Room-temperature single-electron charging and surface polarization in tunneling spectroscopy of high-T_c superconducting thin films

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The tunneling spectroscopy of both $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $TlBa_2Ca_2Cu_3O_{9\pm\delta}$ (Tl-1223) superconducting thin films was studied using scanning tunneling microspectroscopy. The marked staircase structure in the current-voltage characteristics showed the manifestation of single-electron charging of two series-coupled mesoscopic tunnel junctions. For YBCO films, the step width across the zero-bias voltage (ΔV_0) was larger than that of other steps (ΔV_n), with $\Delta V_0 \cong 1.5\Delta V_n$, as the bias voltage exceeded a threshold value. Such a step-widening anomaly, however, was not seen in Tl-1223 films. Preliminary surface polarization measurements showed that the polarization is much more hysteretic for YBCO than for Tl-1223 films, suggesting that the anomalous widening of ΔV_0 may originate from the polarization-induced residual charging effect. [S0163-1829(98)09841-5]

The gaplike structure in scanning tunneling microspectroscopy (STM), though frequently inferred to be evidence of superconductivity,[1–3] could also be a manifestation of single-electron charging (SEC) effects.[4–7] It has been demonstrated[5] that, in a typical SEC system, the multiple-peak tunneling features similar to those observed in high-T_C superconductors (HTS's) were unambiguously reproduced. On the other hand, McGreer *et al.*[3] have demonstrated that the feature of the Coulomb staircase can also be affected by a gap opening in the superconducting electrode. The effect manifests itself by a widening of only the width of the zero-bias voltage step, ΔV_0, with $\Delta V_0 = e/C + 8\Delta$. Here, $\Delta(T)$ is the superconducting gap of the material.

In this paper, we will first show that, in a typical STM measurement, the tip and the HTS film surface may naturally form a system consisting of two series-coupled mesoscopic tunnel junctions. Features of a Coulomb staircase in the tunneling current-voltage characteristics (IVC's) associated with the SEC effect were observed even at room temperature. In particular, when the bias voltage, V_t, was increased to exceed a certain level, the width of ΔV_0 became larger than that of the other steps (ΔV_n), with $\Delta V_0 \approx 1.5\Delta V_n$. This anomalous widening of ΔV_0, although apparently not of the same origin as found in Ref. 3, was unique to all the $YBa_2Cu_3O_{7-\delta}$ (YBCO) films studied and was absent in the $TlBa_2Ca_2Cu_3O_{9\pm\delta}$ (Tl-1223) films. Preliminary polarization-*E*-field measurements on both the YBCO and Tl-1223 films suggest that it might be due to a surface polarization-induced residual charge existing in degraded YBCO surfaces.

The YBCO films were deposited *in situ* on various substrates, including MgO, $LaAlO_3$ (LAO), $NdGaO_3$ (NGO), and $SrTiO_3$ (STO) by pulse laser ablation.[8] It is noted that all the films are of high quality with the *c* axis normal to the film surface. Typically, the zero-resistance transition temperatures, T_{c0} were in the range 87–90 K with $J_c(77\ \mathrm{K}) > 10^6$ A/cm^2 in all cases. The YBCO films appeared to be granular on a fine scale with an average ''island'' size of about 100 Å in diameter.[9] The Tl-1223 films, on the other hand, were prepared by a two-step (i.e., dc-sputtering and postannealing) process.[10] These films were having T_c's$\approx$108–110 K and $J_c(77\ \mathrm{K}) \geqslant 10^6$ A/cm^2, as well. Nonetheless, the films were even more granular than the YBCO films. It is noted that the tunneling configuration in our case is very similar to the Pb-oxide system studied by McGreer *et al.*[3] In our case, manipulation of junction parameters such as the junction capacitance can also be achieved by varying the distance between PtIr tip and sample surface through the changes of V_t's.

Both the topographic and spectroscopic information were obtained simultaneously by operating the STM system in the scanning probe mode (SPM). In this mode, a fixed V_t was first chosen to set the tip-surface distance, then, after turning off the feedback circuit, the IVC's were taken by ramping the voltage from $-V_t$ to V_t. In this way the tip-sample distance was fixed while taking the tunneling IVC's. In each operation, a total of 16 IVC curves were recorded over an area of 100 Å$\times$100 Å. Thus each data point is representing an average of 16 curves and should give an indication of film homogeneity. In addition, as pointed out by van Bentum *et al.*,[11] the presence of a much larger stray capacitance in the leads far away from the point contact should not affect the effective capacitance of the rather blunt tip (usually with a radius in the order of $\sim$100 Å), significantly. Finally, all of the tunneling characteristics were taken at room temperature and in air.

