RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 9 1 MARCH 1994-I

Charging effect in partially oxygen-depleted superconducting Y-Ba-Cu-O thin films

W. Kula* and Roman Sobolewski

Department of Electrical Engineering and Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14627

(Received 7 December 1993)

We report our studies on the charging effect in metal-insulator-superconductor, thin-film structures with thick (~100 nm), partially oxygen-depleted $YBa_2Cu_3O_y$ (YBCO) channels. The devices were fabricated in YBCO-on-$SrTiO_3$ films with a laser-writing patterning technique. The $SrTiO_3$ substrates were used as gate insulators. A number of test structures, consisting of the oxygen-deficient (superconducting at 10–60 K) channel and fully oxygenated (superconducting above 85 K) source and drain electrodes, were measured. We found that the electric field applied to our as-fabricated structures complexly affected their superconducting properties, causing both reversible and irreversible modifications of the channel's critical temperature and critical current. The channel sensitivity to the electric field disappeared in our samples after several days of room-temperature aging; however, it could be subsequently recovered, again only temporarily, by hydrogen doping. The charging effect was particularly pronounced in structures with the lowest critical temperatures of the channel. We associate the behavior observed in our samples with charge-transfer effects related to electric-field-enhanced changes of the crystalline order in oxygen-deficient YBCO.

The charging effect in thin superconducting films has been the subject of some research in the past few decades.[1] In the early 1960's, Glover and Sherill[2] observed a 10^{-4}-K shift of the superconducting transition temperature T_c in their ~10-nm-thick Sn and In films, caused by the application of an electric field as high as 3×10^5 V/cm. The effect was later reproduced by Stadler,[3] who, using a ferroelectric substrate to enhance the charging of an ultrathin Sn film, obtained a T_c shift of 0.0013 K. He also demonstrated that this shift was directly related to the electron-concentration change at the superconductor surface. Experimental studies on high-temperature superconductors (HTS's) revealed a significant charging effect both in ultrathin (at most few-elementary-cells thick) epitaxial and granular $YBa_2Cu_3O_y$ (YBCO) films.[4–7] In the epitaxial films, the researchers observed up to 20% modulation of the normal-state resistance, a 2-K shift of T_c, and a 50–90 % modulation of the critical current density J_c.[4,5] Even more impressive, a 25–30 K T_c shift was reported for YBCO films containing intrinsic or fabricated weak links.[6,7] It should be noted, however, that although the ultrathin-film geometry allows one to modulate the total number of carriers in the film and makes the charging effect very pronounced, any practical applications of ultrathin YBCO films are questionable, due to their poor reproducibility and low long-term stability.

Theoretical studies[8,9] have shown that the response of a superconductor to the electric field strongly depends on the value of the parameter:

$$\tau=\lambda_{el}/\xi_0 , \quad (1)$$

where $\lambda_{el}\sim 1/[N(E_F)]^{1/2}$ is the electric-field penetration depth in the superconductor, $N(E_F)$ is the density of states at the Fermi level, and ξ_0 is the bulk superconducting coherence length. Since noticeable changes of the superconducting order parameter cannot occur on distances shorter than ξ_0, only in materials with $\tau>1$ may one expect a significant modification of the superconducting properties in the electric-field penetrated surface layer. Detailed calculations of the field effect in superconductors, performed by Kechiantz,[8] showed that the charge-induced T_c shift, ΔT_c, at the surface penetrated by the electric field is proportional to τ^2. In metallic superconductors, the large value of $N(E_F)$ and ξ_0 result in $\tau\ll 1$, which explains why experimentally measured ΔT_c in, e.g., In or Sn is extremely small. In HTS's the situation is more promising since $N(E_F)$ is about one order of magnitude smaller than that in metals and ξ_0 is very short. In fact, for the parameters used in Ref. 8, we have $\tau\sim 1$ and the estimated ΔT_c is of the order of several degrees. Even higher values of τ are expected in YBCO with a reduced oxygen content ($6.5<y<6.9$) since in such films T_c is suppressed and $N(E_F)\propto T_c^2$.[10]

