Direct Visualization of Current-Stimulated Oxygen Migration in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films

Stefan Marinković,[†] Alejandro Fernández-Rodríguez,[‡] Simon Collienne,[†] Sylvain Blanco Alvarez,[†] Sorin Melinte,[¶] Boris Maiorov,[§] Gemma Rius,^{||} Xavier Granados,[‡] Narcís Mestres,[‡] Anna Palau,^{*,‡} and Alejandro V. Silhanek^{*,†}

[†]*Experimental Physics of Nanostructured Materials, Q-MAT, CESAM, Université de Liège, B-4000 Sart Tilman, Belgium*

[‡]*Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC, Campus UAB, 08193 Bellaterra, Spain*

[¶]*Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium*

[§]*Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

^{||}*Institute of Microelectronics of Barcelona (IMB-CNM, CSIC), Campus UAB, 08193 Bellaterra, Spain*

E-mail: palau@icmab.es; asilhanek@uliege.be

Abstract

The last years have witnessed major 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. In this work, we focus on the investigation of oxygen doping in an extended region through current-stimulated oxygen migration in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting bridges. The underlying methodology is rather simple and avoiding sophisticated 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 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 of cuprates involves diffusion of oxygen atoms with the applied current. The resulting fine control of the oxygen content would permit a systematic study of complex phase diagrams and the design of electrically addressable devices.

Keywords

electromigration, ybco, superconducting nanoconstrictions, memristor, high-*tc* superconductor

The physics of copper oxide superconductors continues to be one the most fascinating scientific topics since their discovery in the late 80's.¹ This notoriety can be arguably attributed to a superconducting transition temperature greatly exceeding those of any known superconductor at room pressure, the plethora of unconventional electronic phases and the yet unsettled origin of the pairing mechanism.² It is not uncommon that slight changes in the stoichiometry of complex oxides lead to large variations of its properties. The interplay 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 challenge to precisely control the oxygen stoichiometry and consequently to establish an accurate phase diagram.³ 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 leading priority in superconductor science.⁴

In this work, we explore the possibility to tune the oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) by mass-selective migration of oxygen atoms induced by large electrical 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.⁵ For instance, the crystalline structure of YBCO changes from orthorhombic to tetragonal, while the c -axis lattice parameter increases by lowering the oxygen content.

Results and Discussion

Electromigration process

The investigated superconducting samples are YBCO thin films, patterned to form narrow bridges with two different designs as shown in Figure 1(a,b). In all cases the narrowest section of the transport bridges was $\sim 1\text{-}2\ \mu\text{m}$ wide. Figure 1(c) shows an optical microscopy image of an entire device and Figure 1(d) shows the associated magneto-optical image for the same device obtained at $T = 4.5\ \text{K}$ and $\mu_0 H = 0.95\ \text{mT}$. This image evidences the magnetic flux expulsion from the superconducting parts of the sample with bright blue 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 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 $1 \mu\text{m}$ wide. In (b) the central bridge is $0.8 \mu\text{m}$ wide and the two symmetrical arranged side bridges are $3 \mu\text{m}$ wide. Panel (c) shows an optical microscopy image of the entire device. Inset: cross-section at the voltage pad showing the epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ film grown on a LaAlO_3 single crystal substrate and Ag electrodes. In panel (d) a magneto-optical image obtained at $T = 4.5 \text{ K}$ and $\mu_0 H = 0.95 \text{ mT}$ for the device in panel (c) is shown.

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 Figure 1(a) is shown in Figure 2(a). At low currents, *i.e.* within the range between point pristine and point A, the $R(I)$ exhibits a smooth nearly reversible increase mainly due to Joule heating effects. At about 12 mA , corresponding to a current density $J \approx 8 \text{ MAcm}^{-2}$, 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. The inset in Figure 2(a) shows the time evolution of the circulating current through the sample which takes place on the scale

of several hours.

Note that although these measurements have been done at constant bath temperature, the local temperature at the constriction can be substantially higher. Using finite element simulations we can estimate the local temperature at point A as $T_{\text{loc}} \sim 525$ K (see Supporting Information). This value represents an estimation 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 1273 K,⁶ recrystallisation is observed ca. 1073 K,^{7,8} oxygen loss starts at around 673 K⁹ while oxygen movement and ordering is present at even lower temperatures.¹⁰ Therefore, the combination of high temperature and high current density is expected to induce directed diffusion of oxygen atoms.

