pressure and room temperature.

2.1.1 Crystallographic Description

For a complete crystallographic description [29] of $YBa_2Cu_3O_{7-\delta}$, two idealized unit cells can be used, as shown in Figure 2.2. For $\delta \approx 0$ the material is in an orthorhombic ($a \neq b$, (a, b) < c) configuration in the *Pmmm* space group, whereas for $\delta \approx 1$ the material is described as tetragonal (a = b < c) in the *P4/mmm* space group⁵. The cell parameters are functions of δ [7] (and by proxy functions of quenching temperature and oxygen partial pressure [22]) and around 3.85 Å for a and b and up to 12 Å for c. The b axis is slightly larger than a for orthorhombic materials, and the tetragonal c is larger than its orthorhombic counterpart. The atomic positions in the displayed sketch are named in accordance with well known literature.

Both structures feature the square-planar CuO_2 plane in O(2) - Cu(2) - O(3), but only the orthorhombic structure is superconducting [26]. In the tetragonal structure (essentially, $YBa_2Cu_3O_6$) the basal copper is coordinated with six oxygen atoms into octahedra that do not exert any charge transfer on the Cu(2) planes, as the interaction between Cu(2) and the apical O(4) is much weaker in this structure. The orthorhombic O(1) - Cu(1) chains on the other hand couple with the Cu(2) planes and influence superconductive behavior [23, 30], which is evidenced by the known relation between T_c and the ratio of the Cu(2) - O(4) and Cu(1) - O(4) bond lengths [31].



Figure 2.2. Visualization of the orthorhombic (left) and tetragonal (right) unit cells of $YBa_2Cu_3O_{7-\delta}$. The orthorhombic unit cell corresponds to low δ values. Literature suggests that the change to tetragonal material happens at δ close to 0.55 [7]. The 1st and 2nd neighbor interactions are shown as black and gray bars, respectively and atomic positions are named in accordance to literature [22]. Crystallographic *a* and *b* parameters are the same for tetragonal structures. In the orthorhombic structure Cu(1) - O(1) form chains and O(2) - Cu(2) - O(3) form planes.

As pointed out above, real YBCO samples can never be fully oxygenated, as electroneutrality needs to be maintained. Using neutron diffraction on samples with varying δ , Jorgensen *et al.* [7] have shown that, close to the orthorhombic-tetragonal transition, the site occupancy for O(1) drops, while O(5) (corresponds to the twinning position shown in Fig. 2.3 **a**), at $[\frac{1}{2},0,0]$) starts being increasingly populated, until finally combining in the tetragonal O(1) position. According to their and the conclusions

 $^{^{5}}$ Notation according to the International short symbols standard in crystallography, also known as Hermann-Maguin notation. The *P* designates a primitive Bravais lattice, the numbers and lowercase letters indicate symmetry elements - rotations along *c* and mirror planes respectively

of others [15, 22, 32] it is agreed that the vacancies in the orthorhombic superconducting $YBa_2Cu_3O_{7-\delta}$ system clearly prefer the O(1) position in the copper chains (as shown in Fig. 2.3 **b**)), thereby tuning the Cu(1) - O(4) - Cu(1) bond lengths and the doping levels in the CuO_2 planes. This means that real materials can be described as two lattices, one hosting all the truly periodic atomic positions (*Y*, *Ba*, Cu(1,2), O(2,3,4)) and another one hosting the $O(1) - V_0^2$ lattice, where V_0^2 are the vacancies⁶.

It is well documented that the switching from orthorhombic to tetragonal crystals, while dependent on individual sample history, usually happens at δ values larger than 0.5 [7, 22]. Note that this information is obtained by preparing a multitude of samples and comparing their structures, instead of comparing a single sample with varying properties.



Figure 2.3. Visualization of the *CuO* chains of YBCO, atoms shown in same colors as in Fig. 2.2. **a)** The twinning positions available to O(1) are shown as squares in the $[\frac{1}{2}, 0, 0]$ position. A possible oxygen movement from an O(1) to a twinning position is shown. **b)** A random vacancy distribution in the *CuO* plane.

Crystal Anisotropy

There is an inherent difference between the *a* and *b* cell parameters for any orthorhombic cell, but it is not nearly as emphasized as the difference between them and the *c* of YBCO, which is almost three times larger. Considering the layered structure and the strain in real samples [33], it is to no surprise that the resistance [34], the dielectric response [35], oxygen mobility [36–39], and even the superconductivity [40] in YBCO behave in an anisotropic fashion.

The resistivity in the *ab* plane ρ_{ab} increases linearly with temperature, both for YBCO [41] and related structures, like BiSCCO⁷ [42, 43]. Essentially, transport in this plane is shown via Hall response to be *p*-type, which contrasts with the results for Hall response in the *c* direction [44] for perovskite superconductors. Additionally, transport parallel to *c* was reported to behave in a multitude of ways for various cuprates, from metallic to semiconducting and mixed, with the mechanism posing a source of controversy for several years [45].

Recording the full resistivity tensor of YBCO is a delicate measurement, because of $\frac{\rho_c}{\rho_{ab}} \gg 1$ and any measurements along *c* being easily influenced by in-plane conduction channels. Additionally, real samples tend to make *a* – *b* twins [32, 46, 47] using the position shown in Fig 2.3 **a**), creating twinning planes shared between *a* – *b* and *b* – *a* oriented crystals, as shown in Fig. 2.4. This can lead to interference

⁶Kröger-Vink notation. A vacancy on the oxygen site has a +2 charge indicated by the ⁵.

⁷Bismuth-strontium-calcium cuprate.



Figure 2.4. Visualization of a a - b/b - a twinning plane in the *CuO* chains of YBCO.

between the in-plane components. Friedmann *et al.* [48] have published a complete overview of the resistivity components, complimenting other studies proving metallic behavior of ρ_c [40], constant $\frac{\rho_c}{\rho_{ab}}$ ratios for a wide range of temperatures and a strong metallic contribution from the *CuO* chains [49]. Finally, it has been shown that the resistivity is strongly directional with the *CuO* chains dominating to the normal conduction, resistivity being lowest along *b* [50], and transport along the *c*-axis happening through a peculiar tunneling mechanism, further elaborated on in section 2.3.2.

Apart from the very intriguing anisotropic dependencies of transport in YBCO, another quite directional behavior is oxygen diffusion [38]. As mentioned above, early studies have determined that Ovacancies prefer to stay in the *ab* plane, but since then it has been shown by tracer diffusion studies that mobility is also greater in-plane, indicating a clear difference first in energy requirement for movement in the *ab* plane and along *c* [36], and later between *b* and *a* [37]. With D_x being oxygen diffusivity in direction *x*, D_a has been shown to be smaller than D_b by a factor of almost two orders of magnitude. This has since been studied and confirmed further by molecular dynamics simulations [51].

Lattice Vibrations

The lattice vibrations of YBCO have received considerable attention [52], initially being determined using acoustic measurements [53] and more recently using Raman characterization [54] or specific heat data [55].



Figure 2.5. Z-vibrational antipolar optically active Raman modes of YBCO: +O(2,3), O(2,3), Cu(2), Ba and apical O(4) phonon modes. O(4) A_g occurs at 500 cm⁻¹.

Experimental optical phonon spectra have been recorded in the IR⁸ and far-IR parts of the spectrum for both $YBa_2Cu_3O_{7-\delta}$ [56] and $YBa_2Cu_3O_6$ [57]. The results of these studies show a distinct fingerprint of at least 10 distinct modes for the orthorhombic material, and show a difference in vibrational behavior of the CuO_2 planes between the two phases.

Given the peculiarity and discussed anisotropy of YBCO crystals, a significant number of Raman active modes is observed, and specifically the one at 500 cm⁻¹, shown in Fig 2.5, related to the antipolar motion of the apical oxygen $(O(4)A_g)^9$, was shown to be strongly dependent on oxygen doping and present in both orthorhombic and tetragonal material [59]. Raman spectroscopy has since been shown to be a viable way of characterizing samples for epitaxial strain [60, 61], oxygen content [62], quality control for device production [63], and electromigration [64], to be discussed in the following chapter.

2.2 Material Synthesis

Preparation of YBCO samples and devices can be done in a variety of ways, from simple solid state sintering methods to more complex controlled deposition techniques [65]. The choice of technique and parameters will, as earlier mentioned, heavily influence the resulting properties. It is useful to keep in mind that almost all synthesis methods for any RE123¹⁰ complex oxide can usually be used for Y123, due to the easy substitution and similar sizes of rare earths.

In particular, oxygen content is probably the most important property to be controlled during synthesis. This can be achieved either through controlling the reactant stoichiometry going into the reaction, or by preparing richly oxygenated samples and modifying them, usually by annealing in controlled atmospheres. An early overview of annealing effects can be found in [66]. Optimally doped ($\delta = 0.04$) YBCO can be obtained by annealing a sample in oxygen at 400° C.

Numerous flux melting (solid state) [67] methods are proposed for preparing powdered rare earth perovskites to be later sintered into bulk. Notably, the first known syntheses were based on melting of oxides and carbonates of the involved metals, along:

$$\frac{1}{2}RE_2O_3 + 2BaCO_3 + 3CuO \xrightarrow{\Delta} REBa_2Cu_3O_{7-\delta} + 2CO_{2(g)}$$
(2.2)

In recent years the carbonates of *Ba* and *Cu* have been replaced with nitrates in solid state synthesis, as the nitrous gases leave the system more easily and do not have any stable side-products with barium (unlike the carbonate), giving smaller amounts of impurity phases.

$$RE(NO_3) + 2Ba(NO_3)_2 + 3Cu(NO_3)_2 \xrightarrow{\Delta} REBa_2Cu_3O_{7-\delta} + 11NO_{2(g)} + 2O_{2(g)}$$
(2.3)

Note that such a synthesis is a twofold function of oxygen pressure, first as a product and second in the composition of the complex oxide. Details on single crystal growth can be found in Ref. [68].

Furthermore, the quality of these solid state samples can be improved by cold and hot seeding methods, wherein a favorably structured seed crystal is put in contact with the melt at various temperatures

⁸Infra-red.

⁹In group theory description [58], *A* designates Raman active phonon modes which are singularly degenerate (onedirectional) and parallel to the principal axis *c*. The subscript *g* (ger. *gerade* - even) designates that the mode is symmetric upon inversion.

¹⁰Compounds structurally equivalent to $YBa_2Cu_3O_{7-\delta}$ with the yttrium atom substituted for another rare earth.

(therefore hot and cold) to control the crystal growth [69]. The melt is directionally cooled in oxygen flow in a process known as oxygen controlled melt growth, giving samples with higher phase purity and sharper transitions [70]. Thin film YBCO can be grown with a known crystal orientation by controlling the substrate temperature during annealing [71].

In order to avoid the inhomogeneity from solid state annealing methods, numerous "wet" precursor methods have been proposed [72], including sol-gel, freeze drying, spray drying and organometallic methods. They are all based on using solutions to obtain a good dispersion of the ingredients in the precursor powder. After that, a single annealing or reacting step usually gives a high-quality material. One very notable method is the citrate route [73], wherein the cations are complexed with citric acid and deposited in an organometallic powder. The citrates burn at relatively low temperatures leaving as a solid state product the REBCO sample. A good overview of wet precursor synthesis using organometallic intermediate steps can be found in [74].

A well known and deservedly popular approach is chemical solution deposition (CSD), which can give high quality epitaxial films. The trifluoroacetate precursor synthesis method first described by Gupta *et al.* [75] and reviewed by Obradors *et al.* [76, 77] is an excellent example of this. Herein a precursor is synthesized with trifluoroacetate, which yields stoichiometric fluorides after burning that can be readily reacted with water into oxides to be annealed. This completely avoids the formation of the hardly soluble *BaCO*₃. An interesting alternative that avoids the use of fluorides is polymer assisted CSD as proposed for GBCO by Wang *et al.* [78].

High quality YBCO thin films (and bulk devices [79]) can be grown using pulsed-laser deposition [80–82] from targets prepared in numerous ways including the above. Molecular beam epitaxy is also possible and uses either oxygen flow or organometallics as precursor molecules [83, 84].

2.3 Electrical Properties

As the oxygen content controls the electrical properties of the sample, we will use the term doping to refer to the oxygen stoichiometry $(7 - \delta)$ of the material. We shall discuss why this is appropriate, and how it can eventually be related to the actual hole carrier concentration in the superconducting planes.

