Single Electron Tunneling Effect in YBCO Films

J. I. Kye, W. K. Park, B. I. Kim and Z. G. Khim

Department of Physics, Seoul National University, Seoul 151-742


Memory Division, Samsung Electronics, Suwon 440-600

(Received 4 October 1995, in final form 26 February 1996)

We have measured the tunneling spectra of c-axis-oriented YBCO films prepared by the sputtering method. In some spots, the spectra show periodic current steps at the corresponding voltages of $V = (2n + 1)\delta V/2$ or $V = n\delta V$. We have measured $\delta V$ with the variation of the sample-to-tip distance. The resulting voltage period $\delta V = e/C$ increases as the sample-to-tip distance increases. This behavior is explained by single electron tunneling. The simulated conductance, with the assumption of a normal state density of states for both the metal grains and the YBCO surface layer, shows a good agreement with the experimental result, indicating that the surface layer of YBCO is in a normal state due to oxygen deficiency.

I. INTRODUCTION

Electron tunneling in a superconductor has proved to be a very powerful mean for investigating superconducting properties due to its ability to probe the local density of states (DOS). For example, the magnitude of the superconducting energy gap and pairing interactions, such as the electron-phonon interaction, in conventional low-temperature superconductors has been successfully obtained from the analysis of the tunneling conductance. For this reason, various types of tunneling experiments have been attempted for the study of superconducting properties of high-$T_c$ superconductors (HTS). Unlike the tunneling spectra of low-$T_c$ superconductors, however, tunneling spectra of high-$T_c$ superconductors so far have shown a variety of spurious structures, such as linear background conductance above the energy gap, multiple gap-like peaks, and strongly smeared conductance inside the gap region [1].

Figure 1 shows a typical $dI/dV$ curve obtained from a YBCO thin film which shows multiple gap-like peaks as well as a linear background conductance beyond the energy gap. Similar multiple gap structures or periodic conductance peaks have often reported in high-$T_c$ superconducting materials [2]. These spurious structures observed in the tunneling conductance of HTS are, sometimes, attributed to the intrinsic nature of HTS, such as their non-s-wave gap symmetry [3] or the Josephson coupling effect between the layers of HTS [4]. At the same time, these spurious structures are also attributed to extrinsic effects, such as the degradation of the surface [5] or the coverage of the surface by a normal layer, resulting in a distributed energy gap [6].

Another possible explanation for the spurious tunneling conductance is the formation of a serially coupled tunnel junction due to the granular nature of HTS. For a tunnel junction with an extremely small capacitance between electrodes such that the capacitive charging energy $E_c = e^2/2C$ is greater than thermal energy $k_B T$, the tunneling of a single electron will increase the system energy by an amount of $e^2/2C$. Consequently, electron tunneling will be suppressed at a bias lower than $e/2C$; this is commonly known as the Coulomb blockade effect [7]. If there is a small metallic droplet between the tunneling electrodes, thus forming a serially coupled tunnel junctions, the I-V characteristics of such a system can show a current step with equal voltage interval $\delta V = e/C$ corresponding to the accumulation of successive extra electrons in the metallic droplet, an effect which is known as the Coulomb staircase [7].

The capacitance between the electrodes must be very small for the realization of the Coulomb staircase effect. Frequently, small metal droplets or granular systems were employed for the study of such a single electron tunneling (SET) effect [8]. As new techniques for the device fabrication are developed, it is becoming possible to make submicron electronic devices where the discreteness of the electronic charge plays an important role [9]. One can also observe the SET effect in a superconducting film surface. In this case, a small metal droplet, which is evaporated on a thin film, and the scanning tunneling microscope (STM) tip make the double tunnel junction [10]. With improvements in the STM technique, one can
take advantage of its exceedingly fine lateral resolution, better than 10 Å, and the vertical control capability for tunneling measurement. Thus, the low temperature STM is quite suitable for energy gap measurements as well as for transport measurements of small junctions.