Using neutron diffraction on samples with varying δ , Jorgensen *et al.*⁵ and others¹¹ have shown that the vacancies in the orthorhombic superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system clearly prefer the O(1) position in the copper chains, thereby tuning the Cu(1)-O(4)-Cu(1) bond lengths and the doping levels in the CuO₂ planes (see Supporting Information for the labeling of the atomic sites). This means that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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)-VO lattice, where VO are the vacancies at the O(1) site position. It is known that vacant sites, rather than interstitials, are involved in the diffusion of oxygen atoms most likely following a O(1)-VO-O(1) hopping path. More details on the vacancy mechanism of oxygen diffusion in the CuO chains can be found in Ref.¹²

Direct visualization of oxygen migration

In order to unveil the directed migration of oxygen atoms, we resort to optical imaging at cryogenic conditions. Figure 2(b) shows false coloured differential optical microscopy images obtained at 105 K, revealing the evolution of the area affected by the electromigration (darker region). The labels correspond to the points indicated in Figure 2(a). 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).^{13,14} 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 majority charge carriers (holes) flow from right to left in the same direction as oxygen vacancies (*i.e.* towards the cathode). A close inspection of 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 2: (a) Resistance of a YBCO device similar to the one in Figure 1(a) 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 ~ 525 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. (b) 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). Positively charged oxygen vacancies move towards the cathode (-) and negatively charged oxygen atoms move towards the anode (+). The labels correspond to the points indicated in panel (a). 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 redesigned the device geometry as presented in Figure 1(b). This structure consists of a narrow central bridge symmetrically surrounded by wider bridges, each bridge individually addressable by corresponding voltage

contacts. In Figure 3(a) we plot the normalized resistance $R(T)/R(200\text{ K})$ 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 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 $R(200\text{ K})$ of the pristine sample as the normalization factor.

A strikingly different electrical response is observed after electromigrating the sample as shown in Figure 3(b). Similarly as for the device in Figure 2, 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 induced relative change, in Figure 3(b) we replot the universal $R(T)/R(200\text{ K})$ for the pristine sample with black data points. The left and central bridges exhibit a radically different trend after electromigration. The left bridge shows a substantial increase of the normal state resistance and a clear decrease of the superconducting critical temperature as well as a broadening of the transition width. Interestingly, the central bridge still exhibits a superconducting transition at $\sim 30\text{ K}$ 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 Supporting Information) 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 . Note that the superconducting transitions at the left and central bridges exhibit broad distributions $\delta T_c \sim 20\text{ K}$ reinforcing the idea of a highly inhomogeneous state, as proposed in Ref.¹⁵ In

Figure 3: Normalized resistance $R(T)/R(200\text{ K})$ 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. In panel (b), the universal response for the pristine sample is replotted with black open circles. Inset in panel (b): optical microscopy image obtained after electromigration process. 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. Evolution of the critical temperature T_c (c) and the carrier density, n (d) at different regions of the YBCO constriction. The colour code of the data points corresponds to the signal picked up at the coloured regions in the insets. For the sake of clarity the numbering indicates the voltage contacts addressed in each measurement.

addition, 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 an extended electromigration process is shown as an inset in Figure 3(b). This image was taken at 105 K in bright field with the analyzer adjusted to optimize the 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.^{13,14,16–18} Kircher *et al.*¹³ 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. In addition, far field measurements of *c*-axis normal films show an increase of reflectivity where oxygen content has been depleted.¹⁴ 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.

Precise tuning of the oxygen diffusion through the sample may be achieved by applying subsequent electromigration runs in order to progressively increase the oxygen vacancies concentration on the central and left bridges. Figure 3(c) shows the evolution of the critical temperature obtained with a low voltage criterion of 100 nV for the three bridges (right, left and central with data points coloured according the sketch in the inset) and after four sequential electromigration runs. In addition, Figure 3(d) shows the evolution of the carrier density, n , obtained from Hall measurements at 105 K using transverse voltage contacts located at the edges of the central bridge as illustrated in the inset.

The observed dependence of both T_c and carrier density is fully consistent with the interpretation corresponding to oxygen atoms diffusing towards the anode and oxygen vacancies flow towards the cathode during the EM process. In other words, the doping level 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 Figure 3 in order to estimate the hole doping p , *i.e.* the number of holes per copper atom in the CuO₂ 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.¹⁹ In Figure 4 we reproduce the data from Ref.¹⁹ together with the $T_c(n)$ obtained from the electromigration measurements presented in Figure 3(c,d). In view of the fact that T_c and n have been probed at different parts of the bridge, in Figure 4 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 fair 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. Nevertheless, care must be exerted in comparing our data obtained in thin films and with carrier density estimated from 105 K measurements, to those of Ref.¹⁹ corresponding to single crystals and with hole doping obtained at 300 K.