2.3.1 Doping Effects

Soon after the $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ structures were determined, studies of intermediate compounds were started [26, 85, 86], showing an order-disorder phase transition from oxygen-ordered (orthorhombic) to oxygen-disordered (tetragonal) material at $\delta \approx 0.5$ [87]. At lower doping levels, YBCO behaves as an antiferromagnetic insulator while with increasing doping the normal state resistivity becomes a stronger function of temperature [31], with significant anisotropy in the resistivity tensor and peculiar spatial organization of conductance in the material [88–90]. Total loss of superconductivity happens at $\delta \approx 0.55$ [29, 91], where precise estimates depend on sample history. The cell parameters are also dependent on oxygen content, as described above.

Samples whose oxygen doping is controlled via quenching temperature tend to show a straightforward dependence between quenching temperature and critical temperature [22]. This translates into a relationship between T_c and oxygen content in the samples, since the latter is a function of quenching

temperature. In contrast to that most samples prepared in optimal doping and then modified by various means at lower temperatures, show a distinct, two plateau behavior [7, 22, 29, 31, 91]. Therein, the critical temperature remains nearly invariant in two ranges, a high- T_c (\approx 90 K) plateau at $\delta \approx 0.1$ and a low- T_c (\approx 60 K) plateau at $\delta \approx 0.45$, as shown in Fig. 2.6. Importantly, the T_c does not uniquely depend on δ , but also on the ordering of the O(1)- V_O^{-1} sublattice.



Figure 2.6. Experimental dependency of superconducting critical temperature on oxygen stoichiometry. The lower dashed line represents a material with equal distribution of vacancies across the plane, and the upper dashed line corresponds to a material with alternating full and empty chains (ortho-II). All real materials should display a behavior between these two. Adapted from [92].

Recent works describe several "Ortho" phases [85] which correspond to the orthorhombic lattice with a fraction of *CuO* chains removed. Upon investigating ordering in these phases with neutron and high energy X-ray diffraction coupled with Monte Carlo simulations, Anderson *et al.* [93] have shown that the order in most of these phases is only short-ranged (except in the true orthorhombic and tetragonal, and the regularly deficient ortho-II phase), thereby describing these structures as quasi-phases "frozen" during cooling.

While it is clear that changing oxygen content induces an order-disorder phase change, the order of it is disputed. The continuous changes in cell parameters, resistivity, T_c , etc. indicate a transition of at least second order. On the other hand the presence of distinct superlattice reflections in the diffraction samples at various δ values might still show evidence of a first order transition obfuscated by vacancy ordering between the phases [91].

Neutron diffraction studies show progressive vacancy ordering with decreasing δ , caused by the removal of *CuO* chains from the *ab* plane. Both the metallic contribution to the conductivity and the hole doping to the *CuO*₂ planes disappear as do the chains, and the tetragonal material behaves as an antiferromagnetic insulator, instead of a superconducting metal. With some chemical naiveté we can explain this by the material trying to avoid trifold coordinated copper, which is an energetically unfavorable state of the element.

Liang *et al.* [92] have proposed a method for directly relating the carrier doping in the CuO_2 superconducting planes, calculated using the bond valence sum approach dependent on bond lengths. They have shown a very good dependency of the hole doping with the *c* cell parameter, and a reasonably good dependency with critical temperature. As elaborated above, both these properties are functions of the oxygen doping [94], and the authors show that oxygen content directly controls the conductance of the material through the hole carriers concentration with:

$$p = 11.491y + 5.17 \cdot 10^9 y^6 \tag{2.4}$$

$$1 - \frac{T_c}{T_{c,max}} = 82.6(p - 0.16)^2$$
(2.5)

where $T_{c,max}$ is the maximum critical temperature of the material, p is the number of holes per copper atom in the CuO_2 planes and $y = 1 - \frac{c}{c_0}$ with c_0 the lattice parameter at ambient conditions for $\delta = 1$. In order for Eq. (2.5) to work the critical temperature needs to be corrected with a factor provided by the authors for the δ range between the two plateaus, but it works well with highly and weakly doped materials.

2.3.2 Transport and Metal-to-Superconductor Transition

Keimer *et al.* [4] have reviewed the current understanding of the microscopic origin of hightemperature superconductivity in cuprates and highlighted how the p-T phase diagram of YBCO arises as a consequence of magnetic and superconducting ordering. These authors show the existence of three distinct regions apart from the superconducting one including an insulating, quasi-semiconducting and metallic behavior developing at low, medium and high doping, respectively.



Figure 2.7. Experimental resistance in the *ab* plane as a function of temperature for a 0.1 μ m × 1 μ m × 5 μ m constriction of optimally doped YBCO prepared by pulsed-laser deposition on lanthanum aluminate. The measurement setup is described in the experimental section.

In underdoped YBCO, spin coupling between edge-sharing CuO_2 squares sets in limiting the carrier mobility in the material and making it an antiferromagnet. This leads to Mott insulation, as the material technically has unbound electrons available to transfer current, although it can not due to the mentioned magnetic interactions. The interesting concept here is that this antiferromagnetic ordering, that is the spin density wave, is suspected to play an important role in the coupling of electrons into Cooper pairs [95]. This fits neatly into the fact that with overdoping, the T_c of YBCO drops, as the antiferromagnetic ordering between units weakens.

To understand the local charge picture during the metal-to-superconductor transition in a more chemically intuitive way, Magnuson *et al.* [23] have recently employed X-ray absorption spectroscopy and resonant inelastic X-ray scattering, together with simulations in ligand field theory to reconstruct the orbital configurations and populations during the temperature driven metal-to-superconductor transition in YBCO. What these authors have observed, amounts to a self-doping via charge transfer across the apical oxygen between the two different copper atom types, evidenced by the disappearance of the metallic, higher oxidized band of the copper chains at the metal-to-superconductor transition, and the appearance of a new, doped configuration in the planes. This appears to be possible due to favorable energetic and spatial conditions of the $d_{y^2-z^2}$, $d_{z^2-r^2}$ and p_z orbitals of Cu(1), Cu(2) and O(4) respectively.

Generally, conductance is the highest along *b*, then *a* and lowest in the perpendicular *c* direction in the normal state (see Section 2.1.1). Most samples will display fairly resistive conduction in the normal state and a transition width for the metal-to-superconductor transition of about 1 K, as shown in Fig. 2.7. Transport along the *c* axis was shown to occur through "plane-hopping" tunneling currents. This was first theoretically studied with the influences of different scattering mechanisms for interlayer transport by Kumar *et al.* [96]. Finally it is shown that the discrepancy from a straightforward temperature power-law for ρ_c can be attributed to a disorder parameter which is controlled by the in-plane scattering, and therefore $\rho_c \propto \rho_{ab}$. These authors have also proposed that the ratio $\frac{\rho_c}{\rho_{ab}} \propto \delta$.

2.3.3 Superconductivity

The earliest conclusions on the microscopic origin of superconductivity in YBCO came from flux quantization in SQUID's¹¹ [97] and the showing of phase coherence across a junction with a conventional superconductor [98]. These measurements have shown that some of the conclusions from BCS superconductors carry over to cuprates: charges are paired in Cooper pairs and an electrical phase coherence can exist across the interface between YBCO and a BCS superconductor.

The upper critical field of YBCO is an anisotropic value that can reach up to 140 T along the *c* axis and up to a whopping 900 T in the *ab* plane direction at zero temperature [99]. Using magnetic levitation measurements, Xu *et al.* [100] have determined the temperature dependence of the London penetration depth. Similarly, using microwave absorption experiments, Jiang *et al.* [101] have revealed anisotropic values for both characteristic lengths in YBCO as:

$$\lambda_{ab} = 1800 \text{ Å}$$
 $\xi_{ab} = 25 \text{ Å}$ $\lambda_{c,86.5K} = 26000 \text{ Å}$ $\xi_c = 8 \text{ Å}$

at 0 K. Here λ is the London penetration depth, ξ being the coherence length with a subscript indicating the crystallographic axes. Only λ_{ab} is extrapolated to 0 K as the authors used surface resistivity measurements on *c*-axis aligned samples to deduce them. λ_c was measured at 86.5 K using magnetically modulated microwave absorption measurements.

¹¹Superconducting quantum interference device.

YBCO is a type-II superconductor in the sense that it shows incomplete field expulsion above a certain magnetic field applied [102]. The motion of the magnetic vortices that arise in such materials can be detrimental to the needed high current density in applications [103], and their manipulation remains an active field of study [104–106]. Specifically, arranging implanted antidots [107] or similar columnar defects can be used to control the vortex behavior [108–110] and, in specific conditions, even increase the critical current density of the material.

In discussion of microscopic theory of superconductivity of cuprate superconductors, they have often been given the epithet of being unconventional, due to the fact that conventional BCS theory seems insufficient to fully describe them. Early calculations have shown that the reduced symmetry of the CuO_2 planes should influence the spatial distribution of the superconducting pair-formation function. As a consequence, the pair-density wave function seems to adopt an anisotropic shape in momentum space [111]. That the superconductivity truly is confined in such materials was first unquestionable after observation of Josephson junction-like behavior along the *c* direction of cuprate superconductors [112].

A convenient way of testing the pairing symmetry is using the shift in electrical phase induced in parallel conventional-unconventional superconductor interfaces, if they are connected in such a way that they do not meet along the same crystallographic direction. This phase shift is proportional to the pair-formation energy gap in both materials. As the gap in an unconventional superconductor is directionally dependent, we essentially probe for the expected phase shift at angled junctions [113, 114]. In the late nineties evidence that the pairing symmetry in YBCO is lowered [115, 116] has been provided through both various SQUID-interferometry [117–119] and magnetometry [114] experiments on crystal interfaces, twinning boundaries and various interfaces with BCS superconductors, as well as by studying phase coherence across Josephson junctions [120] and magnetic field modulation in the material [100, 121]. Recent scanning tunneling spectroscopy studies have also shown that more conventional field expulsion can be achieved locally by utilizing strong vortex pinning effects [122]. Another experimental technique that has seen increasing use in recent years is angular resolved photoemission spectroscopy, which has both high enough energy and angular resolution to probe the energy states of the carriers in superconductors. Together with tunneling microscopy techniques, it has provided the strongest evidence for unconventional pairing function symmetry in YBCO [4].

2.3.4 Photoconductivity

Tuning the oxygen content of $YBa_2Cu_3O_{7-\delta}$ is not the only way to influence its electric properties, as illumination also changes them [123] through what has come to be called photodoping [124]. Enhanced photoconductivity (another term for the same effect), was first extensively studied in $GdBa_2Cu_3O_{7-\delta}$ [125, 126] and shown to induce superconductivity in underdoped samples [127], and to have an intriguingly long relaxation time.

Similar studies in YBCO have shown the same behavior [128], with anisotropic changes between ρ_{ab} and ρ_c [129]. Notably, photodoping occurs in medium doped (and to some extent in the metallic phases), not in optimally or overdoped materials [130, 131], and depends strongly on temperature. The latter is well-illustrated by Stockinger *et al.* [132] who have shown a steady increase in carrier concentrations with long-term illumination for temperatures between 70 and 290 K but a saturation of the increase in carrier mobility at around 250 K followed by a steady decrease. They also show that the ratio $\frac{\Delta \rho_c}{\Delta \rho_{ab}}$

changes significantly with change in temperature [129], enhanced (depleted) at low (high) illumination temperatures. They suggest that at higher temperatures the influence of photoassisted oxygen ordering [133] becomes the main mechanism by lowering the *c* axis parameter and facilitating the tunneling between the CuO_2 planes, decreasing both ρ_c and $\frac{\Delta \rho_c}{\Delta \rho_{ab}}$. The low temperature behavior is according to them accounted for by thermally assisted oxygen diffusion through the *CuO* chains, backed by the considerations of Ref. [131]. This is not enough to explain the observed behavior, as it fails to capture the increased anisotropy of the resistive tensor. Therefore, the authors have suggested a charge transfer model between the copper plane and copper chains, with photogenerated electrons being trapped either in oxygen vacancies or free oxygen bands, and the photogenerated holes being contained in the *CuO*₂ planes (similar to what happens at the metal-to-superconductor transition).

