Femtosecond reflectivity of 60 K Y-Ba-Cu-O thin films

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(Received 15 June 1993; accepted for publication 8 December 1993)

We report systematic studies of the femtosecond transient reflectivity at 2 eV in partially oxygen-depleted Y-Ba-Cu-O thin films exhibiting the resistive superconducting transition at 60 K. Our measurements, performed at room temperature, reveal that in 60 K films, the Fermi level in the Cu-O plane lies approximately 2 eV above the filled copper $d^9/d^{10}$ band. By mapping the transient optical response across a 1 cm$^2$ film, we show that the position of the Fermi level is very sensitive to the apparent local variations of the film oxygen content, which gives rise to dramatically different transient optical responses. We also observe a strong transient reflectivity dependence on intensity, which can be attributed to the shift of the Fermi level caused by nonequilibrium hole heating.

In this letter, we report a series of femtosecond reflectivity measurements on 60 K YBCO thin films performed at room temperature. We selected films with $T_c \approx 60$ K since their $T_c$ values are relatively insensitive to small variations of the material oxygen content and they fill the gap between our previously tested oxygen-rich and oxygen-poor samples. By mapping the transient response across the 60 K sample, we show that the optical response (corresponding to a nearly resonant $d-E_F$ transition) depends strongly on the pump-spot location. This dependence, in turn, demonstrates that $\Delta R/R$ is extremely sensitive to the "local" oxygen content. A strong intensity dependence on the transient $\Delta R/R$ response is also observed, which we attribute to a Fermi-level shift associated with nonequilibrium hole heating.

In this work we used a number of 150-nm-thick epitaxial YBCO films deposited on LaAlO$_3$ by in situ rf single-target sputtering at the Westinghouse Science and Technology Center. All as-deposited films exhibited 0.5-K-wide superconducting transitions at about 90 K, with critical current densities exceeding 2 MA/cm$^2$ at 77 K. Subsequently, the films were partially deoxygenated to obtain 60 K samples. The best results were obtained by furnace annealing of the films in 10 mTorr of O$_2$ for 20 min at 400 °C. Resistivity vs temperature measurements of the annealed samples (Fig. 1) show that our films had exhibited a narrow superconducting transition at exactly 60 K.

FIG. 1. Resistance vs temperature curve for a 60 K YBCO sample. The superconducting transition width is about 1.8 K.

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The optical measurements were performed in a conventional pump/probe configuration, using 100 fs, 2 eV pulses generated at 8.5 kHz by an amplified colliding-pulse mode-locked laser. The laser beam was focused to a 30–50-μm-diam spot and the pump-beam intensity was varied between 5 and 500 μJ/cm². Thus, even for the largest beam intensity, the average power delivered to the sample was well below 5 W/cm², excluding any material modifications due to laser-beam-related oxygen migration and/or oxygen absorption/desorption. The cross-polarization arrangement of the pump and the probe beams rejected the stray light from the pump beam and also eliminated coherent artifacts. A high-sensitivity, lock-in-based differential detection scheme allowed us to achieve a good signal-to-noise ratio.

Figure 2 shows the time-resolved ΔR/R traces measured for a 60 K YBCO sample at 2 eV, together with the 2 eV ΔR/R signals obtained earlier by us⁸ for the oxygen-rich (Tₓ=90 K) and oxygen-deficient (Tₓ=27 K and Tₓ=0 K) samples. The trace for the 60 K sample clearly represents a “missing link” between the results for the oxygen-rich and oxygen-depleted films. For the oxygen-rich sample, ΔR/R displays a positive response, while in oxygen-deficient samples, the response is negative. Our results are qualitatively very similar to those of Fig. 2 in Ref. 1, which shows the ARIR signals measured on a Cu sample for different probe-beam energies. The waveform corresponding to the probe-beam energy of 2.15 eV in Ref. 1 is strikingly similar to the 2 eV signal observed by us for the 60 K YBCO film. This latter observation strongly suggests that for the 60 K YBCO the position of Eₓ is indeed about 2 eV above the Cu d state.

In this letter we use a simplified band structure for YBCO, as in Ref. 3, i.e., conducting carriers (holes) completely occupy the Cu d⁹/d¹⁰ band and partially fill the O p band up to Eₓ. Recent spectroscopic data confirm the adequacy of this model for partially oxygen-depleted YBCO.⁹,¹⁰ The model also fits well with our thermomodulation (Fermi smearing) data. When the 2 eV pump pulse heats the carriers, it modifies the electronic occupancy near Eₓ on a time scale typically shorter than the excitation pulse width. The “smearing” decreases (increases) the occupancy of states below (above) Eₓ. Thus, a probe monitoring the transition from the filled Cu d⁹/d¹⁰ band to the O p band below (above) Eₓ measures a positive (negative) change of absorption that results in a positive (negative) change of reflectivity (ΔR). The sign reversal between the Tₓ=90 K curve and the Tₓ=27 K curve is, therefore, a consequence of the down shift of Eₓ when the oxygen content decreases, which, in turn, directly corresponds to a reduction of total carrier (hole) density in Cu-O planes.