Compelling evidence that EM selectively displaces oxygen atoms can be obtained from micro-Raman spectrometry. This technique enables the local quantification of oxygen content along the YBCO constriction after different electromigration runs.²⁰ Green points in Figure 5(a) show the spots where the micro-Raman signal has been collected. The Raman shift in the 500 cm⁻¹ mode accounts for the c -axis motion of the apical oxygen atoms [O(4)] bridging the CuO chains and CuO₂ planes^{21,22} (see Supporting Information). This relationship originates from the variation of the c -cell parameter with δ . Indeed, an expansion of the unit cell occurs (increase of the c -parameter) when the oxygen content $x = 7 - \delta$ decreases and therefore the frequency of the O(4) phonons is shifted downwards with a linear dependence on x , as a result of bond softening.^{22,23} Figure 5(b-d) display the evolution of the O(4) phonon frequency measured for three different cases corresponding to the pristine state

Figure 4: 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.¹⁹ (empty squares).

(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 $x=6.95$.

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.

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 , and (ii) changes the carrier density as well as the carrier mobility. In addition, a long relaxation time, of the order of days at room temperature, is observed once the illumination is turned off.²⁴ 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.²⁵ The essential mechanism behind this effect implies the photodoping of the CuO₂ planes by electron-hole pair excitation involving two possible scenarios for the electron trapping mechanism, namely photoassisted oxygen ordering²⁶ and trapping at oxygen vacancies.²⁷

Figure 6(a-c) summarizes our findings after continuous illumination with 550 nm wave-

Figure 5: 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 centre 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.

length on an already electromigrated sample (similar to the state shown in the inset of Figure 3(b)). A direct comparison with the response of the sample without illumination shows that during continuous photoexcitation the transitions at ~ 90 K remain unchanged while the broad transitions at lower temperatures are enhanced. Indeed, photoexcitation leads to a slight increase of T_c (the white curve shifts to the right) and to a 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 6: Normalized resistance $R(T)/R(200\text{ K})$ 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. Panel (d) shows the percentage change of the central bridge resistance with respect to the initial value as a function of time. The pristine sample exhibits no resistance change during illumination at 200 K (empty squares) whereas after electromigration clear photodoping is observed (green 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.

Let us now investigate the time evolution of the photo-induced changes in conductivity in the central bridge before and after electromigration. Figure 6(d) shows the percentage change of the central bridge resistance with respect to the initial value R_0 as a function of time. Note 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 photo-

conductivity is persistent and no relaxation is observed. By increasing the temperature to room temperature (inset Figure 6(d)) and turning off the illumination, the photo-enhanced state undergoes a very slow relaxation process. All these findings are in agreement with the investigations performed in oxygen-deficient YBCO samples by Markowitsch *et al.*²⁸ and others.^{29,30}

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 electrical drive (anti-electromigration). Although this technique seems to work fairly well for elemental materials,^{31–36} its success in YBCO has shown to be rather limited.³⁷ In order to illustrate this effect, starting from the EM sample (inset of Figure 3(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 Figure 7(a-f) while panel (g) shows the evolution of $R(I)$ during the EM process. A complete video can be found in the Supporting Information. 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 reveals some partial healing effect. By taking differential images, *i.e.* subtracting consecutive images (Figure 7(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 by the EM shows partial healing during anti-EM. The fact that this healing effect takes place in a restricted zone might indicate loss of oxygen from the sample.

Experimental measurement of oxygen tracer diffusion in the $a - b$ plane of single-crystal YBCO³⁸ suggests an activation energy $E_0 = 0.97 \pm 0.03$ eV for the oxygen atoms whereas the

Figure 7: (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 labels (R, I) in panels (a-f) correspond to the coordinates along the $R(I)$ curve shown in panel (g). (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. Panel (j) shows simulation images of the evolution of the oxygen concentration starting from the pristine state, as the voltage is ramped up with time.

in-plane oxygen diffusion constant has been measured to be $D = 1.4 \times 10^4 \exp(-E_0/k_B T) \mu\text{m}^2\text{s}^{-1}$ with k_B the Boltzmann constant. Finite element simulations of the heat transport indicate that the local temperature during the EM can be as high as 700 K for which $D \sim 1.45 \times 10^{-3} \mu\text{m}^2\text{s}^{-1}$. For the images in Figure 7 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 $30 \mu\text{m}$. Several effects can be invoked to justify this discrepancy. Firstly, complementary measurements³⁹ 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 constant in the a direction which could account for the observed rapid diffusion. Secondly, a higher diffusion has been reported in Ref.⁴⁰ resulting from an applied electric field. Thirdly, oxygen motion is accelerated by defects such as twin boundaries and/or grain boundaries.