As summarized by Markowitsch *et al.* [124], photodoping of YBCO with visible or ultraviolet radiation leads to significant changes in the electronic properties: the free carrier concentration increases, the carrier mobility changes (as a function of the illumination temperature) and in properly doped samples, the T_c increases. Furthermore, the relaxation below 250 K is almost unobservable (persistent photoconductivity) and it is very slow at higher temperatures (on the scale of days). The authors also establish a clear link between the mechanisms of enhanced photoconductivity and *c*-axis tunneling transport, by showing that the conductance in that direction is independent of carrier mobility, and only a function of their concentration.

Yang *et al.* [134] have recently demonstrated a simple photovoltaic device based on the coupling of metallic (*n* conductor) electrode with YBCO, where they have clearly shown the appearance of a voltage across two electrodes when one of them is illuminated with a laser (Note that YBCO has an extremely low Seebeck coefficient thus ruling out any heating effect [135]). In the authors device, the electrons generated by illumination get condensed into pairs and flow without resistance, while the holes travel to the metallic electrode and create a voltage across the device. While technology based on this effect seems far from maturity, it provides an interesting alley of studying both proximity and interface effects in metasystems.

2.4 Applications

Advances in synthesis and product quality, together with the exciting physics of complex oxides [136] have promising implications for the future of applications for high- T_c superconductors [137]. The mentioned chemical solution deposition method, for example, has potential to be used in upscaled fabrication of coated conductor wires [138] (the bleeding edge of applied superconductor technology) due to its low cost and ease of use, as displayed by Holesinger *et al.* [139]. The most recent coated conductor wires are being improved by engineering pinning centers into the material to allow for larger critical current densities [103, 140].

The electric field has numerous effects on YBCO thin films that can be exploited for use in microelectronics, reviewed by Ahn *et al.* [141], and that are becoming more and more interesting as our understanding of electrical oxygen doping effects grows. Devices such as superconducting transistors, switches, sensors and memories can be imagined based on these effects. One important consideration is that cycling electric fields in such materials always lead to some locally irreversible oxygen migration which can deteriorate the samples [142]. Maybe the most interesting of these applications is resistive switching [143–145], wherein an applied electric field causes a change of resistance across a device, which can be reversed by reversing the polarity of the applied voltage. Such devices have numerous applications in microelectronics as they can be used as non-volatile bits. It should be noted that any application with a YBCO-metal interface needs to consider the intrinsic doping effects of such an interface [146]. Apart from fields applied from electrodes, it has been shown that ionic liquid gating can produce even stronger switching behavior [147, 148].

We will discuss the outlook on applications of electrically controlled oxygen migration in YBCO further at the end of Chapter 3.

CHAPTER 3

Electromigration

Electromigration can be described as mass transfer in a conductor due to momentum exchange from carriers to ions in the lattice. It was first studied in the late fifties [149] but rose in prominence as the main cause behind the failure of integrated circuits (IC) after their deployment in the sixties. As all atomic migrations in a crystal are controlled by fairly high activation energies E_A (~1 eV for most metals) [150], the high current densities *J* needed for electromigration could not be achieved in conventional wires due to melting caused by Joule heating. Indeed, a single electron, traveling in a conductor between two scattering events, will gain an average amount of energy expressed as:

$$E_{e^-} = \rho e J l \tag{3.1}$$

where ρ is the resistivity, *e* the unit charge $1.602 \cdot 10^{-19}$ C, and *l* is the electron mean free path. As ρ for common metals is of the order $10^{-6} \Omega \text{cm}$ and *l* is of the order of tens or hundreds of nm, from Eq. (3.1) it can be concluded that very high *J* (of the order of $10^4 - 10^7 \frac{\text{A}}{\text{cm}^2}$) are needed to match the energy of atomic diffusion.

Early IC's, with 10 mm lead widths [151] and film thicknesses of several 100 nm, were the first "wires" that dissipated heat well enough to reach sufficiently high current densities for electromigration to set in before melting, as the intimate contact between film and substrate and their large surface-to-volume ratio make heat evacuation quite efficient. Leading microchip manufacturer IBM is estimated to have spent over 8 billion US dollars¹ in the sixties combating the problem [151]. Early fixes included electromigration resistant Au - Cu alloys and thicker films, but electromigration remains a major concern in IC design even today. Many advances in understanding, preventing and utilizing electromigration have been made over the years, not only in simple metals, but also in alloys, interstitials, solid solutions [152] and complex oxides (see Sec. 3.2).

In this chapter we will present a brief literature review on electromigration, starting with the extensively studied elemental metals and finishing with a focused look on the effect in YBCO and related

¹Adjusted for inflation from 1966 to 2020 using the provided data for the consumer price index for all urban consumers in the month of March of the US Bureau of Labor Statistics for the respective years.

perovskite-like materials.

3.1 Physical Background

Electromigration is most likely to occur in materials with positive temperature coefficients of resistance, that is in metallic conductors. These materials both have large carrier concentrations and respond to temperature increase by increasing scattering event frequency, instead of promoting further electrons to their conduction bands. Accordingly, Huntington and Grone [153] used manually indented gold tapes (cooled at the electrodes to room temperature) to study mass flux during electromigration in metals, which was more recently reviewed by Lloyd [154].



Figure 3.1. Sketch of the forces acting on an atom in an electromigration process. F_E indicates the force on the positive ion exerted by the electric field and F_{wind} corresponds to the average force produced by the momentum transfer of the electron-ion collision. The atom upstream from the vacancy has a lowered activation energy for movement downstream and will do so when the total force reaches sufficient values.

The activation energy for atomic diffusion is significantly reduced at grain boundaries, defects and vacancies [155], making these sites more favorable for atomic movement. In the absence of any temperature, concentration or stress gradients to cause diffusion, mass exchange is random in all directions (net momentum is zero). Under applied current, electrons flow from cathode to anode with an average energy according to Eq. (3.1) and will upon scattering transfer their momentum to an atom (ion). If that atom is on an appropriate position in the crystal lattice, next to an imperfection, it is susceptible to move downstream. Electromigration, a stochastic effect, does not only occur when $E_{e^-} \ge E_A$. On a local scale, an atom might already be above their minimum energy due to thermal vibrations and electrons might transfer only the reminder of the energy requirement for diffusion.

The average force that is experienced by an atom from the momentum of moving electrons colliding with it, the electron wind force [156], is opposed by the applied field (the ion is charged), as shown in Fig. 3.1. As both these forces are functions of the electric field *E*, the resulting total can be expressed as:

$$F = F_{\text{wind}} - F_E = q^* E \tag{3.2}$$

where q^* is the effective charge and *E* is the applied field. As $E = \rho J$ and taking q^* to be equal to Z^*e , Huntington [157] gives the total electromigration force:

$$F = Z^* e \rho J \tag{3.3}$$

where *e* is the elemental charge, ρ the resistivity, *J* the current density. The effective valence² Z^* , a term indicating the magnitude and direction of the momentum exchange [158], is given as:

$$Z^* = \frac{1}{2} \frac{\rho_d N}{\rho N_d} \frac{m^*}{|m^*|}$$
(3.4)

with ρ_d the specific defect resistivity given by $\rho_d = |m^*|/ne^2\tau_d$ with *n* the electron density and τ_d their relaxation time after momentum transfer with a point defect [153]. ρ is the metal resistivity, *N* the metal ion density, N_d the density of defects and m^* the effective mass of the carriers participating in the momentum exchange. The sign of Eq. (3.3) is controlled via the sign of the charge carriers (contained in m^* , which is negative for holes).

Considering carrier movement in the lattice as damped through scattering we can treat the force as proportional to drift velocity v (instead of acceleration in an undamped medium). Using this we express the carrier mobility μ as a function of force $\mu = \frac{v}{E}$ and the drift velocity due to electromigration v_{EM} as:

$$\nu_{EM} = \mu Z^* e \rho J \tag{3.5}$$

Diffusion is a thermally activated process and we can therefore apply Einstein's relation between the diffusivity coefficient *D* of a charged particle, mobility in the medium and temperature $D = \mu k_B T$ (k_B the Boltzmann constant) to get:

$$\nu_{EM} = D \frac{Z^* e \rho J}{k_B T} \tag{3.6}$$

and the vacancy flux Θ_V is expressed using the vacancy concentration c_V :

$$\Theta_V = -c_V v_{EM} = -c_V D \frac{Z^* e \rho J}{k_B T}$$
(3.7)

Soon after Huntington and Grone's work Bosvieux and Friedel [159] published an analytic study of perturbation through momentum transfer from carriers to defects in a metal lattice under applied current. They have found matching results to those of Huntington and Grone for the case of a point defect-like interstitial in the lattice, within the assumptions of their model.

An infinitely long and perfectly homogeneous conductor (with invariant Θ_V) would never fail due to electromigration, as vacancy accumulation only occurs on sites of flux divergence. In real samples these sites are easily identified as imperfections in the crystal (impurities, vacancies, grain boundaries, *etc.*), surfaces and interfaces between materials. Specifically contacts and electrode surfaces are favorable positions for EM damage. Materials with electron majority carriers accumulate voids at the cathode [155] while those with a majority of holes wear at the anode, as shown in Fig 3.2. Reversal of the current reverses the mass flux [160] making partial healing effects possible in many materials [161].

Blech *et al.* [160, 162] were the first to study the mechanical effects of electromigration by mapping the stresses experienced by *Al* thin films on *TiN* substrates using X-ray topography. They have shown that the sample experiences strain as a consequence of the mass transport, with stress being compressive

²The term "effective valence" is a known misnomer, as it does not relate to the valence state.



Figure 3.2. Flux divergence always occurs on material interfaces and electron conducting metals will accumulate material near the anode and deplete it close to the cathode. This leads to both a vacancy concentration gradient and mechanical strain in the material.

at the anode and tensile in the cathode region, as shown in Fig. 3.2. Compression of a part of a crystal mechanically drives vacancies away, as compensation for the exerted stresses. For the same reason, vacancies diffuse towards areas of tensile stress (as atoms are pushed away). In other words, the tendency towards thermal equilibrium directs vacancy diffusion towards areas of tensile stress. This explains why voids form before hillocks, as thermal stresses in real samples tend to be tensile.

In an attempt to formalize the above scenario, the vacancy concentration gradient $\frac{\partial c_V}{\partial x}$ should be taken into consideration with the expression in Eq. (3.7) and the total mass flux Θ_m can now be written:

$$\Theta_m = D\left(\frac{\partial c_V}{\partial x} - c_V \frac{Z^* e\rho J}{k_B T}\right)$$
(3.8)

We can express the time dependency of the system using the continuity equation:

$$\frac{\partial c_V}{\partial t} = \frac{\partial \Theta_m}{\partial x} \tag{3.9}$$

The diffusivity *D* is also a function of temperature following Arrhenius' kinetics $D = D_0 e^{\frac{-E_A}{k_b T}}$. This is important to keep in mind when considering the effect temperature has on the continuity equation:

$$\frac{\partial c_V}{\partial t} = \left. \frac{\partial \Theta_m}{\partial x} \right|_T + \left. \frac{\partial \Theta_m}{\partial T} \right|_x \frac{\partial T}{\partial x} \tag{3.10}$$

The continuity equation above indicates that the effects of temperature gradients may play as important a role as the effects of concentration gradients in the material. As Joule heating in the material is proportional to J, and heat removal from the sample is proportional to the surface-to-volume ratio, changes in conductor cross-section are expected to cause the largest divergence of Θ_m .

J. R. Black [163] conducted one of the most important empirical studies on electromigration and has found that the mean time of failure for a conductor wire susceptible to electromigration is inversely proportional to the current density. Black's equation behaves as a half-life for any number of deployed micro-conductor wires and is more recently given [154] as:

$$t_{\frac{1}{2}} = A J^{-n} e^{\frac{\Delta H}{k_B T}} \tag{3.11}$$

where $t_{\frac{1}{2}}$ is the median time of failure, ΔH is an experimentally determined activation energy and the preexponential factor *A* is empirically determined and a function of the wire cross-section and temperature [164]. The current exponent *n* is 2 in most cases [165] as it models for void nucleation mechanisms, but it has been shown to be closer to 1 in cases where electromigration is controlled by defect growth [166] (*e.g.*, very narrow bridges) instead of nucleation.