We have also mapped the transient ΔR/R signal across our 60 K film with 1 mm spacing (the probe spot size was 30 μm). Figure 3 displays the traces obtained at different locations along the center of the film, as shown in the inset. It is clear that as we move from the film edge toward the center, the ΔR/R signal changes its sign from negative to positive. Based on Fig. 2, this result implies that the position of Eₓ up shifts with respect to the 2 eV probe energy. Since the position of Eₓ is closely related to the oxygen content, Fig. 3 shows that in our sample the local oxygen content is higher in the film center than at its edges. We want to emphasize that one can exclude a gradual (long term) ordering of oxygen vacancies in our films, which is usually observable in quenched, oxygen-deficient YBCO samples. Our 60 K samples were slowly cooled, and we performed our measurements during the period of several months after the films were prepared. The oxygen vacancies in such a case are expected to be fully ordered.

Since the total free-carrier density in YBCO Cu-O planes is more than one order of magnitude less than that in metals such as Cu, one should expect that in YBCO the effect of
nonequilibrium heating will be much more pronounced. In pump-probe experiments, the pump intensity determines the degree of nonequilibrium heating (in other words, the carrier temperature) by modifying the carrier distribution around $E_F$. The change of the initial carrier temperature also slightly affects the position of $E_F$, leading to the pump-intensity-dependent $\Delta R/R$ response. For example, in the free electron model, $E_F$ (or, more accurately, the chemical potential) of the electron gas has a quadratic dependence on the ratio between the electron temperature and the Fermi temperature. Since the Fermi temperature is usually very high (e.g., $\sim 10^4$ K for noble metals), the associated Fermi shift is very small and not observed in pump-probe experiments. On the other hand, in partially oxygen-depleted YBCO the Fermi temperature is in the range of $\sim 10^3$ K, which makes the dependence of the $\Delta R/R$ response on pump intensity measurable.

Figure 4 shows that the $\Delta R/R$ signal strongly depends on the pump intensity and reverses its polarity with increasing intensity. In particular, at the highest pumping intensity (500 $\mu J/cm^2$), $\Delta R/R$ resembles that of the oxygen-rich sample (see Fig. 2). The observed effect is large, but we should remember that in 60 K YBCO, even small $E_F$ shifts will result in substantial differences in $\Delta R/R$, since the $\Delta R/R$ response is most sensitive when probing very close to $E_F$. We also note that the measured intensity dependence is a fully reversible process, in the sense that when the intensity is reduced to its initial low level, the $\Delta R/R$ temporal response changes accordingly. This result excludes the possibility of any stoichiometric changes in our film (e.g., change in the oxygen content) caused by the intense pump beam. On the other hand, the intensity-dependence measurements performed on different spots of the same sample revealed that the optically induced $E_F$ shift is equivalent to a change of the film oxygen content. This is fully understandable since $E_F$ is sensitive to both the oxygen content and the pump intensity and, in the 60 K sample, we probe the hole states that lie close to $E_F$. This latter observation opens an interesting possibility of a direct energy “calibration” of the intensity induced $E_F$ shift in YBCO. By measuring the exact position of $E_F$ at different points on the 60 K sample (e.g., using the white-light system) and comparing the results to the intensity data, one should be able to relate the intensity-induced increase in hole temperature with the associated $E_F$ shift. More detailed discussion and experimental results will be presented elsewhere.

In summary, we have performed systematic studies on the transient optical response in 60 K YBCO thin films at room temperature. We observed that in such samples the Fermi level lies approximately 2 eV above the Cu $d^9/10$ band, and in the hole picture, $E_F$ is down shifted (up shifted) as the oxygen content decreases (increases). By mapping the transient optical response across the 60 K sample, we have shown that the position of $E_F$ relative to the 2 eV interband ($d$-$\pi$) transition is very sensitive to the local oxygen-content changes. We have also observed that the increase in the pump intensity enhances the nonequilibrium hole heating, leading to a substantial up shift (in the hole picture) of $E_F$.

The authors would like to thank Dr. J. R. Gavaler from the Westinghouse Science and Technology Center for providing us with the high quality YBCO thin films. This work was supported by the Army Research Office Grant DAAH04-93-G-0211 and by the New York State Institute on Superconductivity Grant No. R12762. W. Xiong acknowledges the support from the Laboratory for Laser Energetic’s Frank Horton Graduate Fellowship Program.

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