Modelling

Simulation of the oxygen diffusion process has been modelled by using the partial differential equation solver developed by COMSOL Multiphysics® Modeling software. We used a 2D domain with a three-bridge structure, mimicking the experimental geometry considered in the experimental pattern shown in Figure 1(b). Two top contacts were located at both ends of the simulated domain in order to electrically polarize the sample. The right contact (anode) was grounded while a step function from zero bias voltage was applied to the left contact (cathode).

In the oxygen diffusion framework we are considering two driving forces, a first one associated to the gradient of the chemical potential depending on the concentration of diffusing oxygen ions ($D\nabla c$, with D the diffusion coefficient and c the oxygen concentration) and a second one associated to the electrical field ($-\nabla V$). According to those driving forces, the evolution of the oxygen concentration at each point of the domain can be determined by the following equation :

$$\dot{c} = \nabla \cdot (D\nabla c + zuFc\nabla V), \quad (1)$$

with $z=-2$ the oxydation state of oxygen ions, u the Nernst-Einstein ratio ($u = D/RT$) with R the gas constant, and F the Faraday constant. We assume a diffusive regime in a continuous medium approximation with oxygen redistribution within the closed system but without external exchange. The effective diffusion coefficient has been considered isotropic although varying in space through the dependence of the temperature induced during the electromigration process. We assume a typical thermally activated process $D=D_0\exp(-E_0/k_B T)$, with $D_0= 1.4 \cdot 10^4 \mu\text{m}^2\text{s}^{-1}$ and $E_0 = 0.97 \text{ eV}$.³⁸ The temperature distribution along the bridge has been evaluated according to the values obtained during the electromigration process as shown in the Supporting Information. The oxygen concentration limits have been established according to the maximum ($\delta=0$) and minimum ($\delta=1$) oxygen doping, considering the volume of the limiting structures, being 66910 mol m^{-3} and 56616 mol m^{-3} , for the orthorhombic and tetragonal phases, respectively. We have started the simulations with an initial underdoped homogeneous oxygen concentration of $c_0 = 60734 \text{ mol/m}^3$ to better visualize the effect of oxygen diffusion through the channel. The electric potential is determined from the constitutive relation $\mathbf{E} = -\nabla V = \mathbf{J}/\sigma$ and the charge conservation equations $\nabla J = q$, with $\mathbf{J}$ the electric current density, σ the electric conductivity and q the electronic charge density. The electric conductivity has been directly correlated with the local oxygen concentration, using a linear function $\sigma(c) = 10^2 \text{ Sm}^{-1}$ if $c < c^*$ and $\sigma(c) = 10^2 + 632(c - c^*) \text{ Sm}^{-1}$ otherwise, which phenomenologically describes the change between the optimally doped and underdoped states. Here $c^* = 61614 \text{ mol m}^{-3}$.

Figure 7(j) shows the resulting evolution of the oxygen concentration as the voltage is ramped up with time on the left contact whereas the right one remains grounded. A complete video of the process is included in the Supporting information. As experimentally observed, oxygen vacancies flow from left to right thus generating an oxygen depleted region spreading from right part of the current leads to the middle bridge.

Conclusion

To summarize, we have demonstrated the possibility to locally deoxygenate $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by applying high current densities 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 imbedded 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 films⁴¹ and YBCO films deposited on miscut substrates⁴² with bridges oriented at different 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 resistance switching memory devices with improved performances.

Methods

Sample Fabrication. Epitaxial 100 nm thick $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films were grown with the c -axis aligned perpendicular to the film plane, either by chemical solution deposition⁴³ or

by pulsed laser deposition on LaAlO_3 single crystal substrates. For both type of deposition methods, similar results were observed and therefore no distinction have been made here. For ensuring ohmic electrical contacts, 200 nm thick Ag electrodes were sputtered and annealed by heating in an oxygen-rich environment. Films were patterned to form narrow bridges with a 4-point geometry, for both resistivity and Hall-measurements, by photo-lithography followed and dry ion-beam etching. More than 20 samples with sharp superconducting transitions at $T_c \sim 90$ K, were analyzed in this work.