Blech *et al.* [167, 168] have also shown that the concentration gradient and mechanical backstress from material build-up result in a threshold product of Jx (x being stripe length) below which electromigration halts at equilibrium. The product is proportional to the pre-exponential factor in Eq. (3.11) [164] (*e.g.* an *Al* stripe under 1 $\frac{MA}{cm^2}$ will not suffer electromigration damage if shorter than 30 µm). This critical stripe length is known as Blech's length and is a very important consideration in modern IC design for protection against electromigration.

Many other researchers have proposed more specific and detailed models for electromigration in metals [169–172]. The recent paper by de Orio *et al.* [164] offers a good overview of the models of electromigration including more recent software-driven numerical models used in the semiconductor industry.

Considering for the effects of electromigration in designing microcircuitry will stay important until a room temperature superconductor compatible with semiconductor technology emerges [151]. From a research perspective, Eq. (3.10) tells us that the narrowest constrictions we can fabricate in a device (which will also have the highest temperature gradients) will be the first position where atoms will migrate. This allows for precise experimental schemes to study the effect further in material specific applications.

3.2 Selective Electromigration in Oxides

Electromigration is not solely limited to metallic conductors and their derivatives, as the effect has been observed in a number of other materials. Transition metal oxides represent a special case for consideration, due to the significant difference in the diffusivities of the various atomic species in the material. Notable examples are ruthenates, titanates [173], manganates [174], vanadates [175] and cuprates [64].

Considering how diffusion is facilitated by vacancies in a crystal and the special vacancy preference for the chain-oxygen position in YBCO (as elaborated in Sec. 2.1.1) it is expected that atomic migration in this compound will be dominated by oxygen transport. This is crucial for mechanical considerations, as in this situation mass flux is selective to only one of the species, drastically reducing the possibility for void and hillock formation. Instead, what is observed is oxygen stoichiometry change between different regions of the wire under electromigration, eventually resulting in conductivity change without significant topological changes (see Sec. 2.3.1).

Initial studies [176, 177] in YBCO samples were carried out soon after the discovery of high- T_c superconductivity in cuprates, confirming that oxygen movement dominates electromigration in YBCO. The first bulk study by Govinda Rajan *et al.* [176] carried out at 473 K, with low current densities (50
$\frac{A}{cm^2}$) and over long periods of time (30 days) reported decomposition of their samples at the anode and composition change at the cathode, leading the authors conclude that oxygen movement is directed towards the cathode. The first (c-aligned) thin film study done soon after by Vitta *et al.* [177], carried out in the superconducting state (86 K), at very high current densities, seemed to confirm the previous findings about the direction of oxygen movement and reported copper movement following the redistribution of oxygen. Both of these studies showed oxygen anion movement towards the cathode, which will contrast with later studies. This discrepancy can be somewhat explained by the fact that the bulk material study was carried out at elevated temperatures and low current densities, while the thin film was studied in the superconducting state (main carriers are electrons, not holes).

Moeckly *et al.* [64, 178–183] were the first to thoroughly study electromigration in YBCO giving more insight into the actual direction of movement for vacancies and atoms. The researchers have initially shown [178] with simple electrical characterization that two different regimes exist for YBCO: at current densities below a threshold (~5 $\frac{A}{cm^2}$), microbridge conductivity is improved, while higher *J* results in vacancy accumulation in the constriction (decreasing the conductivity). Furthermore, the authors have also estimated the activation energy needed for oxygen migration (~0.8 eV), and have shown the filamentary structure of the disordered regions after electromigration. The authors have also shown that degraded samples can at least partially be healed by heating in an oxygen atmosphere, while simple heating of fresh samples does not degrade them significantly without applying current.

In Ref. [64] preliminary micro-Raman characterization has shown that the movement of the oxygen anion is, in fact, towards the anode during above-threshold electromigration, as seen from their optical images in Fig. 3.3. Moeckly and his collaborators [180, 181] also studied the behavior of the superconducting weak links resulting from the filamentary growth of the disordered region during electromigration, providing further information needed to model the effects of electromigration in YBCO.



Figure 3.3. Electromigration in YBCO is selective towards the oxygen in the basal *CuO* chains of the material. As electromigration progresses it gives rise to a deoxygenated region on the cathode (right) side of the observed constriction. YBCO with larger δ is more reflective creating optical contrast. Image series, taken from [64], shows optical microscopy images taken during progressive electromigration of a YBCO constriction.

The use of electrical fields to cause electromigration in $YBa_2Cu_3O_{7-\delta}$ was then studied by applying

voltages (~1-3 V, several nA current) using the metal cladding of a near-field scanning optical microscope as a tunneling electrode. Huerth *et al.* [182, 183] made use of the correlation between reflectivity and oxygen vacancy concentration to estimate the compositional change following electromigration. As oxygen exchange across grain boundaries is quite limited, the authors conclude that electrostatic effects alone can not account for the effect, as the applied field spreads across these boundaries whereas current transport is limited. They note the importance of hot electrons ($E_{e^-} > 1 \text{ eV}$), and suggest a mechanism in which collisions between them and the oxygen atoms can break bonds (or promote electrons to antibonding orbitals). This, in turn, causes electromigration whenever the atom is properly placed close to an imperfection and if the relaxation time of the excitation is long enough for the displacement to actually occur.

Healing of degraded materials can be achieved in oxide conductors just as in metallic ones, and improvement of superconductive properties can be achieved with the effect as has been shown recently by Baumans *et al.* [161] for $La_{2-x}Ce_xCuO_4$ (LCCO)³. In another study [184] on YBCO, the authors have shown that the temperature dependence of the electromigration threshold current density $J_{EM}(T)$ intersects with the dependence of the superconductive critical current density $J_c(T)$ at a temperature T^* . This means that for temperatures below T^* the electromigration threshold will be crossed before the material accesses it's dissipative superconductive state, leading to material degradation.

3.3 Applications

Although the initial motivation for the study of electromigration was increasing the longevity of consumer electronics, more recent approaches have somewhat turned to the application of the phenomenon for nanofabrication and material research and functionalization.

Electromigrative mass flux in metals has been used in fabricating nanogaps and nanoconstrictions [185, 186], where special consideration needs to be given to heat diffusion in order to control the process. The resulting constrictions and gaps can be used as host sites for molecular electronics [187]. The different electrical quantum states in tiny conductor contacts become accessible if their sizes are comparable to the electron De Broglie wavelength, offering a potentially fruitful via of study for both computing applications and fundamental research. Such constrictions have been demonstrated using electromigration [188, 189]. Using nanogaps fabricated by electromigration has also been shown to be viable for fabrication of various devices on chips, for example directional light emitting antennas [190], or very fine DC SQUID's [191].

Various properties of superconductors have been shown to be controllable by electromigration. Baumans *et al.* [192] have shown that electromigrating superconducting bridges can change the nature of the phase slips occurring in superconductors, from thermal to quantum. Additionally, conventional and unconventional superconductors with degraded properties can be at least partially healed through bias reversal as shown for *Al*, *Nb* and LCCO in [161]. Another interesting application is the fabrication of superconducting weak links using EM, as shown by Lombardo *et al.* [193] for *Nb*. As functional oxides can exchange oxygen across interfaces, tuning of magnetic properties of layered structures has also been demonstrated using electromigration [174].

³LCCO also shows a vacancy preference for the oxygen position, see reference.

One of the most obvious effects achievable by EM is changing the resistance of conductors, either by opening and closing gaps (metals) [194, 195], or by changing the composition of the material (oxides) [196]. This effect (resistive switching) is promising for a number of applications (*e.g.* non-volatile bits, transistors [197] and memristors [198]) and has been demonstrated in a number of materials [199].

The special case of Mott insulating oxides provides another special aspect of resistive switching demonstrated for transition metal oxides in general [200] and perovskites in particular [201–203]. Such effects have recently been demonstrated in electrochemically gated YBCO devices by Palau *et al.* [145], showing very effective resistance retention across cycles and a probable oxygen exchange between the material and the electrolyte. The nature of the interaction of the electric field and oxide materials is most probably explained by invoking oxygen vacancy movement, as electrostatic effects alone can not account for the large change in properties in these materials. This has been theoretically shown in a $SrTiO_3/SrRuO_3$ multilayer structure via first-principle calculations by Jeon *et al.* [173].

3.3.1 Control

The stochastic nature of electromigration makes process control somewhat difficult. Maintaining appropriate current densities during the process is not straightforward and often relies on software-controlled feedback loops and incremental adjustments. In a situation where *J* is incrementally increased in an observed junction by increasing the source current (current-controlled electromigration), like in most experimental and fabrication techniques, Joule heating will increase the local resistance even before the electromigration threshold is reached. After electromigration, that is either caused by gap formation (metals) or stoichiometry change (oxides). Increased junction resistance R_j increases junction Joule heating ($P \propto I^2 R$, with *P* being heating power) creating a positive feedback loop that can result in excessive heating, melting and breaking if not taken into consideration in experiment design. To avoid this, the time evolution of R_j is monitored and kept at a steady pace with software loops designed to compensate for excessive heating (thermal runaway) by adjusting the level of applied current in real time. These considerations are absent if electromigration is achieved through short current pulses (allowing the junction to cool between pulses), which can be very useful in determining the onset of electromigration.

In order to avoid thermal effects (melting, deoxygenation, etc.), a very slow increase in the applied voltage, and consequently current is preferred to avoid exponential resistance increase. Therefore, a constant value of dR_j/dt or dG_j/dt (t being time and G conductance) is needed for electromigration to stay under control, and is usually represented by a process variable p. This variable is usually given as some function of the junction resistance, with variations intended to better model the behavior of the complete circuit involved in the process.

Furthermore, selecting a point where the electromigration is to be halted can be difficult, again due to the stochastic nature of the material. Seemingly identical samples may fail after different process times and have varying threshold values. One approach that has been implemented by Zharinov *et al.* [204] is defining a critical conductance value at which the process is to be stopped. The software resulting from the authors work is used in the experimental section of this work and will be explained in detail in the following chapter.

3.4 Frontiers

In view of the broad versatility that electromigration offers in fabrication technologies, it could eventually take part in device manufacture if appropriate control can be achieved on a large scale. While study of EM control remains of primarily academic interest, it might become an interesting approach to achieve material healing or switching, both of which require current alternation. Mastering even just direct electromigration may open the possibility of achieving very small lead sizes in microelectronics application, and the fabrication of previously unachievable devices (based around nanogaps) for novel applications (see Sec 3.3).

The prospect of non-volatile bits based on electromigrative switching with much greater stability and reduced power cost compared to semiconductor flash memories has already piqued the interest of the electronics industry. While these devices do not have commercial applications as of yet, they seem to be good candidates for the next generation of random access memories.

The properties of high- T_c (and conventional) superconductors have been reproducibly controlled with electromigration to some extent, allowing for switching between superconducting and normal states of the material. This has important implications for fundamental research and may hold promise for future application. Using electromigration as a fabrication technique could be of useful for the fabrication of SQUID's and other devices made of superconducting materials and their composites. Electromigration allows for more precise control of constriction size and chemistry, and a number of geometries and functional structures can be imagined through the application of the technique to induce change in certain regions of a superconductor.

The modern perspective on electromigration as more than a simple inconvenience in device application has steadily been gaining momentum in the last twenty years. There is hope for further understanding to come from studying the effect in more different and diverse materials.

CHAPTER 4

Experimental Details

The electromigration and photoexcitation of over 15 individual YBCO constrictions was studied in this work, using a number of electrical measurements and observation techniques. All studied samples were fabricated in the facilities available to A. Palau's group at ICMAB¹, Bellaterra, Spain. The experimental data was acquired either in the facilities of EPNM², ULiège (single- and multi-terminal transport, magneto-optical imaging, scanning electron microscopy, optical microscopy, all photoexcitation and relaxation trials) or ICMAB, Bellaterra (high magnetic field transport and Hall measurements, micro-Raman characterization). This chapter offers a description of all used samples and experimental techniques.



Figure 4.1. **a**) Schematic representation of the used single constriction sample geometry. Illustrated circuitry corresponds to the current source in an electromigration experiment. **b**) Complete sample layout including the bonding pads of the single constriction devices. **c**) Schema of a triple constriction device. **d**) Optical microscope image of a whole triple constriction device with visible *Ag* bonding pads (dark). **e**) Scanning electron microscope image of a pristine device with the triple constriction design.