Fig. 1. Typical tunneling conductance of a YBCO film as obtained by the STM method. One can notice double peaks at 25 meV and 75 meV as if there are two different energy gaps in YBCO.

Fig. 2. AFM image of the YBCO film shows the Coulomb staircase (9.6 × 9.6 µm). The grain size ranges from ∼ 100 Å to several thousand Å.

In this experiment, we have measured the tunneling spectra using a STM at various spots of YBCO films deposited on SrTiO$_3$ or MgO by the sputtering method to elucidate the nature of the tunneling spectra and the surface layers of the HTS. Depending on the tunneling spot in the same YBCO film, we obtained energy gap structures or a Coulomb staircase in the tunneling characteristics. Experimental data were compared with theoretical calculations, and the conductance variation with the tip-to-sample distance was measured.

II. EXPERIMENTAL PROCEDURE

The sample studied in this work is a c-axis-oriented YBCO film which was deposited on a MgO(001) substrate by the dc- sputtering method. The partial pressures of the argon and the oxygen gases were 60 mTorr for each. The substrate temperature during film deposition was held at 700°C. The film was annealed in-situ at 450°C and 600 Torr. The surface of the YBCO film appeared very smooth. The atomic force microscope image of the film, however, revealed the formation of small droplets with sizes ranging from ∼ 100 Å to several thousands of Å as shown in Fig. 2. The critical temperature of the YBCO film was 90 K. In order to reduce the surface degradation, YBCO film was mounted on a
Fig. 4. Even with the variation of the sample-to-tip distance, the nearly identical tunneling conductance on the same spot implies that the observed structure in the conductance is due to intrinsic energy gap of the YBCO film.

Sample holder immediately after sputter deposition. After mounting the sample onto the sample holder which was incased in a cylinder, the cylinder was filled with a helium exchange gas.

The mechanical part of the low-temperature STM system was mounted in a long cylindrical stainless tube to reduce the thermal drift effect. The cylindrical stainless tube was then immersed in a liquid helium cryostat; hence, the mechanical part of the STM was not in actual contact with the liquid helium. Mechanically sharpened Pt-Rh wire was used as the STM tip. To examine the conductance of a nearby spot, we retracted and moved the tip to the new spot. Stable tunneling current was obtained with a typical effective tunneling resistance on the order of 1 MΩ at 4.2 K. The magnitude of the tunneling resistance in this work indicates that the tunneling is not vacuum tunneling, but point-contact-type tunneling, thus leading to a rather stable tunneling barrier. The diameter of the point contact tip was estimated to be about 10 µm from SEM image. The tunneling spectra were measured using the usual lockin technique. The magnitude of the modulation voltage was 1 mV with a sweep rate of about 20 seconds. Even with the feedback signal turned off during the tunneling measurement, the tunnel junction remained stable for at least several minutes at 4.2 K.

III. RESULTS AND DISCUSSION

Figure 3 shows typical results for the tunneling conductance at various positions in the YBCO film. In general, three different types of tunneling conductances (Figs. 3 (a), (b), and (c)) were observed in the same film, depending on the tunneling site. For tunneling through a large grain, we obtained a tunneling conductance similar to the one in Fig. 3 (a). On the other hand, for tunneling through a small grain, we obtained the tunneling conductance of Fig. 3 (b).

The tunneling conductance of Fig. 3 (a), which was obtained from a large grain site, is believed to be due to the energy gap structure of the superconductor. The reason is that, even with a change in the sample-to-tip distance for this spot, we obtained nearly identical conductance curves. By adjusting the sample-to-tip distance, one can control the tunneling current at a given bias. In other words, if the distance becomes larger, the tunneling current becomes smaller for a given bias. Thus, the magnitude of the tunneling current can give an indirect estimate of the sample-to-tip distance. As shown in Fig. 4, the tunneling conductances obtained with different tunneling currents or sample-to-tip distances are almost identical, implying the structure in the conduc-
The conductance curve is an intrinsic property of the superconductor. From this result, the energy gap of YBCO is estimated to be about $\Delta_{\text{peak}} = 20 \text{ meV}$.