Electromigration Procedure. The electromigration process was induced by a home-made software to keep the change in conductance dG/dt in a pre-set range. Details of the controlled feedback loop can be found in Ref.⁴⁴ Most of the electromigration runs have been carried out at 105 K for the ease of accessing the superconducting state ($T < 90$ K). An electromigration process performed at higher bath temperatures, besides the fact that it is triggered at lower current densities, does not provide substantial changes to the final result. The resistance of the pristine sample as a function of temperature shows a linear decrease with residual resistivity ratio $\rho(300 \text{ K})/\rho(100 \text{ K}) \approx 2.7$ and resistivity $\rho(100 \text{ K}) = 100 \mu\Omega\text{cm}$. This pronounced linear $R(T)$ dependence allows us to use the sample as a thermometer and thus estimate the local temperature during electrical stress at high current densities.

Magneto-Optical Microscopy. The optical images were obtained in cryogenic conditions with 50x magnification objective followed by a x2 magnification lens and collected in dark field mode with a continuous green illumination filtered from a Hg lamp. The microscope objective of 50x has a numerical aperture $\text{NA} = 0.50$ and working distance of 10.6 mm. The NA of 0.5 corresponds to a polar angle of $\theta = \arcsin(0.5) \approx 30^\circ$, meaning that the largest component of the electric field is in the ab -plane of the film. Direct visualization of the magnetic flux landscape was obtained by magneto-optical imaging. This technique is based on the Faraday rotation of linearly polarized light in a 3 μm -thick Bi-doped yttrium iron garnet (indicator) with in-plane magnetic domains, placed on top of the investigated sample. Since the rotation of polarization is proportional to the local magnetic field component B_z

normal to the sample plane, the use of an analyzer oriented perpendicularly to the initial direction of polarization results in images where the intensity is proportional to B_z . The images are acquired with a CCD camera and have a pixel size of $1.468 \times 1.468 \mu\text{m}^2$. Post-image processing was done to remove the inhomogeneous illumination and field-independent background, using the ImageJ software. More information about the setup can be found in Ref.⁴⁵

Hall Coefficient Measurements. Temperature-dependent resistance and Hall coefficient were measured using a physical property measurement system (PPMS, Quantum Design). Electrical contacts were made by wire bounding. The Hall coefficient was obtained at 105 K from transverse voltage between two opposing contacts, applying a magnetic field ramp from -9 T to +9 T along the c -axis. The carrier density was calculated as $n = 1/(qR_H)$, where $R_H = (t/I)dV_H/dB$, is the Hall coefficient, t the sample thickness, I is the applied current and dV_H/dB the linear slope of the Hall voltage with the magnetic field.

Raman Spectroscopy. Raman scattering experiments were performed at room temperature in the backscattering geometry using an Xplora Horiba Jobin-Yvon micro-Raman spectrometer equipped with a high sensitivity air cooled CCD (charge-coupled device) as the detector. The 532 nm laser line was used for the measurements. The incident laser beam was focused to a $1 \mu\text{m}$ spot using an $\times 100$ microscope objective on the sample. The laser power was kept below 1.0 mW to avoid laser-induced heating. The spectrometer resolution was 2 cm^{-1} . The polarization of the electric field of the incident and scattered light was kept parallel to the crystallographic a -axis of the YBCO layer.

Acknowledgement

The authors acknowledge the financial support from the Fonds de la Recherche Scientifique - FNRS, Spanish Ministry of Economy and Competitiveness through the Severo Ochoa Programme for Centres of Excellence in R&D (SEV-2015-0496), SUMATE project (RTI2018-

095853-B-C21), co-financed by the European Regional Development Fund, the COST programme NanoCoHybri (CA 16218), and from the Catalan Government with 2017 SGR 1519. The work of A. Fernández-Rodríguez has been done in the framework of the doctorate in Materials Science of the Autonomous University of Barcelona (UAB) and is supported by the Spanish Ministry of Economy (BES-2016-077310). The work of A. Silhanek is partially supported by the grant CDR J.0151.19 of the F.R.S.-FNRS. S. Blanco Alvarez, S. Melinte, and A. Silhanek acknowledge financial support through the grant PDR T.0106.16 of the F.R.S.-FNRS. S. Marinković acknowledges support from F.R.S.-FNRS (Research Fellowship ASP). The authors thank the ULiege Microscopy facility CAREM for the SEM investigations.

Supporting Information Available

Simulation of the inhomogeneous temperature distribution along the bridge before electromigration, further information concerning resistance changes after irreversible electromigration, room temperature micro-Raman spectra obtained at different spots along the transport bridge, scanning electron microscopy imaging of the electromigrated samples, video of real-time tracking of the electromigration process, and video of the simulated oxygen displacement during electromigration.