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²Experimental Physics of Nanostructured Materials

4.1 Microstructured YBCO thin films

Two sample geometries have been studied: devices with a single constriction as shown in Fig. 4.1a) and multi-terminal devices with three constrictions in series as shown in Fig. 4.1c) and e). The complete sample layout with the contact pads for the single constriction is shown in Fig. 4.1b) and for the multi-terminal device in Fig. 4.1d). The samples were *c*-axis aligned YBCO films with 100 nm thicknesses grown on $LaAlO_3$ (lanthanum aluminate, LAO) single crystal substrates. All used devices exhibit a clear metal-to-superconductor transition at ~87-90 K (transition width ≤ 1 K) after microstructuring.

Single Constriction Device

Single constriction devices were grown via chemical solution deposition as described in Ref. [76]. In this method, an anhydrous alcohol solution of the trifluoroacetates of *Y*, *Ba* and *Cu* is prepared, then dried to powder form in a controlled atmosphere before combustion. The trifluoroacetates deposit homogeneous powders that can be sintered to give high quality films, and the method avoids the creation of the insoluble carbonate of barium. After combustion at medium temperatures the remaining powder is a mixture of the oxides and fluorides of the metals (notably, BaF_3) which is then sintered with controlled oxygen partial pressure and substrate temperature to give well aligned films.

The deposited films are patterned using UV photolithography in poly(methyl methacrylate) (PMMA), as seen in Fig. 4.2. After PMMA development, feature definition was done with a reactive ion etch in *Ar* plasma. 200 × 200 μ m² bonding pads were sputtered with 200 nm of *Ag* and annealed under oxygen at 450 °C to reduce contact resistance. The bridges of these samples were ~1-2 μ m wide and ~2-3 μ m long. Perpendicular voltage leads were patterned on one side of the constriction as shown in Fig. 4.1**a**).

Triple Constriction Device

The second layout consists of three constrictions connected in series with the innermost dimensions (width×length) being 1 μ m × 5 μ m and the outer ones 3 μ m × 10 μ m. All constrictions are accessible from both sides with voltage terminals, making for a total of 8 voltage connections to the constrictions and enabling both transport and Hall effect measurements. A scanning electron microscopy of the three bridges is shown in Fig. 4.1e).

Samples in this design were fabricated using pulsed laser deposition wherein a prefabricated YBCO target is hit with energetic laser radiation in a vacuum chamber and the scattered metal ions are directed towards a cooled substrate, where they deposit. This method controls both the film quality and crystallographic orientation in one step. The targets were prepared with conventional solid state methods. Device patterning was done via reactive ion etching in *Ar* plasma. Silver contacts were sputtered on the connection pads to 200 nm thickness and subsequently annealed at 450 °C to ensure Ohmic contacts.

4.2 Low Temperature Experiments

In view of the fact that we are interested in the evolution of the superconducting state after electromigration, it is essential to be able to access cryogenic conditions with variable temperature. The Montana Instruments commercial closed-cycle helium cryostation of EPNM located at the Faculty of



Figure 4.2. Illustration of the sample etching process. A 100 nm-thick film of *c*-aligned YBCO is deposited on a LAO substrate **a**). PMMA is applied as a photoresist **b**) and is lithographed. The irradiated section of the PMMA becomes soluble to the developing solvent (PMMA is a positive resist). The soluble PMMA is lifted with a developer solvent **c**). The PMMA layer protects the YBCO below it from ion bombardment during reactive ion etching **d**), which leaves the desired geometry in the film. Finally, the remaining PMMA is lifted with a stronger solvent leaving only the patterned YBCO **e**) on the substrate.

Physics (ULiège) was used for these purposes. An overview of the disjointed sample holder of the system, a feature that allows optical access in cryogenic conditions is shown in Fig. 4.3.

Several window stages serve as protection against radiation and thermal exchange around the sample. A good thermal coupling between the sample, the chipholder and the sample mount is essential during the whole experiment. This is achieved by securing the chip to the chipholder via silver paint (SPI supplies, Conductive silver paint) as a contact and a glue, and by applying small amount of appropriate vacuum grease (Apiezon N with a thermal conductivity of $0.1 \text{ Wm}^{-1}\text{K}^{-1}$) between the chipholder and the sample stage. The sample stage is made of oxygen-free high thermal conductivity copper (C101) with a thermal conductivity of $630 \text{ Wm}^{-1}\text{K}^{-1}$. The system can settle at a minimum 3.5 K and stay relatively stable up to 200 K (10 mK stability). The refrigeration system is based on a Grifford-McMahon cycle.



Figure 4.3. Schematic representation of the cooling stage of the Montana Instruments closed-cycle helium cryostat used for the low temperature experiments in this study. Reproduced from Ref. [205].

The samples investigated at ICMAB, Bellaterra, Spain were measured in a commercial Quantum Design physical property measurement system (PPMS), which also includes current and magnetic field sources, as well as characterization equipment. This instrument allows for better temperature stability, has a higher cooling power and higher magnetic field capabilities than the cryostat used in ULiège.

4.3 Imaging

A number of imaging techniques have been used to asses sample quality and electromigration effects: optical, magneto-optical, scanning electron and micro-Raman microscopies were performed.

4.3.1 Optical Microscopy

Optical microscopies were performed either at cryogenic conditions or on the cryostat sample mount at room temperature, using a Olympus BXFM modular microscope mounted with a digital camera. The microscope is operated with a *Hg* lamp through a green filter, a light polarizer, and an analyser on the ocular end. An objective with 50× magnification was used for maximum imaging resolution. This lens has a numerical aperture of 0.5 (polar angle $\theta = 30^\circ$) and a working distance of 10.6 mm.



Figure 4.4. Illustration of the two applied optical imaging modes and their distinction. In bright field mode **a**) all of the incident light (red arrow) is allowed to the imaged surface and reflected photons (blue arrow) are collected indiscriminately. In dark field mode **b**) a shield is used to allow only a part of the incident beam to impinge on the surface at a higher angle. The photons collected in this scenario need to have a higher scattering angle, giving a better image of surface roughness and texture at the cost of image brightness.

The system allows to perform imaging in bright field and dark field modes, as shown in Fig. 4.4. In the bright field mode most of the light reflected from the surface is collected indiscriminately. It should be noted that the light is polarized before impinging on the sample and the operator can place an analyser (precision 0.1°) on the ocular side to select the collected light polarization. Bright field imaging gives a good visual inspection of the surface. The alternative, dark field mode, offers the possibility of selectively collecting the light that scatters with a higher incident angle (by blocking the middle of the incident

ray). Collecting only the scattered photons that traveled along the edge of the incident light cone before impingement gives a darker image but the acquired image is weighted towards topological contrast. This is because the topological imperfections on the sample surface are the sites that scatter the most light.

4.3.2 Magneto-Optical Imaging

Magneto-optical imaging (MOI), which allows for visual inspection of the magnetic field expulsion in a superconductor as shown in Ref. [206], was performed on all used samples. Herein, an indicator crystal (*Bi* doped yttrium iron garnet, $Y_3Fe_5O_{12}$) is positioned over the superconductor. The optically active layer is 3 μ m thick and has in plane magnetic domains. Linearly polarized light passing through this film is rotated by an angle proportional to the local magnetic field. The indicator is grown on a 450 μ m thick $Gd_3Ga_5O_{12}$ glass substrate and is covered with a 100 nm thin film of *Al* serving as a mirror, as schematically shown in Fig. 4.5. Using the optical microscopy setup described in Sec. 4.3.1 polarized light is cast on the indicator, reflected on the mirror and is collected with the analyser set to a perpendicular direction to the initial polarization. This way, the intensity of the reflected light is a function of the local magnetic field B_z perpendicular to the plane of the sample. The pixel size in the used system is 1.468 ×1.468 μ m².



Figure 4.5. Illustration of the working principle of employed the magneto-optical imaging technique. An indicator crystal, *Bi* doped yttrium iron garnet grown on a transparent substrate and covered with a metallic mirror, is positioned over the sample. Polarized light is cast through the structure. The polarization plane of the light is rotated, according to the Faraday effect, by the local magnetization of the indicator crystal which in turn is dependent on the local magnetization of the sample below it. By applying a magnetic field on a superconducting sample, this technique allows the direct imaging of magnetic field expulsion.

As given in Ref. [206], magnetic fields can be distinguished to a resolution of 10 μ T and the spatial resolution of the method is proportional to the distance between the sample and the indicator crystal. In usual mounting conditions this amounts to a spatial resolution between 2 and 10 μ m. The system is calibrated above the T_c of the sample, and operated at low temperatures to access the superconducting state. The maximum applied field, limited by the available instrumentation to 5 mT, needs to stay below the saturation value of the indicator which is μ_0 H ~ 100 mT.

4.3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is employed to obtain high resolution visualizations of the nanoscale features of the investigated devices before and after electromigration. To that end, the Raith Pioneer Two Electron Beam Lithography System of the EPNM group was used. The instrument has multiple available detector lenses, an electron gun with acceleration voltages of up to 30 kV and can apply probing currents from 3 pA to 20 nA.



Figure 4.6. Simplified illustration of the working principle of the performed scanning electron microscopies. **a**) Schematic of the most important parts of the SEM. The system is operated in vacuum. Electrons are ejected from a heated filament in the electron gun using an operator controlled acceleration voltage in the acceleration column. Further along the beam path the electrons get focused using an array of condensers, magnetic and electrostatic lenses before finally impinging on the sample. The beam is moved in the scanning plane with additional scanning coils (not pictured) and the response of the detectors is recorded for all positions. Two detectors were employed in the measurements, the InLens detector (blue accent) is positioned inside the lens and the Everhart-Thornley (SE2) detector (red accent) is at an angle. The former collects electrons with higher energies. **b**) Illustration of an electron path through the interaction volume with six inelastic and one elastic scattering. Only secondary electrons (SE) emitted close to the sample surface can be detected, as SE energy is generally insufficient to traverse more than several atomic layers. SE emitted after initial forward scattering of the primary electrons (SE1) have relatively high energy and are detected with the InLens detector. The lower energy secondary electrons (SE2) emitted after scattering of a backscattered electron (BSE) on its way out of the sample are collected by the Everhart-Thornley detector. In a scanning electron microscope electrons are ejected from a (Joule) heated *W* filament using a column of acceleration coils. The energy that is imposed on the electrons is proportional to the voltage in the column. The electron beam is focused using condenser coils, magnetic and electrostatic lenses before impinging on the sample surface as shown in Fig. 4.6**a**).

Incident (primary) electrons have very high energies and scatter on the atoms of the sample. If they scatter transferring a portion of their energy to an atom, they excite it³ causing it to emit a secondary electron (SE) with lower range and energy (2-50 eV). Such, inelastic events occur more frequently than elastic scatterings in which the kinetic energy of the primary electrons is mostly preserved, but the scattering angle is large (backscattering). An example of a primary electron path through the interaction volume is given in Fig. 4.6b). Secondary electrons can not leave the sample bulk due to their low energies, and only those emitted close to the sample surface get collected by the detectors. The electrons that get emitted or backscattered can be detected using various detection systems tuned to electron energy and angle. The sample can be moved in the plane and scanning coils (not pictured) are used to recording the detected signal for every pixel of an observed frame, by incrementally moving the incident beam. Insulating samples can accumulate charge on the surface leading to faulty imaging, and some samples need to be covered with a thin metallic film to increase the number of SE emissions to make imaging possible.

The Pioneer Two was operated with two detectors. The primary detector (InLens, SE1) is located inside the lens with the primary electron beam and collects secondary electrons emitted with relatively high energies (SE1) from initial forward scattering events, as shown with blue accent in Fig. 4.6**b**). The InLens detector has no large volumetric depth and is best for visualizing sample surfaces. The second detector (Everhart-Thornley⁴, SE2) is located outside the electron beam lens and collects secondary electrons emitted with lower energies (shown with red accent in Fig. 4.6**b**). These are electrons that were emitted close to the surface after scattering of a backscattered primary electron (SE2). The SE2 detector can be understood as providing volumetric information about the sample.

The SE2 detector of the Pioneer Two offers a resolution in the range of 10's of nm. It is surpassed by the InLens detector which has a resolution in the nm range. The actual performance is dependent on a given sample's material composition.