The surface polarization were measured using a Sawyer-Tower circuit[12] comprised of a Tektronix AWG2020 GS signal generator, a TDS520 oscilloscope, and a built-in 10 nF reference capacitor, C_t. The frequency of the voltage source was 1 kHz. Two droplets ($\approx$2 mm in diameter) of silver paint were first applied onto the film surface as probe contacts. The polarization density **P** underneath the area covered by the silver paint was calculated and was used to estimate the effective residual charge in the junction.

The typical tunneling IVC's for YBCO films obtained at room temperature are shown in Fig. 1. Notice that, although the thermal noise is significant, the SEC effect-induced Coulomb staircase in the IVC's [curve *(a)*] is evident. Although

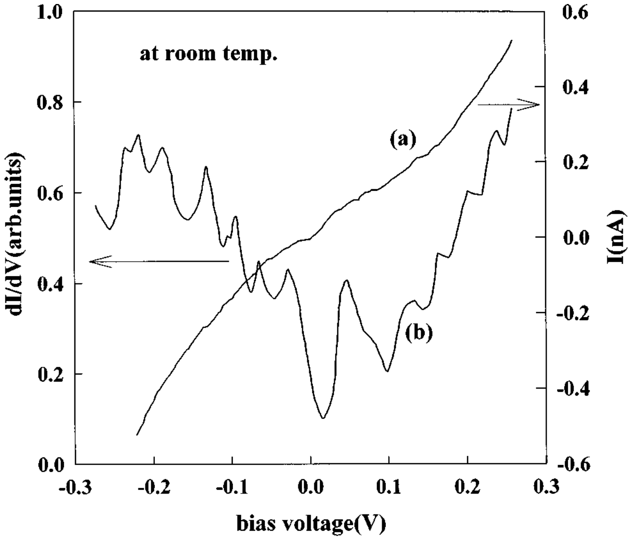

FIG. 1. The typical room-temperature tunneling characteristics obtained by STM for YBCO and Tl-1223 films.

the room-temperature SEC effects have been demonstrated very recently in some complicated material systems,[13,14] we believe to the best of our knowledge that the present results are the first to be observed in HTS films.

It should be pointed out that, physically, in order to observe SEC effects, there are two necessary prerequisites:[6] (1) the thermal energy has to be much smaller than the charging energy, $k_BT<E_C$, and (2) the tunneling resistance has to be much larger than the quantum resistance, $R_t>R_q \equiv \hbar/e^2 \cong 4.3$ kΩ. In our case, the tunneling resistance $R_t \approx 10^8$ Ω, thus, condition (2) is automatically satisfied. Whereas the charging energies, as given below, are all in the order of k_BT, and seemingly fail to meet the conditions. The apparent discrepancy, we believe, may be due to the fact that in most theoretical considerations condition (1) was a result of treating the thermal fluctuation classically. As a result, the power spectrum incorporated in the theories was mostly with the familiar Johnson-Nyquist form. However, as pointed out by Ben-Jacob, Mottola, and Schön,[15] in regimes where the quantum effects and discreteness of the underlying charge transfer processes are both important, the spectrum differs dramatically from the Johnson-Nyquist form. The net effect is a significant suppression of thermal fluctuations and the discreteness of single charge transfer is expected to be completely smeared out only when $R_t \leqslant (\hbar/e^2)e^2/Ck_BT$. This may be the reason why even when $e^2/Ck_BT \leqslant 1$ the SEC effect can still be seen if R_t is large enough.

In order to delineate that the observed features are indeed due to the SEC effect more quantitatively, the dI/dV vs V is shown in curve *(b)*. The multiple peak structure clearly exhibits the typical Coulomb staircase structure expected for a series-coupled two-junction model system.[9] Furthermore the analyses gave a nearly constant spacing of $\Delta V_n = 31 \pm 2$ mV (except the zero-bias step) for $V_t = -0.3$ V. This corresponds to a junction capacitance $C = e/\Delta V_n \cong 5.2 \times 10^{-18}$ F and a charging energy $E_C = e^2/2C \cong 16$ meV, respectively. Taking the effective area of the PtIr tip to be between $S = \pi r^2$ (for planar) and $S = 2\pi r^2$ (for hemispherical) with $r \cong 100$ Å and the average tip-sample distance $d \cong 10$ Å (from the specified values listed in the manual), the simple parallel plate formula could give a estimated capacitance in the range of $C \cong 3 \times 10^{-18}$ F to $C \cong 6 \times 10^{-18}$ F, which is in fair agreement with that inferred from ΔV_n. The agreement further indicates that the observed tunneling IVC's are indeed manifestations of SEC effects.