This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

References

1. Bednorz, J. G.; Müller, K. A. Possible High T_c Superconductivity in the Ba-La-Cu-O System. *Z. Phys. B - Condens. Matter* **1986**, *64*, 189–193.
2. Keimer, B.; Kivelson, S. A.; Norman, M. R.; Uchida, S.; Zaanen, J. From Quantum Matter to High-Temperature Superconductivity in Copper Oxides. *Nature* **2015**, *518*, 179–186.

3. He, G.; Wei, Z.; Feng, Z.; Yu, X.; Zhu, B.; Liu, L.; Jin, K.; Yuan, J.; Huan, Q. Combinatorial Laser Molecular Beam Epitaxy System Integrated with Specialized Low-Temperature Scanning Tunneling Microscopy. *Rev. Sci. Instrum.* **2020**, *91*, 013904.
4. Jin, K.; Suchoski, R.; Fackler, S.; Zhang, Y.; Pan, X.; Greene, R. L.; Takeuchi, I. Combinatorial Search of Superconductivity in $Fe-B$ Composition Spreads. *APL Mater.* **2013**, *1*, 042101.
5. Jorgensen, J. D.; Veal, B. W.; Paulikas, A. P.; Nowicki, L. J.; Crabtree, G. W.; Claus, H.; Kwok, W. K. Structural Properties of Oxygen-Deficient $YBa_2Cu_3O_{7-\delta}$. *Phys. Rev. B* **1990**, *41*, 1863–1877.
6. Taïr, F.; Carreras, L.; Camps, J.; Farjas, J.; Roura, P.; Calleja, A.; Puig, T.; Obradors, X. Melting Temperature of $YBa_2Cu_3O_{7-x}$ and $GdBa_2Cu_3O_{7-x}$ at Subatmospheric Partial Pressure. *J. Alloys Compd.* **2017**, *692*, 787–792.
7. Obradors, X.; Puig, T.; Pomar, A.; Sandiumenge, F.; Piñol, S.; Mestres, N.; Castaño, O.; Coll, M.; Cavallaro, A.; Palau, A.; Gázquez, J.; González, J. C.; Gutiérrez, J.; Romà, N.; Ricart, S.; Moretó, J. M.; Rossell, M. D.; Van Tendeloo, G. Chemical Solution Deposition: A Path towards Low Cost Coated Conductors. *Supercond. Sci. Technol.* **2004**, *17*, 1055–1064.
8. Shi, D. Q.; Ko, R. K.; Song, K. J.; Chung, J. K.; Choi, S. J.; Park, Y. M.; Shin, K. C.; Yoo, S. I.; Park, C. Effects of Deposition Rate and Thickness on the Properties of YBCO Films Deposited by Pulsed Laser Deposition. *Supercond. Sci. Technol.* **2004**, *17*, S42–S45.
9. Farnan, G. A.; McCurry, M. P.; Walmsley, D. G.; Li, Z. Z.; Raffy, H. Transport Properties of $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$. *Supercond. Sci. Technol.* **2001**, *14*, 160–167.
10. Veal, B. W.; Paulikas, A. P.; Shi, Y., H. and Fang; Downey, J. W. Observation of

- Temperature-Dependent Site Disorder in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ below 150°C . *Phys. Rev. B* **1990**, *42*, 6305–6316.
11. Werder, D. J.; Chen, C. H.; Cava, R. J.; Batlogg, B. Oxygen-Vacancy Ordering and Microstructure in Annealed $\text{Ba}_2\text{YCu}_3\text{O}_{7-\delta}$ Superconductors. *Phys. Rev. B* **1988**, *38*, 5130–5133.
 12. Tu, K. N.; Yeh, N. C.; Park, S. I.; Tsuei, C. C. Diffusion of Oxygen in Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Ceramic Oxides. *Phys. Rev. B* **1989**, *39*, 304–314.
 13. Kircher, J.; Kelly, M.; Rashkeev, S.; Alouani, M.; Fuchs, D.; Cardona, M. Anisotropy and Oxygen-Stoichiometry Dependence of the Dielectric Tensor of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Phys. Rev. B* **1991**, *44*, 217–224.
 14. Moeckly, B. H.; Buhrman, R. A.; Sulewski, P. E. Micro-Raman Spectroscopy of Electromigration-Induced Oxygen Vacancy Aggregation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Appl. Phys. Lett.* **1994**, *64*, 1427–1429.
 15. Moeckly, B. H.; Lathrop, D. K.; Buhrman, R. A. Electromigration Study of Oxygen Disorder and Grain-Boundary Effects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. *Phys. Rev. B* **1993**, *47*, 400–417.
 16. Sulewski, P. E.; Noh, T. W.; McWhirther, J. T.; Sievers, A. J.; Russek, S. E.; Buhrman, R. A.; Jee, C. S.; Crow, J. E.; Salomon, R. E.; Myer, G. Free-Carrier Relaxation Dynamics in the Normal State of Sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. *Phys. Rev. B* **1987**, *36*, 2357–2360.
 17. Zhao, G. L.; Xu, Y.; Ching, W. Y.; Wong, K. W. Theoretical Calculation of Optical Properties of Y-Ba-Cu-O Superconductors. *Phys. Rev. Lett.* **1987**, *36*, 7203–7207.
 18. Kamaras, K.; Porter, C. D.; Doss, M. G.; Herr, S. L.; Tanner, D. B.; Bonn, D. A.;

