Micro-Raman spectroscopy of electromigration-induced oxygen vacancy aggregation in YBa$_2$Cu$_3$O$_{7-\delta}$

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We describe the results of micro-Raman spectroscopy and optical microscopy studies of basal-plane chain-oxygen vacancy motion in YBa$_2$Cu$_3$O$_{7-\delta}$ thin films under the influence of a high current bias near 300 K. Above a threshold level this bias causes vacancy aggregation and then long-range displacement, leading to an enhancement of oxygen order in the region of highest current density and the complex accumulation of oxygen vacancies in the region where the electromigration force is near the threshold level.

The study of oxygen ordering phenomena in the high-$T_c$ material YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) has recently garnered much interest. The charge-transfer model of carrier doping to the Cu-O planes has been successful in describing the effect of basal-plane oxygen content, and experiments involving quenched oxygen-deficient samples of YBCO 2-5 have highlighted the ease with which oxygen rearranges in the basal plane at room temperature. Despite the successful prediction of ordered phases of the basal-plane oxygen vs $\delta$ it is not clear how oxygen orders dynamically on a local scale or whether microdomains of differently ordered phases can coexist. Given the very short YBCO superconducting coherence length, of particular concern is the extent to which oxygen defects aggregate, especially under the influence of stress and in the vicinity of structural defects. Studies of oxygen electromigration in YBCO thin-film microbridges 7-9 have shown how localized oxygen disorder can be generated and how its existence is manifested in the transport characteristics of YBCO films, grain boundaries, and interfaces. Here we report the results of a microscopic Raman scattering investigation of oxygen vacancy diffusion under electrical bias in YBCO microstructures. These results illustrate the unusual diffusion dynamics of oxygen in YBCO in the presence of a weak force and demonstrate the often detrimental tendency of basal-plane oxygen vacancies to aggregate.

The films in this study were deposited by laser ablation onto MgO substrates to thicknesses between 140 and 210 nm. These films are free of high-angle grain boundaries and can support large supercurrent densities ($J_c$,$>$2X10$^6$ A/cm$^2$ at 77 K). Rutherford backscattering measurements utilizing resonant oxygen channeling indicate that these films possess a higher degree of oxygen order than films containing high-angle grain boundaries. Standard photolithography and ion milling were used to define microbridges of YBCO with widths of 1, 2, 5, or 10 $\mu$m and a length-to-width ratio of 3:1.

We have previously reported the remarkable effects produced by applying high dc currents ($>$2X10$^6$ A/cm$^2$) to these microstructures at room temperature. Below a threshold bias of about 5 V, the Raman modes of YBCO are well known, and the peaks observed in this scattering geometry due to its temperature dependence which makes it extremely weak at 300 K;7 it is

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FIG. 1. Optical image of an electromigrated microbridge ($J_{\text{ext}} > 5 \text{ MA/cm}^2$) and corresponding micro-Raman spectra. The spectra indicate that the bright ring (b) is oxygen depleted with respect to the bulk film (a). The less-bright region (c) appears oxygen disordered, while the bridge (d) is more oxygen ordered than the bulk.

just barely apparent in Fig. 1(a). The differences in the Raman spectra for the brighter region to the left of the bridge (b) are all consistent with a region of depleted oxygen content. This is most dramatically indicated by the large shift of the apical oxygen mode from 502 cm$^{-1}$ (nearly fully oxygenated, $\delta < 0.1$) to 488 cm$^{-1}$ ($\delta = 0.5$). This mode is known to be a strong indicator of oxygen content and usually shows a linear variation from about 502 to 475 cm$^{-1}$ as $\delta$ changes from 0 to 1 (fully oxygenated to fully oxygen deficient).\textsuperscript{13-16}

We also observe that the 338 cm$^{-1}$ mode increases dramatically in intensity, the Cu(2) mode shifts from 150 to 142 cm$^{-1}$ and increases in intensity, and the mode at 435 cm$^{-1}$ (not easily seen in the bridge) shifts up to 453 cm$^{-1}$. These features are regularly observed for oxygen-deficient samples.\textsuperscript{13-16} In addition, we observe that the Fano line shape of the 338 and 117 cm$^{-1}$ peaks seen in the fully oxygenated regions changes to a symmetric Lorentzian shape for the oxygen-depleted regions. Since the asymmetric Fano profile results from the interaction of phonons with a continuum of electronic excitations,\textsuperscript{12} our observation indicates a severe reduction of the carrier concentration in the oxygen-depleted regions. Thus, we conclude that the current bias causes the migration of oxygen atoms and the subsequent aggregation of oxygen vacancies, resulting in oxygen depleted regions.