4.3.4 Micro-Raman Microscopy

Micro-Raman microscopy, a spatially resolved variant of Raman spectroscopy, was used in order to get the best available chemical quantification of the oxygen distribution in the constrictions after an electromigration process. The technique is based on inelastic scattering of light with matter (Raman scattering) that results in a change in both light direction and polarization. Delicate optical systems need to be arranged to discern the Raman shifted photons from those coming from elastic (Rayleigh) scattering. The energy (frequency) shift between the laser and the detected light is correlated to its corresponding (molecular or crystal) excitation. In the case of a solid state system this excitation corresponds to a

³Excited atoms also radiate X-rays or emit Auger electrons after secondary electron emission, and many setups allow for qualitative analysis of SEM images using respective spectroscopies. Details are omitted from the text for simplicity.

⁴The working principle of the Everhart-Thornley detector is that of conversion of the electron signal to light using a scintillator and applying a photomultiplier to amplify the normally low signal of lower energy secondary electrons (SE2). The SE2 are collected using a positive voltage in front of the scintillator.

phonon. Infra-red and visible light is usually employed, but other wavelengths may become appropriate in various systems. The technique is similar to general infra-red spectroscopy, albeit more specific to the anisotropic (Raman) vibrations of a system.

The micro-Raman experiments were performed at IMB-CNM⁵, a sister facility of ICMAB, in the clean room available to G. Rius. The used instrument was a Xplora Horiba Jobin-Yvon micro-Raman spectrometer equipped with a digital detector. A 532 nm laser line was used for excitation by focusing it to 1 μ m², at a power of 1 mW, using a 100× magnification lens.

As the Raman spectrum of YBCO is well known (see Sec. 2.1.1), the 500 cm⁻¹ peak in the spectrum was used for characterization of δ . With decreasing δ content, the peak is downshifted and we can, to some extent, quantify the oxygen distribution in the material.

4.4 Electromigration and Electrical Characterization

All electrical measurements were performed in the Kelvin 4-terminal geometry, as shown in Fig. 4.7**d**). Herein the current is supplied across the outer wires and the voltage is measured across inner wires. In this way, the resistance of the circuit and most of the sample is not recorded, and only the part of the sample between the inner wires gives a signal. As almost no current flows through the inner wires⁶, very low absolute resistances can be measured with ease due to lower noise and overall circuit impedance. Additionally, resistance vs. temperature responses measured were obtained using a more sophisticated AC setup. Herein, the driving voltage is supplied across the feed wires using a AC current source (Keithley 6221A) which also communicates a phase-reference signal to the phase-locked amplifiers that perform the sensing. The amplifiers (SRS830 DSP) are digital instruments that transform incoming AC signals into amplified digital DC responses, but only on the AC frequencies locked-in by the reference from the source as shown with the thin line in 4.7**a**). In this manner a very large amount of noise can be rejected from the measurement and low noise electrical characterization can be performed. This configuration was also used for all photoexcitation and relaxation trials. All resistance measurements were performed with currents between 10 and 50 μ A.

Electromigration was controlled via the software protocol described below in Sec. 4.4.3. The DC voltage source used was a Keithley 2440 and the nanovoltmeter a Keithley 2162A. All electrical sources and sensors used for characterization in ICMAB's Quantum Design PPMS were part of the system itself.

4.4.1 Noise Considerations

Any electrical measurement is subject to noise, be it from environmental influences or the circuit itself. For an invariant system, the sensor (voltmeter) will measure its measurand (voltage) at a value oscillating around an average. This is due to noise influences and limited experimental resolution. By recording how the voltage changes over time V(t) and performing a Fourier transform into frequency space we can express the distribution of the spectral power density S_{ω} (in $\frac{V^2}{H_2}$) as:

$$S_{\omega} = \frac{dV^2(\omega)}{d\omega} \tag{4.1}$$

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⁶Using a high-impedance voltmeter or amplifier allows for measurements with insignificant current flow through the sensing wires.



Figure 4.7. Electrical experimental procedures used in this study. **a**) The temperature-resistance response is measured using an AC current source and three phase locked amplifiers as the voltmeters. Temperature control is achieved using the the Montana Instruments cryostation described in Sec. 4.2. A similar circuit was used in the PPMS measurements with a DC feed and nanovoltmeters instead of lock-in amplifiers. **b**) Electromigration is performed at 105 K using a DC voltage source and a nanovoltmeter recording only the innermost bridge. Hall coefficient measurements performed in ICMAB's PPMS using the transverse voltage pads across the innermost constriction are shown in **c**). Characterization is done in the DC regime (magnetic field applied perpendicular to the plane of the sample) and temperature control is achieved using the PPMS' own cryogenic equipment. **d**) A general Kelvin 4-terminal circuit for measuring resistance.

It naturally follows that the distribution of S_{ω} can be sharpened by reducing the measured bandwidth - the range of frequencies included in the registered signal. Indeed, the root mean square voltage noise $V_{\rm rms}$ for a given measurement bandwidth Δv is given as:

$$V_{\rm rms} = \sqrt{S_\omega \cdot \Delta \nu} \tag{4.2}$$

White noise is defined as noise that has invariant spectral power across all frequencies. Other noises are described in literature but will not have bearing on the study at hand. The $V_{\rm rms}$ described above is most useful in studying the noise coming from the circuit. Noise coming from the environment, *e.g.* urban, industrial and cosmic background radiation, is lessened by shielding the sensor.

Several types of noise need to be considered in circuits like the ones in Fig. 4.7. Thermal noise, also referred to as Johnson-Nyquist noise, is present in all electrical circuits above zero temperature due to thermal agitation of carriers. The S_{ω} of thermal noise can be expressed as:

$$S_{\omega} = 4k_B T R \tag{4.3}$$

It follows that Johnson-Nyquist noise is a function of temperature, and will be on the level of nanovolts in the low temperature experiments performed in this study.

Furthermore, current fluctuations appear in a real conductor under applied voltage due to the microscopic nature of the carriers and the crystal. This noise, while white, is distinct from thermal noise

and not a function of temperature. It is of little importance if the current is above the nA range and for small measurement bandwidths, and is expressed as:

$$S_{\omega} = 2eRV_{\rm avg} \tag{4.4}$$

where V_{avg} is the average applied voltage. This kind of noise, due to it's independence on temperature, can become the dominant noise mechanism at very low temperatures.

Lastly, flicker noise is originating from a more complex mechanism dependent on impurities, parasitic carrier recombinations, etc. The S_{ω} of flicker noise is ill-defined, but clearly a function of the applied currents frequency along $S_{\omega} \propto \frac{1}{\nu}$. It is of little consequence in AC measurements, is not a white noise, and is sometimes referred to as "1/*f*" noise due to its frequency dependence.

4.4.2 Sample Handling

In order to perform the described measurements the sample chip must be secured to a sample holder compatible with the experiment setup and bonded with thin *Al* wires to electrical contacts. The sample holder itself consists of a gold-plated square receptacle that is secured into a printed circuit board (PCB) mount with connection pads and pins, as shown in Fig. 4.8 **a**). The PCB mount is home-made to fit both the sample stage in the Montana Instruments cryostation and the bonding platform shown in Fig. 4.8 **b**) and **c**), which also doubles as the storage stage for the sample when it is bonded, but not mounted in the cryostation. Gold contacts in the PCB lead to a total of 16 available pins used as electrical contacts.



Figure 4.8. Equipment for sample handling. **a**) A sample secured on the gold plated receptacle within its PCB mount. **b**) A side view of the bonding platform, with BNC connectors and the dedicated ground connector visible. A top view of the bonding platform is shown in **c**). Reproduced from Ref. [205].

As very small devices tend to be delicate and susceptible to breaking due to any electrostatic discharge (ESD), certain measures needed to be adopted to be able to avoid sample failure. This includes making sure that all bonds on a sample, once it is connected to its holder, stay at the same ground. This approach of avoiding ESD by common ground levels across all instruments and the device is often referred to as the make-before-break (MBB) approach. Fortunately, as YBCO is quite resistive in comparison with metallic devices, it tends to be slightly more resilient to ESD breakage. However, this does not mean that

no samples were killed by ESD during this study, making repeat measurements part of the laboratory experience. Samples that are not connected electrically to their holders do not fail due to ESD.

The MBB approach starts with the wire-bonding of the device. The bonding was performed using EPNM's iBond5000 Series wire-bonder of Kulicke and Soffa. The sample is secured to the receptacle with silver paint to make a good contact, and is put into the bonding stage. The bonding stage is grounded to the same level as the wire-bonder and end-caps (sample-to-ground connections) are inserted into the stage. The sample is then bonded, usually with six bonds (two feed wires and four measurement wires for three 4-terminal measurements) to the gold leads on the PCB. *Al* is used for the contact wires and bonding is performed using a vibrating needle, positioned using a microscope.

When not in use, a small current (nA range) is passed through the bonded sample in the bonding stage, in order to secure it against ground spikes.

For transport, the sample is kept in the bonding stage with inserted ground caps. The same MBR guidelines are kept in place during sample mounting into the cryostation, with all parts of the system being kept at the same ground. Additionally, a grounded air ionizer is used to make sure that no ESD happens during the short time the sample spends floating in the air between bonding stage and cryostation stage. Naturally, the operator is grounded using a metallic wristband connected to the same ground. After the sample is mounted and all shields are in place, a switching board is used to separate the sample from the coaxial connectors used for the instrumentation. Only after all instruments (again on the same ground) are connected is the switch turned and an electrical contact is established between instrumentation and the device. All sensor wiring is done using Bayonet Nelli-Concelman (BNC) coaxial cables, which are well shielded against magnetic and electrical interference.

4.4.3 Data Acquisition Software

Most experimental procedures and all data acquisition was performed using software assistance.

Basic optical, scanning electron and micro-Raman microscopies were performed using the proprietary software provided by the instrumentation manufacturers. Additionally, numerous home-made experimental algorithms programmed in National Instruments (NI) LabVIEW graphical programming environment were used. The virtual instruments (VI) for electrical characterization in EPNM were created by G. Shaw. The electromigration VI, elaborated on below, is produced by Zharinov *et al.* [204] as mentioned in Sec 3.3.1.

Individual sources and sensors are connected to the operator computer using the general purpose interface bus (GPIB) standard, and are issued commands using the standard commands for programmable instruments (SCPI) syntax, interpreted by LabVIEW. Microscopic image analysis is performed using FIJI (an open-source repackaging of ImageJ). Data analysis was performed primarily in Spyder (Python 2.7) and Origin and sporadically in GNU Octave and SciDAVis. Raster image processing was performed in the GNU image manipulation program (GIMP) and vector image processing in Inkscape. Data animation was performed using MATLAB.

Electromigration Control

Electromigration runs were performed using a LabVIEW VI representative of the study in Ref. [204]. Herein a software controlled proportional-integral-derivative (PID) feedback loop is applied to the EM control scheme for continuous current modulation. In a PID scheme, the time evolution of a declared process variable (p) is monitored and compared to a declared setpoint value (of dp/dt) by incrementally calculating an error and adjusting the control variable to keep p as close to the setpoint as possible.



Figure 4.9. Flow chart algorithm of the electromigration process with control variable U and process variable p, as described in the text. The applied bias is adjusted to keep p as close to the desired setpoint as possible, by minimizing the error $e(t) = p - p_{setpoint}$. Two distinct functions are applied depending on whether the error condition is met, or not. f_{PID} is the regular PID increase function, while f_{nl} is the non-linear corrective response. $\epsilon(t)$ is the RMS noise, k a numerical constant and N a counter variable. Taken from Ref. [204].

In Zharinov's scheme the declared process variable is $-(dG_j/dt)/G_j$, where G_j is the junction conductance equal to $\sigma/(\rho l)$ (σ is cross-section and l is junction length). The reasoning for this selection is that the mass flux Θ_m is proportional to the change in cross-section over total cross-section. Additionally, using conductance as a process variable allows the use of quantum conductance G_0 ($G_0 = \frac{2e^2}{h}$) as a normalization factor. This makes sense for the metallic junctions in their study but does not completely align with the samples considered here, whose cross-section does not change during the process. However, the resistivity ρ of the studied YBCO junctions does change, and as it also controls the conductance of the junction, the same schema can be applied.

The control variable is the applied voltage (U), and the PID feedback loop follows the algorithm presented in Fig. 4.9. The VI halts the electromigration automatically upon reaching a threshold value of G_j , set by the operator. U is incrementally increased while monitoring p. The error condition, also manually set by the operator, serves the purpose of hindering uncontrolled electromigration by comparing p to the setpoint.