- Greedan, J. E.; O'Reilly, A. H.; Stager, C. V.; Timusk, T. Excitonic Absorption and Superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. *Phys. Rev. Lett.* **1987**, *59*, 919–922.
19. Liang, R.; Bonn, D. A.; Hardy, W. N. Evaluation of CuO_2 Plane Hole Doping in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Single Crystals. *Phys. Rev. B* **2006**, *73*, 1–4.
 20. Thomsen, C.; Kaczmarczyk, G. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; John Wiley and Sons: Chichester, 2002; p 2651.
 21. Feile, R. Lattice Vibrations in High- T_c Superconductors: Optical Spectroscopy and Lattice Dynamics. *Physica C* **1989**, *159*, 1–32.
 22. Huong, P. V. Microstructure of High-Temperature Superconductor Thin Films As Studied by Micro-Raman Spectroscopy. *Physica C* **1991**, *180*, 128–131.
 23. Ye, J.; Nakamura, K. Quantitative Structure Analyses of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films: Determination of Oxygen Content from X-Ray-Diffraction Patterns. *Phys. Rev. B* **1993**, *48*, 7554–7564.
 24. Osquiguil, E.; Maenhoudt, M.; Wuyts, B.; Bruynseraede, Y.; Lederman, D.; Nieva, G.; Guimpel, J.; Schuller, I. K. Photoexcitation Effects in $\text{YBa}_2\text{Cu}_3\text{O}_x$. *J. Alloys Compd.* **1993**, *195*, 667–670.
 25. Nieva, G.; Osquiguil, E.; Guimpel, J.; Maenhoudt, M.; Wuyts, B.; Bruynseraede, Y.; Maple, M. B.; Schuller, I. K. Photoinduced Enhancement of Superconductivity. *Appl. Phys. Lett.* **1992**, *60*, 2159–2161.
 26. Osquiguil, E.; Maenhoudt, M.; Wuyts, B.; Bruynseraede, Y.; Lederman, D.; Schuller, I. K. Photoexcitation and Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_x$ Films. *Phys. Rev. B* **1994**, *49*, 3675–3678.

27. Federici, J.; Chew, D.; Welker, B.; Savin, W.; Gutierrez-Solana, J.; Fink, T.; Wilber, W. Defect Mechanism of Photoinduced Superconductivity in $\text{GdBa}_2\text{Cu}_3\text{O}_{6+x}$. *Phys. Rev. B* **1995**, *52*, 15592–15597.
28. Markowitsch, W.; Lang, W.; Pedarnig, J. D.; Bäuerle, D. Persistent Photoconductivity in Oxygen-Deficient and Ion-Irradiated $\text{YBa}_2\text{Cu}_3\text{O}_x$. *Supercond. Sci. Technol.* **2009**, *22*, 034011.
29. Guimpel, J.; Maiorov, B.; Osquiguil, E.; Nieva, G.; Pardo, F. Interrelation between Persistent Photoconductivity and Oxygen Order in $\text{GdBa}_2\text{Cu}_3\text{O}_x$ Thin Films. *Phys. Rev. B* **1997**, *56*, 3552–3555.
30. Decca, R. S.; Drew, H. D.; Maiorov, B.; Guimpel, J.; Osquiguil, E. Photoinduced Superconducting Nanowires in $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5}$ Films. *Appl. Phys. Lett.* **1998**, *73*, 120–122.
31. Xiang, C.; Kim, J. Y.; Penner, R. M. Reconnectable Sub-5 nm Nanogaps in Ultralong Gold Nanowires. *Nano Lett.* **2009**, *9*, 2133–2138.
32. Li, Z.; Bauer, C. L.; Mahajan, S.; Milnes, A. G. Degradation and Subsequent Healing by Electromigration in Al-1 wt % Si Thin Films. *J. Appl. Phys.* **1992**, *72*, 1821–1832.
33. Hong, C. F.; Togo, M.; Hoh, K. Repair of Electromigration-Induced Voids in Aluminum Interconnection by Current Reversal. *Jpn. J. Appl. Phys.* **1993**, *32*, 624–627.
34. Kozlova, T.; Rudneva, M.; Zandbergen, H. W. *In Situ* TEM and STEM Studies of Reversible Electromigration in Thin Palladium-Platinum Bridges. *Nanotechnology* **2013**, *24*, 1–18.
35. Baumans, X. D. A.; Lombardo, J.; Brisbois, J.; Shaw, G.; Zharinov, V. S.; He, G.; Yu, H.; Yuan, J.; Zhu, B.; Jin, K.; Kramer, R. B. G.; Van de Vondel, J.; Silhanek, A. V. Healing Effect of Controlled Anti-Electromigration on Conventional and High-Tc Superconducting Nanowires. *Small* **2017**, *13*, 1700384.