Another interesting feature in the tunneling characteristics to be noted is the anomalous widening of ΔV_0. To the best of our knowledge, this has never been systematically addressed before. Figure 2 shows ΔV_n, as a function of V_t for YBCO films. It is noted that each data point in the figure represents a value averaged over 16 IVC's obtained within an area of 100 Å×100 Å. The narrow spread of values is indicative of film homogeneity and the reproducibility of the SEC effect. It is evident that, for $V_t > 0.25$ V, ΔV_0 is constantly larger than ΔV_n's, which remains essentially constant

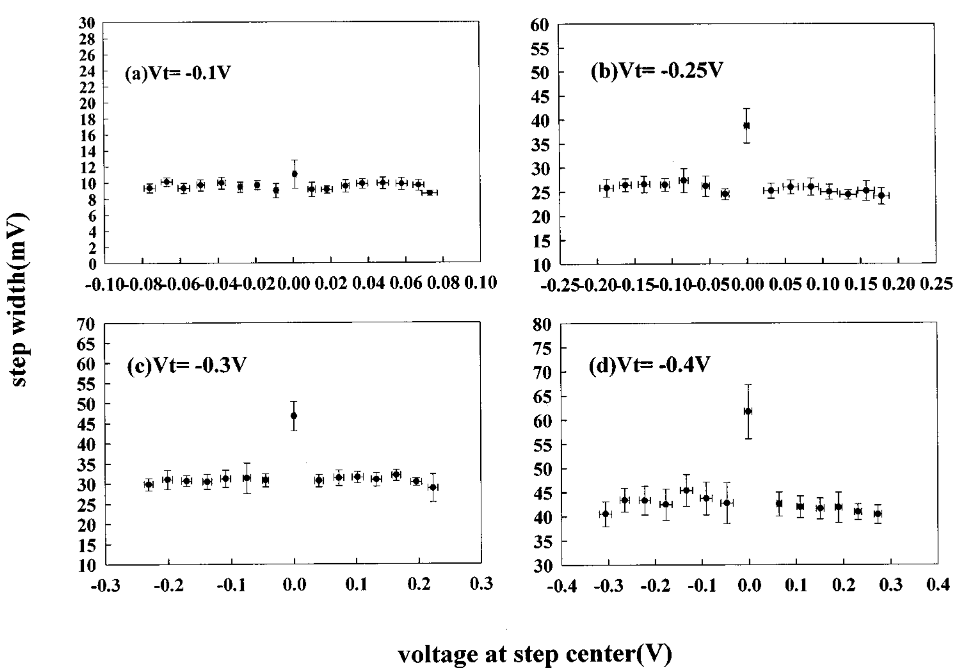

FIG. 2. $\Delta V_n \,(= ne/C)$ of YBCO films as a function of V_t at room temperature. Notice that $\Delta V_0 \cong 1.5 \Delta V_n$ emerged abruptly when $V_t \geqslant -0.25$ V.

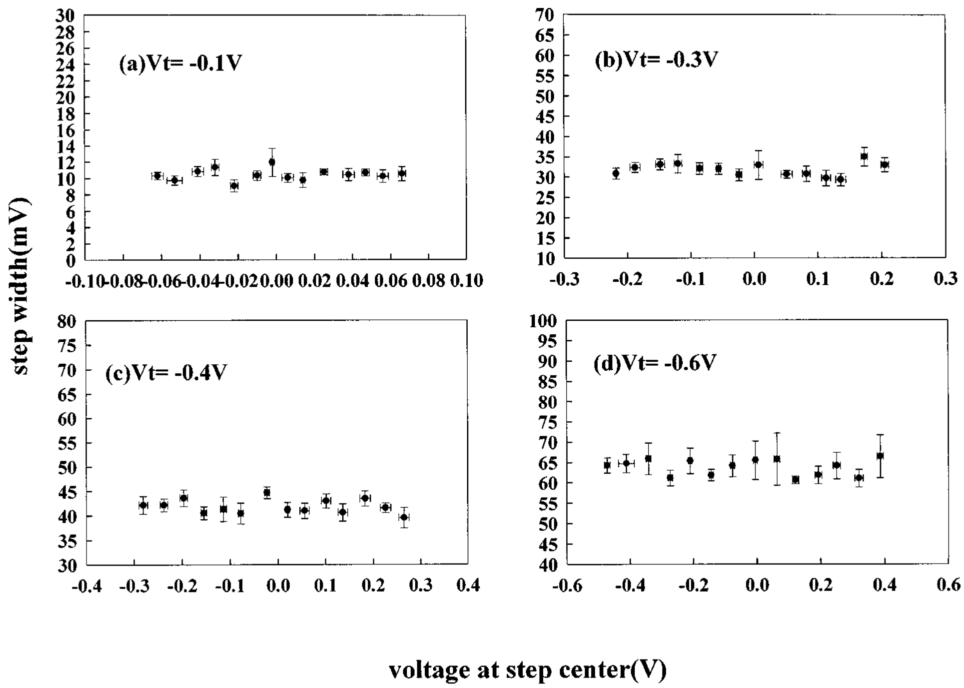

FIG. 3. ΔV_n as a function of V_t for Tl-1223 films at room temperature. Notice the absence of a ΔV_0 anomaly.