The conductance curve of Fig. 3 (b), which shows more than 10 peaks, is attributed to the single electron tunneling effect, while that of Fig. 3 (c) is attributed to the semiconducting region of the sample due to a degraded surface with off-stoichiometric oxygen content. Of course the conductance curve shown in Fig. 3 (b) can also be interpreted as a multiple gap structure or interplanar tunneling between CuO$_2$ planes. However, the tunneling characteristics, such as the voltage interval $\delta V$ between conductance peaks, vary with the sample-to-tip distance, implying that those peaks are due to an extrinsic property. Thus, we assume that there is an isolated metal droplet separated by a thin insulating layer on top of the YBCO film, so the electron tunnels from the tip to an isolated grain and then to the film as shown in Fig. 5. If the capacitance between them is very small such that the single electron charging energy $e^2/2C$ is greater than the thermal energy $k_B T$, then it will be necessary to have extra bias $\delta V = e/C$ for each additional electrons accumulated in the metal droplet, as mentioned earlier.

Figure 6 shows another tunneling conductance obtained at a different spot in the YBCO film. A slightly asymmetric and yet still periodic conductance peaks appear with $\delta V$ about 40 mV.

Simulation of the tunneling conductance was performed following the method developed by Amman et al. [11]. With the applied voltage $V$ across the tip and sample and $N$ extra electrons in the middle metal droplet, the junction voltages are given as

$$V_1 = \frac{C_2}{C_1 + C_2} V - \frac{Ne}{C_1 + C_2} - V_p,$$

$$V_2 = \frac{C_1}{C_1 + C_2} V + \frac{Ne}{C_1 + C_2} + V_p$$

where $V_p$, the Fermi level difference of the metal droplet, is introduced to account for the asymmetry in the conductance.

The ensemble-averaged rate equation for the probability $\rho(N,V,t)$ that there are $N$ extra electron in the metal droplet at time $t$ with applied voltage $V$ is given as
\[
\frac{\partial \rho(N,V,t)}{\partial t} = \left[ r_1(N-1,V) + l_2(N-1,V) \right] \rho(N-1,V,t) \\
+ \left[ l_1(N+1,V) + r_2(N+1,V) \right] \rho(N+1,V,t) \\
- \left[ r_1(N,V) + l_1(N,V) + r_2(N,V) + l_2(N,V) \right] \rho(N,V,t)
\]

(2)

where \( r_i(N,V) \) (\( l_i(N,V) \)) is the electron tunneling rate from the right (left) electrode on the \( i \)th junction. The tunneling rate \( r_2(N,V) \), for example, the tunneling rate from the tip to the metal droplet, will be proportional to the product of the occupied density of states in the tip and the unoccupied density of states in the metal droplet:

\[
r_2(N,V) = \int_{-\infty}^{\infty} \frac{2\pi}{\hbar} |T(E)|^2 N_r(E - E_r) f(E - E_r) N_l(E - E_l) [1 - f(E - E_l)] \, dE
\]

(3)

where \( f(E) \) is the Fermi distribution function and \( N_r(E) \) and \( N_l(E) \) are the density of states of the right electrode and the left electrode, respectively. With \( r_i(N,V) \) and \( l_i(N,V) \), one can obtain the probability \( \rho(N,V,t) \) from the static condition of Eq. (2). Then the tunneling current can be calculated as

\[
I(V) = \sum_{N=-\infty}^{\infty} e[r_1(N,V) - l_1(N,V)]\rho(N,V)
\]

\[
= \sum_{N=-\infty}^{\infty} e[r_2(N,V) - l_2(N,V)]\rho(N,V).
\]

