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Patterned electron beam exposures of YBCO – towards local control of doping

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Abstract

Local control of dopant profiles and ordered doping in high Tc superconductors have the potential to greatly increase the transition temperature, Tc. We report on experiments we used focused electron beams to locally modulate the oxygen dopant concentration in commercial YBCO films (100 nm on LaAlO3). Patterned exposure of YBCO samples to 10 keV electrons and fluences in the 10²⁰ e-/cm² range led to increases of Tc of ~0.4 K, comparable to earlier reports from broad beam exposures in a similar fluence regime. We discuss our results in relation to concepts of local oxygen depletion and chain ordering induced by ionizing radiation and outline possible processing paths to implement a form of modulation doping in YBCO by patterning with intense, short excitation pulses (e.g. of MeV protons).

Keywords: high Tc superconductivity, electron beams, doping

1. Introduction

The quest to increase the transition temperature of superconductors remains an exciting field of basic and applied research following the discovery of cuprates over 30 years ago [Bednorz] and recently with observations of very high
transition temperatures for conventional superconductivity in sulfur hydride under high pressures [Drozdov, Gor’kov]. In this article we report on an experimental study of yttrium barium copper oxide (YBCO, YBa2Cu3O7-x, x=0.4) where we attempted to affect the transition temperature by acting on the oxygen dopant sub-system using focused beams of 10 keV electrons. Tolpygo et al. have reported increases of Tc by up to 2 K following broad beam exposure of thin films of YBCO to 40 keV electrons with an optimal fluence of 5x10^{20} electrons/cm² [Tolpygo]. Tc converged back to the nominal value of 91 K when this optimal fluence was exceeded. The observed changes were explained as due to chain oxygen disordering (formation of vacancies and interstitials in specific lattice positions) which disrupts the conductivity of chains and decreases the hole doping in CuO2 planes. Intriguing effects of oxygen chain order induced by beams of 20 keV electrons where reported by Seo et al. [Seo], where electron bombardments was found to instigate the collective hopping of oxygen atoms either from an interstitial site to a vacant chain site or by reshuffling of chain segments to extend the average length of chains without changing the overall oxygen content. In contrast to these studies with relatively low electron beam energies, irradiation induced Tc suppression due to formation of lattice defects by electron beam energies well above the displacement threshold were reported e.g. by Giapintakis et al. [Giapintzakis].

Recently, formation of (transient) ordered dopant structures where reported from x-ray beam direct writing with lanthanum copper oxides [Poccia].

Also recently, Wolf and Kresin have proposed that ordering of oxygen dopants in YBCO films could lead to large increases in Tc [Wolf]. We now paraphrase the leading arguments of Wolf and Kresin from their article [Wolf]: “Dopants play a dual role in YBCO. On the one hand, they provide the (de-localized) charge carriers (holes) that support superconductivity. On the other hand, oxygen atoms are scattering centers responsible for pair breaking. When oxygen is added to under-doped YBCO, the mixed-valence state of the in-plane Cu leads to plane-chain charge transfer and the appearance of a hole, initially on the Cu site. Because of diffusion, the hole enters the system of de-localized carriers responsible for the metallic and, correspondingly, for the superconducting behavior as pairing of such holes causes superconductivity. But the added oxygen ion and corresponding in-plane Cu also form a defect with pair-breaking impact. The statistical nature of doping leads to a random distribution of dopants and at relatively low doping levels the spatial distribution can be rather broad. As a result, regions with smaller number of dopants can have larger values of Tc. These regions can form superconducting “islands” inside of the normal matrix which have been observe up to temperatures Tc’>Tc.” We can now ask whether we can implement a form of modulation doping in cuprates, where optimally doped regions can provide the charge carriers that would then conduct more freely up to temperatures Tc’>Tc in adjacent under-doped regions. Below, we report on our first attempts to implement this idea in stripe like patterns of adjacent regions of optimally doped and under-doped YBCO formed using beams of low energy electrons.