36. Lombardo, J.; Collienne, S.; Petrillo, A.; Fourneau, E.; Nguyen, N. D.; Silhanek, A. V. Electromigration-Induced Resistance Switching in Indented Al Microstrips. *New J. Phys.* **2019**, *21*, 113015.
37. Baumans, X. D. A.; Fernández-Rodríguez, A.; Mestres, N.; Collienne, S.; Van de Vondel, J.; Palau, A.; Silhanek, A. V. Electromigration in the Dissipative State of High-Temperature Superconducting Bridges. *Appl. Phys. Lett.* **2019**, *114*, 012601.
38. Rothman, S. J.; Routbort, J. L.; Baker, J. E. Tracer Diffusion of Oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. *Phys. Rev. B* **1989**, *64*, 8852–8860.
39. Rothman, S. J.; Routbort, J. L.; Welp, U.; Baker, J. E. Anisotropy of Oxygen Tracer Diffusion in Single-Crystal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Phys. Rev. B* **1991**, *44*, 2326–2333.
40. Palau, A.; Fernández-Rodríguez, A.; Gonzalez-Rosillo, J. C.; Granados, X.; Coll, M.; Bozzo, B.; Ortega-Hernandez, R.; Suñé, J.; Mestres, N.; Obradors, X.; Puig, T. Electrochemical Tuning of Metal Insulator Transition and Nonvolatile Resistive Switching in Superconducting Films. *ACS Appl. Mater. Interfaces* **2018**, *10*, 30522–30531.
41. Arpaia, R.; Andersson, E.; Kalaboukhov, A.; Schröder, E.; Trbaldo, E.; Ciancio, R.; Dražić, G.; Orgiani, P.; Bauch, T.; Lombardi, F. Untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Thin Films on MgO Substrates: A Platform to Study Strain Effects on the Local Orders in Cuprates. *Phys. Rev. Mat.* **2019**, *3*, 114804.
42. Maiorov, B.; Gibbons, B. J.; Kreiskott, S.; Matias, V.; Holesinger, T. G.; Civale, L. Effect of the Misalignment between the Applied and Internal Magnetic Fields on the Critical Currents of “Tilted Coated Conductors”. *Appl. Phys. Lett.* **2005**, *86*, 132504.
43. Obradors, X.; Puig, T.; Ricart, S.; Coll, M.; Gazquez, J.; Palau, A.; Granados, X. Growth, Nanostructure and Vortex Pinning in Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Films Based on Trifluoroacetate Solutions. *Supercond. Sci. Technol.* **2012**, *25*, 32.

44. Zharinov, V. S.; Baumans, X. D.; Silhanek, A. V.; Janssens, E.; Van De Vondel, J. Controlled Electromigration Protocol Revised. *Rev. Sci. Instrum.* **2018**, *89*, 043904.
45. Shaw, G.; Brisbois, J.; Pinheiro, L. B.; Müller, J.; Blanco Alvarez, S.; Devillers, T.; Dempsey, N. M.; Scheerder, J. E.; Van De Vondel, J.; Melinte, S.; Vanderbemden, P.; Motta, M.; Ortiz, W. A.; Hasselbach, K.; Kramer, R. B.; Silhanek, A. V. Quantitative Magneto-Optical Investigation of Superconductor/Ferromagnet Hybrid Structures. *Rev. Sci. Instrum.* **2018**, *89*, 1–21.

Graphical TOC Entry

Mastering of the oxygen doping and carrier concentration is achieved in the strongly correlated complex oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ through current-stimulated oxygen migration. This high-selectivity process is able to target one type of oxygen atoms and therefore tune the electronic response of the material. Direct visualization of the process reveals an inhomogeneous oxygen vacancy distribution with a controllable propagation speed.