(4)

The thick line in Fig. 6 is the theoretical simulation employing the normal state densities of states (which we took as a constant.) for the metal droplet and the YBCO layer. The parameters employed in the calculations were \( C_1 = 4.4 \) aF, \( C_2 = 10 \) aF, \( R_1 = 60 \) M\( \Omega \), \( R_2 = 500 \) k\( \Omega \), and \( V_p = -4.2 \) mV. The calculated I-V and dI/dV curves agree well with experimental results. If we take a BCS-type density of states for the metal droplet or the YBCO layer, the first conductance peak is shifted by \( \Delta \) in the simulated conductance. The absence of a voltage shift by \( \Delta \) in the conductance implies that both the metal droplet and even the YBCO layer are actually in a normal state. The oxygen-deficient top surface layer is believed to have behaved as a normal layer. Also, the absence of a sharp current step in the I-V curve is attributed to the sizable difference in the capacitance of junctions.

If the periodic structure in the conductance curve was really due to single electron tunneling, one would also expect a variation of \( \delta V \) with the sample-to-tip distance as mentioned earlier. That is, as the distance between the sample and the tip increased, the capacitance between them would decrease, and hence \( \delta V = e/C \) would become larger. dI/dV curves in Fig. 7 (a) show the variation of the tunneling conductance with the sample-to-tip distance obtained at a different position from that of Fig. 6. The tunneling currents of 2 nA, 5 nA, and 10 nA specified in Fig. 7 (a) are currents at a bias voltage of 130 mV. Thus, a smaller tunneling current means a smaller capacitance or a wider sample-to-tip distance. The voltage interval \( \delta V \) between the conductance peaks increases from 24 mV to 27 mV as indicated by the slope in Fig. 7 (b). This behavior indicates that the obtained periodic structure in dI/dV is not an intrinsic property

![Fig. 8. Bistability of the single electron tunneling effect observed at the same spot of a YBCO film. Sometimes the tunneling conductance shows \( V = (2n+1) \delta V/2 \) (a); at some other times, it shows \( V = n\delta V \) (b).](image-url)
of sample, but a Coulomb staircase induced by small isolated grains with small capacitances.

To fit the simulated curve to the experimental curve, it is necessary to adopt another parameter called $V_p$, which causes a voltage shift in the $dI/dV$ or I-V characteristics. It is not clear yet why there is a voltage shift. The Fermi energy mismatch of the middle electrode due to polarization in the insulating layer or impurity states in the insulating layer may cause such a voltage shift [12].

Figure 8 shows a bistability in the single electron tunneling effect. Note that two conductance curves obtained at the same spot show a shift in the peak position by $\delta V/2 = e/2C$, evidenced by the variation of the peak position $V = (2n+1)\delta V/2$ and $V = n\delta V$. To explain this bistability, it is necessary to introduce a fractional charge $e/2$ at the equilibrium state, which is quite unrealistic. Further investigation is necessary to elucidate the nature of the bistability observed in ultra-small particles.

IV. SUMMARY

We measured the tunneling spectra of a c-axis oriented YBCO film, which was sputter-deposited on a MgO substrate, by low-temperature STM. The AFM image of the YBCO film surface revealed the formation of tiny grains with sizes ranging from about 100 Å to several thousand Å. The typical tunneling conductance obtained for larger grains had a linearly increasing background conductance and also position-dependent properties similar to other grains.

Further investigation is necessary to elucidate the nature of the bistability observed in ultra-small particles.

The multiple energy gap-like structures observed previously are now believed to be due to the Coulomb staircase effect in HTS film [15,16]. The bistability in the SET effect observed in this work remains as a problem for further investigation.

ACKNOWLEDGMENTS

This work was supported in part by the Ministry of Science and Technology and also in part by the Basic Science Research Institute program (BSRI-95-2416) of the Ministry of Education in Korea.

REFERENCES