Our results demonstrate that the electromigration direction of the basal-plane oxygen is clearly toward the anode,\textsuperscript{18} not the cathode.\textsuperscript{19} As the current density and electric field decrease as a function of distance into the electrodes, a critical value is reached that is not sufficient to continue to promote the long range motion, on an atomic scale, of the oxygen vacancies—hence the sharp delineation between oxygen-depleted and oxygen-rich regions. This observation graphically complements our earlier finding of a threshold electromigration bias for the onset of damage in originally well ordered YBCO.

Real-time microscopic observations of the electromigration-induced changes offer insight into this oxygen diffusion and vacancy aggregation process. Figure 2 shows a series of still photos taken from a video of one such study. In Fig. 2(a) we see a microbridge that is biased slightly below the critical level. Figure 2(b) is taken a few seconds after the bias had been increased to slightly above threshold, which caused the rapid formation of lighter, more reflective regions distributed more or less uniformly over the entire micro-
bridge. Subsequently, as seen in Fig. 2(c), these regions of higher reflectivity begin to migrate towards the cathode and appear to agglomerate into regions of still higher reflectivity, forming a “river delta.” If the bias is maintained for a sufficient time, the delta gradually evolves into a very inhomogeneous pattern on the $\sim 1 \mu m$ scale, as shown in Fig. 2(d). Also observe that the microbridge region (the region of highest current density) is restored to at least its original optical character. Comparison of the Raman signal from the center of a microbridge at the conclusion of an electromigration process [Fig. 1(d)] with that from the bulk of the film [Fig. 1(a)] indicates that as well as possessing similarly high oxygen content, the oxygen order in the microbridge is improved. Evidence for this is a substantial narrowing of the linewidth of the $502 \text{ cm}^{-1}$ mode and a decrease in intensity and downward shift of the $440 \text{ cm}^{-1}$ mode. The 117 and 338 $\text{ cm}^{-1}$ modes also decrease in intensity.

Micro-Raman spectroscopy may also be used to probe distinct regions within the oxygen-depleted areas. Analysis of the visually inhomogeneous region seen in Fig. 1 confirms that the brighter ring at the outer portion of the damaged area is more oxygen deficient ($\delta=0.5$) than the lighter region in the middle of this area ($\delta=0.16$, see spectra b and c). This middle region is slightly oxygen depleted compared with the nearly fully oxygenated bridge, but in addition the peak at $\sim 500 \text{ cm}^{-1}$ is much broader, indicating that the basal-plane oxygen in this region is less well ordered or homogeneously distributed than in the bulk of the film [Fig. 1(a)] or in the center of the bridge [Fig. 1(d)]. Thus, even for regions of high oxygen content, the effect of the force is to cause an inhomogeneous distribution of oxygen.

Our interpretation is that the electromigration bias first locally aggregates basal-plane oxygen vacancies that are initially more uniformly distributed in the film. This occurs to an extent sufficient to alter the optical transitions and Raman modes in these newly formed regions of higher vacancy concentration. The spatial scale of these regions is impossible to discern from optical examination, though there clearly are inhomogeneities on the scale of $\sim 0.25 \mu m$, and, as indicated by transport measurements, also on a much finer scale. Subsequent to the shorter range vacancy aggregation, the electric bias provides a force for the diffusion of the vacancy aggregates toward the cathode where they further agglomerate. This process depletes the microbridge of mobile vacancies and results in an improvement in the oxygen stoichiometry and order in the microbridge.

The formation of regions of oxygen inhomogeneity in the early stages of electromigration indicates the presence of vacancy flux divergence sites caused by a spatial variation in the parameters controlling the oxygen diffusion. These could be related to the thin film microstructure, as is typically the case in electromigration and diffusion. But the migration of the regions of vacancy aggregation along the microbridge and across numerous twin and low-angle tilt boundaries indicates that a dominant factor in the formation and subsequent displacement of these aggregates is variation in the basal-plane oxygen diffusion rates with the local oxygen content and order.

While a threshold bias for the onset of long-range vacancy displacement is rather unusual, more surprising is our finding that an electric field of just $\sim 10^5 \text{ V/cm}$ is sufficient to alter the thermally activated diffusion dynamics from the situation where local rearrangements of relatively well ordered basal-plane oxygen are promoted (below threshold), to the state where longer range oxygen vacancy aggregation is the result (above threshold). We note that a simple edge dislocation can exert an elastic force on an oxygen vacancy at a distance of $\sim 10 \text{ nm}$ from the dislocation core that is equivalent to the force of our observed threshold field. The ability of weak atomic forces to promote oxygen vacancy aggregation, possibly due to long-range interactions between basal-plane oxygen atoms, may be fundamental in explaining the heterogeneous weak-link nature of most YBCO high-angle grain boundaries, interfaces, and surfaces.

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