2. Experiment

We purchased samples with thin films (100 nm) of YBCO on LaAlO3 (100) with a nominal Tc of 90 K. (MTI Corporation, Richmond, CA). Sample dimensions where 10 mm x 10 mm x 0.5 mm. We then sputter deposited Ag/Ti/Au (100 nm/20 nm/ 400 nm) contacts in an electrode layout for four-point probe measurements. Four electrode patterns where deposited per sample. We then exposed areas between the electrodes to 10 keV electrons in an FEI Strata 235 dual beam FIB. The pressure in the vacuum chamber was in the low 10^{-6} Torr range. We selected an electron beam energy of 10 keV guided by simulations using the CASINO program [CASINO] which showed that at this energy electrons deposit most of their kinetic energy in the 100 nm YBCO film. We measured electron beam current values with a home built Faraday cup. Figure 1 shows examples of line patterns from electron beam exposure of samples i) and iii). Sample i) was exposure to an electron beam with a current of 8.6 nA for 10 minutes per line and a total of six lines. The scanning electron micrograph images taken after line patterning show the exposed lines with an apparent width of about 0.75 μm, much larger than the nominal electron beam spot size, which is of order 10 nm at these elevated current levels. We attribute the contrast to changes in the surface composition as a result of high fluence electron exposures. Further, vibrations and drift can contribute to line broadening during extended exposures. With a line width of 0.75 μm, an upper bound of the electron fluence per line is 6x10^{20} electrons/cm² for sample i). Samples iii) was exposed to a 1 nA electron beam also with six lines and 10 min per line. The apparent line widths were 0.5 micron and the upper bound of the fluence per line is then 2.4x10^{20} electrons/cm². The instantaneous local fluence is likely higher, but the 0.5 to 0.75 μm apparent line widths also reflect the range of secondary electrons.
Following e-beam patterning, samples were stored in a low pressure sample storage container and then inserted into a vacuum cryostat for measurements of the temperature dependent resistance.

The cryostat was cooled down to a base temperature of about 4 K and the four-point-probe resistances of three samples on one YBCO chip were measured in parallel during the slow warmup back to room temperature over a period of several hours. The resistance measurements were made using a resistance scanner by applying a current bias of 1 mA. The warm-up rate through the superconducting to normal-state transition was 1.5 mK/s.

3. Results and discussion

In Figure 2 we show temperature dependent resistance data for samples i), iii) and a reference sample on the same chip, sample ii), which had not been irradiated with electrons.
The data show an increase of $T_c$ by 0.4 K for the e-beam patterned samples compared to the control sample that had not been exposed to electrons. We observe a $T_c$ of about 86 K for the control sample, much lower than the nominal value of 90 K. A possible explanation for this discrepancy is aging of the YBCO film due to exposure to ambient moisture during sample preparation and handling. This obvious shortcoming is subject of ongoing work. The observed small increase in $T_c$ was reproduced in several runs. No $T_c$ change was observed for a sample exposed to $-5 \times 10^{19}$ electrons/cm$^2$ in a line pattern.

Compared to the earlier findings by Tolpygo et al. [Tolpygo], our observation of a $T_c$ increase of 0.4 K is significantly lower than the up to 2 K increase for an optimal electron fluence of $5 \times 10^{20}$ electrons/cm$^2$ in broad beam exposures with 40 keV electrons. We do not observe any evidence of local dopant control or the implementation of adjacent regions of optimally doped and under-doped YBCO. And we did not observe the anticipated effect of higher $T_c$ due to carrier diffusion from optimally doped regions into under-doped regions with lower density of scattering centers.

4. Outlook

First results from exposure of commercial thin film YBCO samples to 10 keV electrons in sub-micron line patterns have not shown significant $T_c$ increases. Observed $T_c$ increases were smaller than $T_c$ increases reported earlier for similar fluences for 40 keV electrons in broad beam exposures [Tolpygo]. In next steps, we will design a sample preparation process that further limits exposure to environmental air moisture and will optimize the geometry of temperature sensors to improve accuracy of sample temperature measurements. We see several intriguing opportunities, one being the implementation of a low temperature sample stage in the dual beam FIB which will enable in situ resistance measurements as a function of sample temperature and for a series of electron and ion beam exposure conditions. Scattering of energetic electrons is known to lead to much larger scattering volumes in samples compared to energetic ion beams. In lithography, this so called proximity effect [Wang] can blur the abruptness of features and in our case, it will contribute to the width of the region of beam induced oxygen dopant ordering. An alternative to patterning with energetic electrons are thus ions, e.g. MeV protons or helium ions. Intense pulses of protons or helium ions can deliver rapid local excitations leading to dopant re-arrangements similar to those observed for energetic electron beams but with much higher sharpness and abruptness in masked exposures due to the scattering kinetics of ions vs. electrons [Seidl].

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