Despite the large number of experimental studies on the charging effect in HTS's, our physical understanding of the results obtained so far is still not complete. Interpretations based on the electrostatic nature of the field-induced changes of the free-carrier density (like the Kechiantz's model) account only semiquantitatively for the observed changes of the samples' normal-state resistance and T_c. Simultaneously, the measured J_c modulation is often much larger than that expected. Thus, an additional mechanism—as was suggested by Mannhart *et al.*[4]—related to field-induced changes of the pinning energy at the surface of superconductor, should be also included. Recently, an alternative, "chemical" model of the charging effect in YBCO was proposed by Chandrasekhar, Valls, and Goldman.[11] The authors investigated the chain-oxygen dynamics in the YBCO basal plane, using a Monte Carlo simulation of the asymmetric next-nearest-neighbor Ising model, and showed that the application of an electric field caused a modification of the YBCO crystalline structure by changing the oxygen coordination number of the basal Cu ions. This, in turn, changed the average Cu valence and resulted in the modification of carrier doping in the Cu-O planes. According to Chandrasekhar, Valls, and Goldman[11] the applied field generates a charge transfer, which is related to

the field-induced *ordering* of the chain-oxygen ions (without changing the total oxygen amount), rather than a simple electrostatic response of mobile carriers. Magnitudes, signs, and long time constants of the field-induced YBCO response, calculated within that model, remain in good agreement with those observed in the experiments published so far.

The concept of our charging-effect test structure with a thick, oxygen-deficient YBCO channel is schematically shown in Fig. 1. As we have stated before, oxygen-deficient YBCO is characterized by a low value of $N(E_F)$, which leads to a longer λ_{el} and larger τ. Thus, one may expect a substantial charging effect in devices with thicker, more stable YBCO channels. Our structure consists of a superconducting (with $T_c = 10-60$ K) channel and fully oxygenated ($T_c \approx 90$ K) source and drain electrodes. An electric field is applied to the channel through an insulating layer, which may be either the whole film substrate (as shown in Fig. 1) or a dielectric coating deposited (preferably *in situ*) on top of YBCO film. In the case of a perfect interface between the YBCO and the gate insulator, we should be able to observe the field-induced modulation of T_c in the top, penetrated by the electric field, monolayers of the channel. However, in the real case, structural imperfections and enhanced charge trapping in YBCO close to the gate insulator cause the surface critical temperature T_{cs} to be lower than that inside the volume of the film, T_{c0}. Therefore, in that case one should not expect to observe the field-induced change of the channel T_c since the measured T_c is determined by the T_{c0}, which remains unaffected by the electric field. In this latter situation, however, we may expect field-induced changes of the channel J_c. The structural imperfections in the YBCO surface layer act below T_c as pinning centers and give a substantial contribution to the volume pinning force in the film. Field-induced changes of their pinning energy may, thus, either decrease or increase the total channel J_c, depending on the gate-voltage polarity.

Our test structures were fabricated from 100-nm-thick YBCO films, rf sputtered on single-crystalline $SrTiO_3$ substrates. The as-deposited films were intentionally deoxygenated by furnace annealing for 1–2 h at 330–450 °C in 10 mTorr of O_2, followed by a slow, 30-min cool down to 250 °C and subsequent quenching to room temperature. The above procedure allowed us to reproducibly fabricate YBCO samples with well-defined T_c's between 10 and 60 K. The transistor structure was patterned with the laser-writing technique.[12,13] Drain and source electrodes were patterned by local laser-induced diffusion of O_2 into the film. The oxygen-rich electrodes were 60 μm wide and 3 mm long and were placed about 1 mm apart. Next, the sample's ambient atmosphere was changed from O_2 to N_2, and oxygen-poor areas were laser patterned on both sides of the drain and source. The oxygen-poor regions acted as the borders and electrically insulated at low temperature the transistor's structure from the rest of the film. As a result, we obtained between the drain and source a 1-mm-long and 60-μm-wide, partially deoxygenated transistor's channel. The whole, 0.5-mm-thick, $SrTiO_3$ substrate was used as a gate insulator, with its silver-paint-covered back side acting as a gate electrode. Since the dielectric constant of $SrTiO_3$ at low temperatures may reach 10^3, application of this material as a gate insulator allowed us to achieve significant charging of the superconductor using reasonably low gate voltages. Unfortunately, quasiferroelectric properties of $SrTiO_3$ increased the device's time constant to several seconds, which practically prevented us from performing any time-dependent, charging-effect measurements.

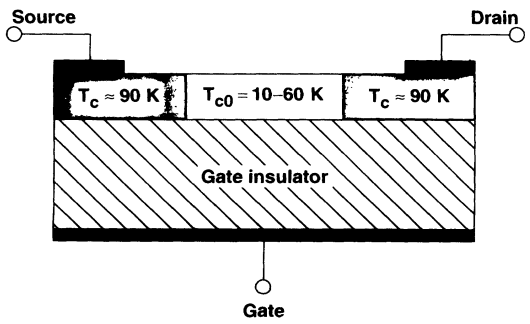

FIG. 1. A schematic of the superconducting charging-effect test structure with a thick, partially oxygen-deficient YBCO channel.