The process itself has two distinct phases. Below the electromigration threshold J_{EM} resistance increase is gradual and due to Joule heating. This initial phase can last hours before the needed current density is reached in a controlled manner. After passing the threshold and electromigration initiation the control parameter is incrementally decreased to maintain a steady mass flux out of the junction.

CHAPTER 5

Results and Discussion

As already anticipated in **Ch. 4**, the investigated superconducting samples are YBCO thin films, patterned to form narrow bridges with two different designs as shown in Fig. 5.1a),b). In all cases the narrowest section of the transport bridges was ~1-2 μ m wide. Fig. 5.1c) shows an optical microscopy image of an entire device and Fig. 5.1d) shows the associated magneto-optical image for the same device obtained at *T* = 4.5 K and $\mu_0 H$ = 0.95 mT. This image evidences the magnetic flux expulsion from the superconducting parts of the sample with bright green areas corresponding to high magnetic fields and dark regions representing low magnetic fields. The homogeneity of the magnetic flux expulsion is a strong indication of the high quality of the YBCO film, confirming its excellent superconducting behavior and absence of macroscopic defects.



Figure 5.1. Scanning electron microscopy images of a single YBCO constriction **a**) and a symmetric three-bridges structure **b**). Electromigration takes place in between voltage contacts where the current density reaches its maximum value. In **a**) the narrowest point of the bow-tie structure is 1 μ m wide. In **b**) the central bridge is 0.8 μ m wide and the two symmetrical arranged side bridges are 3 μ m wide. Panel **c**) shows an optical microscopy image of the entire device. In panel **d**) a magneto-optical image obtained at T = 4.5 K and $\mu_0 H = 0.95$ mT for the device in panel **c**), is shown.

As described in Sec. 4.4.3, the electromigration (EM) process in the constrictions was induced by ramping up the voltage bias while simultaneously monitoring the change in conductance dG/dt. A typical resistance-current curve, R(I), obtained at $T = 105 \text{ K} > T_c$ for the sample of Fig. 5.1a) is shown in Fig. 5.2. At low currents, i.e. within the range between point **pristine** and point **A**, the R(I) exhibits a smooth increase mainly due to Joule heating effects. This section of the curve is nearly reversible. At about 12 mA, corresponding to a current density $J \approx 8 \text{ MA/cm}^2$, a change of sign in the slope indicates that electromigration has been launched, as suggested by the fact that less current is needed to increase the resistance.



Figure 5.2. Resistance of a YBCO device as a function of the circulating current during an electromigration process. The time evolution of the measurement is indicated by the black arrows. The initial temperature in the pristine state is 105 K and increases up to \sim 400 K at point **A**. Controlled feedback operates from point **A** on avoiding thermal runaway. Inset: current circulating through the sample as a function of time during the electromigration process shown in the main panel.

It is worth stressing that although these measurements have been done at constant bath temperature, the local temperature at the constriction can be substantially higher. Using the R(T) dependence of the pristine sample as a thermometer we can roughly estimate the local temperature at point **A** as $T_{loc} \sim 400$ K. This value represents an underestimation reliable only for currents lower than point **A**. Above this point the stoichiometry of the sample changes and a new calibration would be needed for each data point. For the sake of comparison, YBCO decomposition temperature, i.e. the onset of melting, takes place around 1000 °C [16], recrystallization is observed ca. 800 °C [77, 81], while oxygen loss can start already around 400 °C [80]. As elaborated in **Ch. 3**, the combination of high temperatures and large current density is expected to induce directed diffusion of oxygen atoms. In order to unveil this effect, we resort to optical imaging at cryogenic conditions.

5.1 Direct Visualization of Oxygen Migration

Fig. 5.3 shows false colored differential optical microscopy images obtained at 105 K and revealing the evolution of the affected area (darker region) due to electromigration. The labels correspond to the points indicated in Fig. 5.2. The superposed white curve delineates the borders of the transport bridge. The

electromigrated region can also be evidenced in bright-field optical images since the creation of oxygen deficient zones in YBCO films results in increased reflectivity (see text below) [35, 64]. Note that the change of optical response is directional towards the cathode side (-), and therefore cannot be attributed to the symmetrically spread Joule heating. The holes flow from right to left in the same direction than the drift of oxygen vacancies (i.e. towards the cathode). A close inspection to the optical intensity from the affected area actually shows a mixture of high intensity and low intensity spots indicating a rather inhomogeneous redistribution of oxygen vacancies.



Figure 5.3. Differential images showing the evolution of the front of the affected region for an applied current running from right to left as indicated in panel **A**. The label correspond to the points indicated in Fig. 5.2. The superposed white curve delineates the borders of the transport bridge and the vertical black arrows indicate the mean position of the propagating front.

In order to confirm that oxygen atoms are displaced out of the constricted region and correlate optical images with electrical measurements, we have intentionally redesigned the device geometry as presented in Fig. 5.1b). This structure consists of a narrow central bridge symmetrically surrounded by wider bridges, each bridge individually addressable by corresponding voltage contacts. In Fig. 5.4a) we plot the normalized resistance R(T)/R(200 K) as a function of temperature for the three bridges when the sample is in its pristine state. For the sake of clarity, we have indicated with red color the left bridge, green for the central bridge, and blue for the right bridge. The normalized resistance allows us a direct comparison between the central and the side bridges, being the absolute resistance of the central bridge a factor 3.25 higher than the side bridges as expected from geometrical considerations. The perfect overlap of the normalized resistance curves demonstrates that the lateral structuring of the YBCO film has no effect on the superconducting transition and the resistivity of the film. In other words, the pristine sample behaves as a monolithic structure with uniform composition and electrical response. In the rest of the manuscript

we will keep R(200 K) for the pristine sample as the normalization factor.



Figure 5.4. Normalized resistance R(T)/R(200 K) as a function of temperature for the central bridge (green), left bridge (red), and right bridge (blue) for the sample in the pristine state **a**) and after electromigration **b**). The inset in panel **a**) shows a scanning electron microscopy image of the three bridges connected in series, indicating the color code of the voltage signal acquired and the polarity of the current source. The labels **A** and **C** correspond to anode and cathode, respectively. In panel **b**), the universal response for the pristine sample is replotted with black dots. Inset in panel **b**): polarized microscopy image obtained after substantial electromigration process (see App. A.1). The affected area on the cathode side is clearly visible as a bright region starting from the central bridge and extending deep into the current leads to the left.

A strikingly different electrical response is observed after electromigrating the sample as shown in Fig. 5.4b). Similarly as for the device in Fig. 5.3, the polarity of the voltage bias during electromigration corresponds to cathode (-) on the left side and anode (+) on the right side. In order to facilitate the observation of the change in response, in Fig. 5.4b) we replot the universal R(T)/R(200 K) for the pristine sample with black data points. The left and central bridges exhibit a radically different R(T) response. The left bridge shows a substantial increase of the normal state resistance and a clear suppression of superconducting critical temperature. Remarkably, the central bridge still exhibits a superconducting transition at ~ 30 K with a low temperature phase corresponding to a dissipative state and a higher normal state resistance with respect to the initial state. The right bridge remains nearly unaffected with respect to the initial state. Further electromigration (see App. A.1) leads to a full suppression of the superconducting condensate in the left bridge and, more interestingly, to a decrease of the normal state resistance in the right bridge without affecting T_c . There are few observations that worth pointing out here, (i) the superconducting transitions at the left and central bridges exhibit broad distributions $\delta T_c \sim$ 20 K reinforcing the idea of a highly inhomogeneous state as proposed in Ref. [178]; (ii) a clear transition at 90 K remains visible for the affected bridges, indicating that part of the bridge has not been modified by the electromigration process.

An optical microscopy image taken at the end of the extended electromigration process described in App. A.1 is shown as an inset in Fig. 5.4**b**). This image has been taken at 105 K in bright field with the analyzer at its optimal contrast. The affected area on the cathode side is clearly visible as a bright region starting from the middle bridge and extending deep into the current leads to the left. The optical properties of YBCO have been investigated in Ref.[30, 35, 207, 208]. On the one hand, Kircher et al. [35] reported a decrease of reflectance with increasing oxygen content for the electric field parallel to the crystallographic a axis, whereas an increase in reflectance occurs for the electric field parallel to the c axis. On the other hand, far field measurements of c-axis normal films show an increase of reflectivity where oxygen content has been depleted. According to this interpretation, higher reflectivity on the cathode side is indicative of an increase in oxygen vacancies, in agreement with the scenario proposed above.

5.2 Fine Tuning of Oxygen Doping by Electromigration

Precise tuning of the oxygen diffusion through the sample may be achieved by applying subsequent electromigration runs in order to progressively increase the oxygen vacancy concentration on the central and left bridges. Fig. 5.5**a**) shows the evolution of the critical temperature obtained for the three bridges (right, left and central with data points colored according the sketch in the inset) and after four sequential electromigration runs. In addition, Fig. 5.5**b**) shows the evolution of the carrier density, *n*, obtained from Hall measurements using transverse voltage contacts located at the edges of the central bridge as illustrated in the inset.



Figure 5.5. Evolution of the critical temperature T_c **a**) and the carrier density, n **b**) at different regions of the YBCO constriction. The color code of the data points corresponds to the signal picked up at the colored regions in the insets. For the sake of clarity the numbering indicates the voltage contacts addressed in each measurement.

The observed dependence of both T_c and carrier density is fully consistent with the interpretation corresponding to oxygen atoms diffusion towards the anode and oxygen vacancies flow towards the cathode during the EM process. In other words, δ increases on the cathode (-) side and decreases on the anode (+) side. This scenario naturally accounts for the suppression of T_c and reduction of the carrier density on the cathode side. Note that the carrier density exhibits a slight increase on the anode side (blue points) consistent with the scenario where oxygen atoms replenish some vacancies and with the observation of a decrease of normal state resistance on the anode side after several EM steps.

It is interesting to use the information presented in Fig. 5.5 in order to estimate the hole doping p, i.e. the number of holes per copper atom in the CuO_2 planes. Hole doping is a parameter of paramount importance determining the critical temperature of the cuprates for which the $T_c(p)$ and $p(\delta)$ dependences have been experimentally estimated in Ref. [92], as discussed in Sec. 2.3.1. In Fig. 5.6 we reproduce the data from Ref. [92] together with the $T_c(n)$ obtained from the electromigration measurements presented in Fig. 5.5. In view of the fact that T_c and n have been probed at different parts of the bridge, in Fig. 5.5 we plot the average critical temperature between left and central bridges as a function of the carrier density inferred from the left Hall cross. The good agreement between the two independently determined experimental data points encourage us to propose the present method as an appealing approach to fine tune the doping level in cuprates for eventually obtaining a detail mapping of the electronic phases in these materials.



Figure 5.6. Superconducting critical temperature as function of the carrier density and hole doping estimated from the current-induced oxygen migration (filled squares). For the sake of comparison, we reproduce the data from Ref. [92] (empty squares).

Compelling evidence that EM selectively displaces oxygen atoms has been obtained from micro-Raman scattering. This technique enables the local quantification of oxygen content along the YBCO constriction after different electromigration runs [209], as explained in Sec. 2.1.1. Orange points in Fig. 5.7**a**) show the spots where the micro-Raman signal has been collected together with the numbering used for indicating those locations. The Raman shift in the 500 cm⁻¹ mode accounts for the *c*-axis motion of the oxygen atoms [O(4)] bridging the CuO chains and CuO_2 planes [52, 210] (see App. A.3). This relationship originates from the variation of the *c*-cell parameter with δ (Sec. 2.1.1). Indeed, an expansion of the unit cell occurs (increase of the *c*-parameter) when the oxygen content x= 7- δ decreases and therefore the frequency of the O(4) phonon is shifted downwards with a linear dependence on *x*, as a result of bond softening [29, 210]. Fig. 5.7**b**)-**d**) display the evolution of the O(4) phonon frequency measured for three different cases corresponding to the pristine state **b**) and after two successive EM runs **c**)-**d**). For the pristine state (black points) a phonon frequency value of 502 cm⁻¹ is observed, consistent with an optimally doped homogeneous track with an oxygen content of *x*=6.95.



Figure 5.7. O(4) phonon mode frequency measured along the linear scan displayed in panel **a**), for the pristine state and after reaching two different EM states (applied current 16 mA), together with the extracted oxygen content. The center of the constriction is marked with a dotted line. The error bar in the phonon frequency is 2 cm⁻¹ and displayed only for the pristine sample.