Our resistivity versus temperature, $R(T)$, and current-voltage measurements were performed in a four-probe geometry on devices operated in a common-source mode. The devices were mounted inside a continuous-flow helium cryostat and temperature stabilized with the accuracy of 0.01 K. The gate-to-channel leakage current was maintained below 0.1 nA and was negligible as compared to the measurement current. The drain voltage versus channel current, V_D-I_{CH}, characteristics were recorded in a dc current mode for several different values of the sample gate voltage V_g. For the J_c definition, we used an arbitrary criterion of 1 μV/cm.

The temperature dependence of the source-to-drain resistance for a typical, as-fabricated test structure is shown in Fig. 2. The two, well-defined superconducting transitions, one above 80 K and the other with $T_{c0} \approx 16$ K, correspond to the transitions of the source and drain electrodes, and the channel, respectively. We note that both transitions are relatively sharp, confirming high spatial homogeneity of the laser-patterned YBCO regions. A family of V_D-I_{CH} curves, measured at $T = 8.9$ K for V_g from 0 to -400 V, is shown in Fig. 3. We observed that negative V_g significantly enhanced the channel J_c, which in one of the samples increased by 43% for $V_g = -400$ V.[14] Simultaneously, the positive V_g (not shown in Fig. 3) lead to suppression of J_c, although its magnitude was not as high as the enhancement observed for negative V_g's. We want to stress, however, that the above J_c changes were to some extent irreversible, i.e., after removing the gate voltage the channel J_c did not return completely to its initial value. Subsequently, the field-induced J_c changes registered 40 h after the first measurement (Fig. 4) were much less pronounced, although we still observed both the enhancement and suppression of J_c. During the

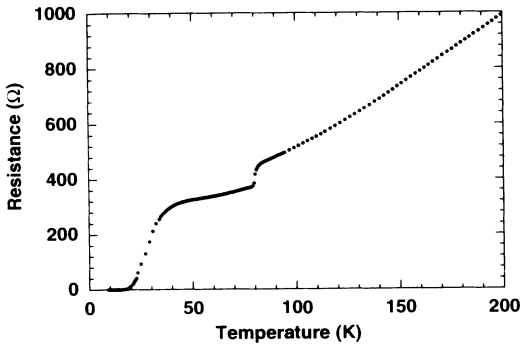

FIG. 2. Temperature dependence of the source-to-drain resistance for the as-fabricated YBCO-on-$SrTiO_3$ test structure.

next few days, the sensitivity of channel J_c to V_g continuously decreased and, finally, about one week after the structure fabrication, we detected no field-induced response of the sample. In addition to J_c modulation, we found that after each measurement session the T_{c0} of the channel increased by about 0.5–1.5 K and, several days after the structure's preparation and the first measurement, T_{c0} saturated at the value of about 8 K higher than that in the as-fabricated sample. The saturation of T_{c0} coincided with the disappearance of the charging effect in the sample. However, the experimental V_D-I_{CH} data presented in Figs. 3 and 4 cannot be solely attributed to the increase of T_c since, as we mentioned before, depending on the sign of the applied V_g, we observed a *decrease* or an *increase* of the channel J_c, which implies a more complicated interaction between the electric field and the YBCO in the channel. On the other hand, the time drift of T_c made any quantitative analysis of our experimental results (e.g., examination of the response asymmetry for positive and negative V_g's) impossible.

All the above features were also observed in the other as-fabricated structures with the oxygen-depleted channel. We noticed, however, that both the field-induced J_c modulation and long-term T_c drift were much more pronounced in samples with low (10–20 K) initial T_{c0}. Simultaneously, structures that were stored for ten or more days before the first measurement, regardless to their channel T_{c0}, showed no charge-induced response.

Our experimental results lead us to a conclusion that the charging effect observed in our samples is most likely related to the field-enhanced modification of the

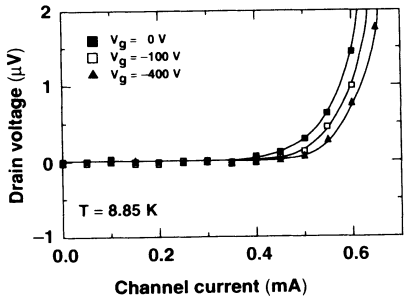

FIG. 3. Drain voltage versus channel current characteristics of the sample from Fig. 2, measured for three different values of V_g at 8.9 K. Lines connecting experimental points are guides for the eyes.

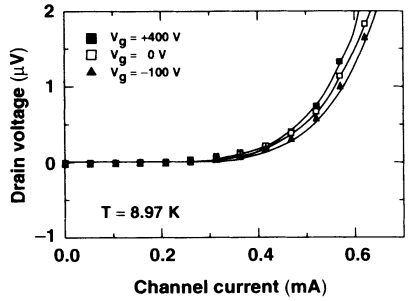

FIG. 4. Drain voltage versus channel current characteristics of the sample from Fig. 2 for several V_g's. The traces were recorded 40 h after the measurement presented in Fig. 3.

channel's crystalline structure, rather than to the simple electrostatic response of mobile holes. We can rule out that the J_c modification was caused by electrostrictive or piezoelectric stresses induced in the $SrTiO_3$ substrate, since those effects should be reversible and should not disappear in the older samples, nor be very sensitive to the sample T_{c0}. Also the possibility of the charging-current-induced electromigration of oxygen inside the channel is unlikely, as the polarity of our response is opposite to that reported in the electromigration experiments.[15] In fact, the charging effect observed by us can only be satisfactorily explained using the previously mentioned model, proposed by Chandrasekhar, Valls, and Goldman.[11] In particular, as in argument for this "chemical" nature of our response, we note the correlation between the sensitivity of our samples to electric field and the slow, persistent, increase of the channel's T_c. A long-term T_c increase in oxygen-deficient YBCO has been reported by several groups and is commonly related to the slow ordering of oxygen vacancies in the Cu-O chains.[16] It seems then reasonable to associate the large charging effect in our as-fabricated structures with their enhanced sensitivity to the electric field due to the film's oxygen system being far from equilibrium. As the oxygen pattern equilibrates, both reversible and irreversible field-induced oxygen-ion rearrangements become, apparently, less plausible, and sample sensitivity to the electric field decreases. Also the fact that the observed changes of J_c and T_c are lower in the samples with higher initial T_{c0}'s seems to confirm the above hypothesis. Both the chain-oxygen sensitivity to the electric field in the Chandrasekhar, Valls, and Goldman model and the long-term self-ordering of oxygen vacancies are much weaker in YBCO with higher oxygen contents.

To further investigate the possible relation between the electric-field sensitivity and the sample's crystalline order, we hydrogenated one of our old, previously tested structures by annealing it for 2 h at 190 °C in a flow of 4% H_2:96% N_2 gas mixture. It is known[17] that hydrogen doping influences YBCO electrical properties, since the H atoms position themselves primarily in interstitial locations outside the Cu-O planes and easily contribute additional electrons to the Cu-O planes, decreasing their free-hole density. On the other hand, such mild hydrogenation should not significantly influence the sample's oxygen content. We found that, indeed, the hydrogenation did not change the laser-written pattern nor the

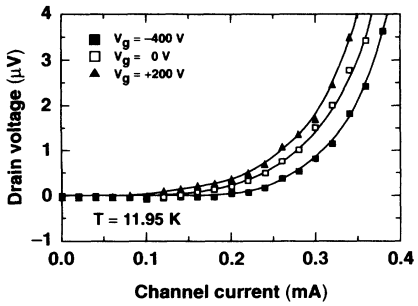

FIG. 5. Drain voltage versus channel current characteristics of a hydrogenated device measured for three different values of V_g at 11.9 K.

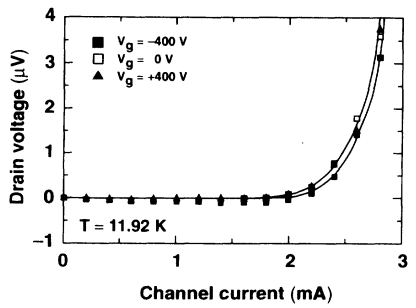

FIG. 6. Drain voltage versus channel current characteristics of the sample from Fig. 5. The characteristics were recorded after 7 days of room-temperature storage of the sample.

drain and source T_c; however, the channel's T_{c0} decreased from 29 to 15 K. Simultaneously, the sample's V_D-I_{CH} characteristics *regained* a sensitivity to V_g, as shown in Fig. 5. The observed J_c modulation was even stronger than in our first, after-the-fabrication measurement of this sample, but once again, this response disappeared almost completely after a few days of room-temperature storage (Fig. 6). At the same time, the sample's T_{c0} increased by 7 K. Although the microscopic origin of the revival of the charging effect in YBCO after the hydrogenation process remains at present unclear for us, it completely excludes any electrostrictive or piezoelectric effects and we strongly believe that it supports our previous conclusion that the charging effect observed in our films is due to the field-induced structural changes in oxygen-deficient YBCO.