After performing controlled electromigration up to 16 mA (EM-1 state) the linear Raman scan across the constriction shows a large down shift of the apical oxygen mode frequency from 502 cm⁻¹ to 490 cm⁻¹, at the central and part of the left side of the bridge. This shift is consistent with a region of

depleted oxygen content, $x \sim 6.65$ towards the cathode. A slight increase in the O(4) phonon frequency is observed at the right side of the bridge confirming a reduction in the amount of mobile oxygen vacancies and consequently, a possible enhancement in the oxygen doping. After subsequent electromigration process with the same current amplitude (EM-2 state), the Raman scan (orange squares), indicates an enlargement of the oxygen depleted region towards the left side of the bridge, consistent with an enlargement of the region where oxygen vacancies are created.

5.3 Photoexcitation

An elegant way to probe the induced inhomogeneous oxygen distribution can be achieved through photoexcitation effects. Indeed, it has been previously shown that illuminating oxygen deficient YBCO films, (i) decreases the normal state resistivity and increases T_c , (ii) changes their carrier density as well as carrier mobility, and (iii) a long relaxation time, of the order of days at room temperature, is observed once the illumination is turned off [130]. More importantly, there is a clear correlation between the oxygen content and the relative change in the resistivity produced by the photoexcitation. More precisely, the lower the T_c of the sample, the larger the relative change in the resistivity [211]. The essential mechanism behind this effect implies the photodoping of the CuO_2 planes by electron-hole pair excitation involving two possible scenarios for the electron trapping mechanism, namely photoassisted oxygen ordering [131] and trapping at oxygen vacancies [212]. These effects were discussed in Sec. 2.3.4.

Fig. 5.8 summarizes our findings after continuous illumination with 550 nm wavelength on an already electromigrated sample (similar to the state shown in the inset of Fig. 5.4**b**)). A direct comparison with the response of the sample without illumination shows that photoexcitation leads to an increase of T_c and reduction of the normal state resistivity at the left and central bridges, consistent with the premise of oxygen depletion in these zones. In contrast to that, for the oxygen rich side (right bridge), the critical temperature remains unchanged whereas the normal state resistivity increases. Note that sample heating due to the illumination process cannot explain a decrease of resistance as observed in the central and left bridges.



Figure 5.8. Normalized resistance R(T)/R(200 K) for the left **a**), central **b**), and right **c**) bridges before (black) and after (white) illumination. Note the different vertical scale range in each panel.

Let us now investigate the time evolution of the photo-induced changes in conductivity in the central

bridge before and after electromigration. Fig. 5.9 shows the percentage change of the central bridge resistance with respect to the initial value R_0 as a function of time. The main panel shows that the pristine sample exhibits no resistance change during illumination at 200 K (yellow squares) whereas after creating an oxygen-deficient region by electromigration, a clear photodoping is observed (black circles). At this temperature, the induced photoconductivity is persistent and no relaxation is observed. By increasing the temperature to room temperature (inset Fig. 5.9 and turning off the illumination) the photoenhanced state exhibits a very slow relaxation process. All these findings are in agreement with the investigations performed in oxygen-deficient YBCO samples by Markowitsch *et al.* [124] and others [125, 127].



Figure 5.9. Percentage change of the central bridge resistance with respect to the initial value as a function of time. The main panel shows that the pristine sample exhibits no resistance change during illumination at 200 K (yellow squares) whereas after electromigration clear photodoping is observed (black circles). Inset: At room temperature and switching off the illumination, the photoexcited sample can relax back to the original state in a much longer time scale.

5.4 Anti-Electromigration

One particularly appealing aspect that could situate voltage-controlled electromigration as a privileged tool of choice for tuning the oxygen content, is the possibility to heal a previously electromigrated sample, by simply inverting the direction of the drive (anti-electromigration). Although this technique seems to work fairly well for elemental materials[161, 194, 195, 213–215], its success in YBCO has shown to be rather limited [184]. In order to illustrate this effect, starting from the EM sample (inset of Fig. 5.4**b**)) we invert the polarity of the voltage in such a way that now the right bridge corresponds to the cathode side and the left bridge to the anode side. Subsequently, we run an anti-electromigration while simultaneously acquiring optical images. A selected set of these images is presented in Fig. 5.10**a**)-**f**) while panel **g**) shows the evolution of R(I) during the EM process. A more in-depth image analysis can be found in App. A.2, as well as SEM images of the junction. At first sight, these images confirm that the previously affected areas due to the EM are not recovered by the anti-EM process. Instead, a new affected region of depleted oxygen extends toward the right (cathode) side. A closer look into the data actually



Figure 5.10. **a)-f)** Optical microscopy images showing the progression of the oxygen depleted zones (bright) during the anti-electromigration process. The time elapsed between consecutive images is about 15 minutes. **g)** Resistance of the central bridge of a YBCO device as a function of the circulating current during the anti-electromigration process. The label (R, I) in panel **a)-f**) can be identified in this curve. **h**),**i**) Differential images illustrating the partial healing (black spots) due to anti-electromigration on a previously affected area by electromigration. The grey curve is a guide to the eye delineating the transport bridge.

reveals some partial healing effect. By taking differential images, i.e. subtracting consecutive images (Fig. 5.10**h**),**i**), one can clearly see a pair of dark (oxygen rich) and bright (oxygen depleted) zones. In other words, the initial affected area caused the EM shows partial healing during anti-EM. However, this healing effect seems to take place in a restricted zone suggesting loss of oxygen from the sample.

Experimental measurement of oxygen tracer diffusion in the a - b plane of single-crystal YBCO [36] suggests an activation energy of 0.97 ± 0.03 eV for the oxygen atoms whereas the in-plane oxygen diffusion constant has been measured to be $D = 1.4 \times 10^4 \exp(-0.97 \text{ eV}/k_B T) \mu \text{m}^2/\text{s}$. As we anticipated above, the local temperature during the EM can be higher than 700 K for which $D \sim 1.45 \times 10^{-3} \mu \text{m}^2/\text{s}$. For the images in Fig. 5.10 the sample was exposed to electrical stress during $\tau = 5000$ s, thus giving a diffusion length $L = \sqrt{D\tau} \sim 2.6 \mu \text{m}$ whereas the actual experimental progression in the time scale of the experiment is about 30 μm . Several effects can be invoked to justify this discrepancy. Firstly, complementary measurements [37] have indicated that the diffusion constant D_b for oxygen motion along the crystallographic *b* axis is at least 100 times larger than the diffusion has been reported in Ref. [145] resulting from the applied electric field. Thirdly, oxygen motion is accelerated by defects such as twin boundaries and/or grain boundaries.

CHAPTER 6

Conclusion and Outlook

To summarize, we have demonstrated the possibility to locally deoxygenate $YBa_2Cu_3O_{7-\delta}$ by applying high current densities *J* in the normal state. The proposed approach complements the widely investigated gate-induced electric field effect in this material. Progressive current-stimulated oxygen diffusion is shown to enable tuning of $\delta(J)$ resulting in rather inhomogeneous distributions of oxygen vacancies. We provide experimental evidence through Hall measurements, micro-Raman and photoconductivity investigations, that the electromigration process allows a selective placement of oxygen atoms. The induced stoichiometry modulations become more stable (i.e. irreversible) as the excess current with respect to the onset of electromigration, increases. The affected areas can be directly visualized by optical and electronic microscopy. This method represents a powerful alternative to fine tune locally the charge carrier density in cuprates.

Considering the fact that the final state after electromigration consists of a disordered material composed of a network of superconductive filaments embedded in a non superconductive matrix, it will require the fabrication of very narrow bridges to isolate a single filament. It would be interesting to carry out similar investigations in untwinned YBCO films [216] and YBCO films deposited on miscut substrates [217] with bridges oriented at several angles with respect to the in-plane crystallographic axis. This would allow to probe the two order of magnitude difference in oxygen diffusion expected between the *a* and *b* axes. The combined effect of current-induced and electric field-effect oxygen diffusion may also be worth investigating in view of applications such as memory switching devices with improved performances.

Looking beyond just YBCO, other complex oxides have the potential to display similar selective migration and photoexcitation effects under applied current. In particular, it might be worth investigating related compounds, *e.g.* Pr_2CuO_4 for which a selective control of volatile and nonvolatile superconductivity has been recently demonstrated via ion-liquid gating [218]. On the other hand, it would be an interesting via to studying the effect of EM on magnetic perovskite-like structures, such as $La_{1-x}Sr_xMnO_3$, to be able to tune the magnetic response through current. Understanding both the effects of the chemical nature of the compound and its structure on the selective migration of its ions might open the door to interesting new functionalities.

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Appendices

APPENDIX A

Additional Results

A.1 Resistance Changes after Substantial Electromigration

Fig. 5.4b) shows the change in resistance for the three bridges connected in series after a gentle electromigration process. When the electromigration is continued further, more radical changes are observed with respect to the pristine sample. Fig. A.1 shows the normalized resistance obtained in the left, central, and right bridges after substantial electromigration. The inset shows an optical image of the final state after this electromigration process. Note that the resistivity of the right bridge has substantially decreased with respect to the pristine sample.



Figure A.1. Normalized resistance R(T)/R(200 K) for the left (red), middle (green), and right (blue) bridges. For the sake of comparison, the universal response for the pristine sample (shown in Figure 5.4) is replotted here with black dots. The inset shows an optical image of the final state after the electromigration process.

A.2 SEM Imagining of the Electromigration Modifications

In order to further assess the changes produced by the electromigration process, we carried out *ex situ* optical and electron microscopy imaging. Figure A.2 shows dark field **a**) and bright field **b**) optical microscopy image without analyzer and illuminated with polarized light. Dark field imaging permits to collect scattered light and thus reveals the surface roughness (Sec. 4.3.1). The fact that the modification of the material is not evidenced by this method seems to indicate that no morphological changes have occurred to the sample. In contrast to that, bright field imaging which is related to the reflectivity of the sample clearly unveils the change of conductivity of the affected regions.

Scanning electron microscopy images collected by In Lens secondary electron (SE) detector and Everhart-Thornley detector, are shown in panel c) and d) respectively (Acceleration voltage 5 kV, aperture size 30 μ m, and working distance 6 mm). The In Lens detector collects mainly secondary electrons which are generated near the upper region of the interaction volume and therefore provide direct information on the sample's surface. No morphological changes are seen in these images. However, the region affected by EM is clearly revealed with bright contrast, indicating an excess of secondary electron emission. Since conductive materials give a high SE yield, one may be led to conclude that the affected regions are more conducting, in contradiction to the initial interpretation based on optical images. However, care should be exerted when interpreting contrast in SEM images [219] which can result from (i) the difference in atomic number of the specimens because the atomic number is related to the penetration depth of conductive specimens for electron irradiation, (ii) strongly depend on the charging effect, (iii) work function modifications, or many other effects [220]. Nevertheless, it is worth emphasizing that the changes observed in the InLens SEM images cannot be ascribed to thermal effects due to Joule heating otherwise the voltage contacts should have been also affected, which is not the case. More precisely, clear filamentary and highly inhomogeneous modifications of the material are observed in the InLens SEM images, in agreement with the discussion of the electrical measurement presented above.



Figure A.2. Dark field **a**) and bright field **b**) optical microscopy image without analyzer and illuminated with polarized light. Scanning electron microscopy images collected by InLens secondary electron detector **c**) and Everhart-Thornley detector **d**).

A.3 Raman Spectra

Figure A.3 shows some representative Raman spectra, obtained for different oxygen doping levels. It is clearly observed that the O(4) phonon mode is shifted to lower frequencies as the oxygen content is reduced. The in-phase O(2,3) mode at 435 cm⁻¹ is not easily observed in optimally doped spectra due to its temperature dependence, which makes it weak at room temperature [221]. However, its intensity increases in the oxygen deficient regions which allow disorder induced $q \neq 0$ scattering to be observed in the Raman experiments [52].



Figure A.3. **a**)-**d**) Typical room temperature micro-Raman spectra obtained at different spots along the transport bridge as indicated by the colored circles in panel **e**). Panel **a'**)-**d'**) show a zoom in of the data presented panel **a**)-**d**). The spectrum in panel **a**) corresponds to the pristine sample whereas those in panels **b**)-**d**) correspond to the electromigrated sample. **f**) Optically active Raman modes along the crystallographic c axis for YBCO. The apical *O*(4) Ag phonon mode occurs at 500 cm⁻¹.