In conclusion, the charging effect in relatively thick, oxygen-deficient superconducting YBCO films was investigated. We found that the application of electric field induced both reversible and irreversible changes of the samples' J_c and T_c. Those changes were present only in the samples freshly deoxygenated or hydrogenated and disappeared after several measurement sessions and/or after about a week of the sample aging at room temperature. Our results indicate that in oxygen-deficient YBCO, the charging effect cannot be explained by simple electrostatic response of mobile holes. The sensitivity of J_c modulation to not only the magnitude, but also the sign of the applied gate voltage and the revival of the charging effect in hydrogenated samples, rule out any secondary effects, such as electrostrictive or piezoelectric stresses in the $SrTiO_3$ substrate or oxygen electromigration in YBCO. Thus, we attribute the observed behavior to the charge-transfer effects related to the electric-field-enhanced altering of the YBCO oxygen ordering. Finally, we want to note that the model proposed by Chandrasekhar, Valls, and Goldman[11] is only applicable to the YBCO crystals. The other HTS's, such as Bi-Sr-Ca-Cu-O or Tl-Ba-Ca-Cu-O are tetragonal and much less susceptible to oxygen manipulation. It would be extremely interesting to perform charging-effect experiments on those latter materials and compare the results with those obtained for YBCO films.

This work was supported by Air Force Office for Scientific Research Grant No. F49620-92-J0075.

*Also at the Institute of Physics, Polish Academy of Sciences, PL-02668 Warszawa, Poland.

[1]See, e.g., A. W. Kleinsasser and W. J. Gallagher, in *Superconducting Devices,* edited by S. T. Ruggiero and D. A. Rudman (Academic, Boston, 1990), p. 325, and references therein.

[2]R. E. Glover III and M. D. Sherrill, Phys. Rev. Lett. **5**, 248 (1960)

[3]H. L. Stadler, Phys. Rev. Lett. **14**, 979 (1965).

[4]J. Mannhart, D. G. Schlom, J. G. Bednorz, and K. A. Muller, Phys. Rev. Lett. **67**, 2099 (1991).

[5]X. X. Xi, Q. Li, C. Doughty, C. Kwon, S. Bhattacharya, A. T. Findikoglu, and T. Venkatesan, Appl. Phys. Lett. **59**, 3470 (1991).

[6]G. Brorsson, Yu, Boikov, Z. G. Ivanov, and T. Claeson, IEEE Transp. Appl. Supercond. **3**, 2922 (1993).

[7]J. Mannhart, J. Ströbel, J. G. Bednorz, and Ch. Gerber, Appl. Phys. Lett. **62**, 630 (1993).

[8]A. M. Kechiantz, in *Progress in High-Temperature Superconductivity,* edited by W. Gorzkowski, M. Gutowski, A. Reich, and H. Szymczak (World Scientific, Singapore, 1990), Vol. 24, p. 556.

[9]J. Mannhart, J. E. Bednorz, K. A. Muller, D. G. Schlom, and J. Strobel, J. Alloys Compd. **195**, 519 (1993).

[10]B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, J. C. Campuzano, C. Olson, A.-B. Yang, R. Liu, C. Gu, R. S. List, A. J. Arko, and R. Bartlett, Physica C **158**, 276 (1989).

[11]N. Chandrasekhar, O. T. Valls, and A. M. Goldman, Phys. Rev. Lett. **71**, 1079 (1993).

[12]R. Sobolewski, W. Xiong, and W. Kula, IEEE Trans. Appl. Supercond. **3**, 2896 (1993).

[13]R. Sobolewski, W. Xiong, W. Kula, and J. R. Gavaler, Appl. Phys. Lett. **64**, 643 (1994).

[14]$V_g = \pm 400$ V was the highest voltage we could safely apply to our sample. Assuming dielectric constant even as high as 10^3 for our $SrTiO_3$ substrate, 400 V corresponds to the electric field of $\sim 10^7$ V/cm at the superconductor surface. This value is several times lower than that reported in the literature for the test structures with thin gate insulators.

[15]B. H. Moeckly, D. K. Lathrop, and R. A. Buhrman, Phys. Rev. B **47**, 400 (1993).

[16]G. Ceder, R. McCormack, and D. de Fontaine, Phys. Rev. B **44**, 2377 (1991).

[17]For a review see, e.g., E. K. Shalkova, Yu. M. Baikov, and T. A. Ushakova, Superconductivity **5**, 22 (1992).