for a fixed V_t, signifying all other primary features for SEC effect-induced Coulomb staircase in series-coupled mesoscopic tunnel junctions. In addition, the linear dependence of both ΔV_0 and ΔV_n on V_t implies that the reciprocal of the capacitance of the system (or the film-tip distance) varies similarly with V_t, as well. In a typical STM, the bias voltage determines the expansion of the *z*-piezo and hence the tip-to-film distance. Thus, our observations would imply that the bias voltage changes the tip-to-film distance linearly. In any case, the results not only lend support for using a simplified parallel plate model for first-order estimations, but also indicate that the SEC effects are governed primarily by the capacitance between the tip and the central electrode grain. It is quite remarkable that all of these features occurred in virtually all the YBCO films studied, regardless of the substrates used.[8] The question to be asked now is whether or not the anomalous widening of ΔV_0 is an intrinsic SEC effect.

Since ΔV_0 reflects the Coulomb blockade effect for the first electron to tunnel through the junction, the present observation may thus be regarded as an increase in the blockade barrier due to mechanisms yet to be identified. One of the possibilities of varying ΔV_0 is the polarization-induced residual charge existing in the surface layer of the film.[16] In our case, this could have occurred when V_t was increased to some threshold value such that the electrical field became strong enough to induce a permanent polarization of the YBCO surface. Although, it is not clear at present how this would affect the SEC process in a quantitative manner, it should be interesting to make a preliminary comparison with other families of HTS films with more robust surfaces. As has been repeatedly demonstrated,[10] the Tl-based superconducting films should serve as good candidates for such a study.

As shown in Fig. 3, for Tl-1223 films, the same studies gave two immediately noticeable features. First, ΔV_n's (hence the effective capacitance) remain exactly the same as those found in the YBCO films for each corresponding V_t. More importantly, there is no anomalous widening of ΔV_0 even when V_t is as high as -0.6 V. It indicates that the same mechanisms were prevailing in both family of films, consistent with the notion that the SEC effects should depend only on the nanoscale granularity and not on the electrode material itself. It also reveals that the anomalous widening of ΔV_0 is not intrinsic to SEC effects but probably relates to the YBCO film surface only.

As a further test, surface polarization on both types of films were studied. Preliminary results obtained with a homemade Sawyer-Tower circuit are shown in Fig. 4. The two types of HTS films did display dramatic differences in surface polarization. For Tl-1223 films, there is no apparent saturation polarization within the range of the applied volt-

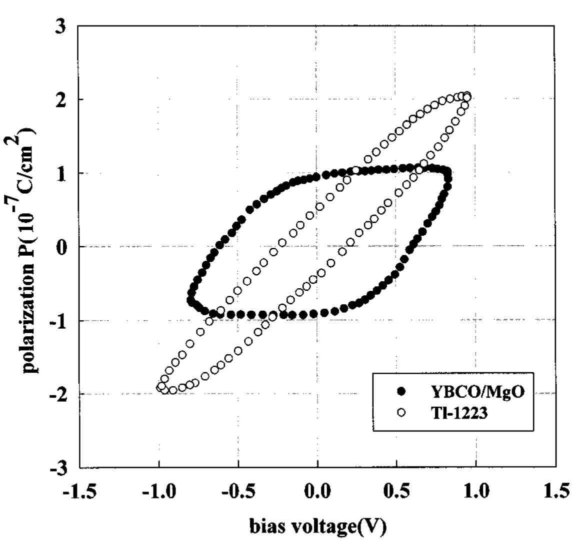

FIG. 4. Distinct surface polarization behaviors between YBCO/MgO and Tl-1223/LAO films.

ages, which are larger than values of V_t applied in the tunneling measurements. The origin of the observed hysteresis loop is not clear at present. However, the shape of the loop suggests that it may just be the phase lag of the circuit. On the contrary, for YBCO films, the polarization behaves much like a typical ferroelectric, with an apparent surface polarization. A rough estimate, by taking the saturation voltage $V_s \cong 0.4$ V and $C_f = 10$ nF, gives $\mathbf{P} \cong [0.4\ (\mathrm{V}) \times 10^{-8}\ (\mathrm{F})]/4\ \mathrm{mm}^2 \approx 10^{-7}\ \mathrm{C/cm}^2$. Thus, for a central electrode about 100 Å in diameter the effective polarization-induced residual charge $Q_{\mathrm{eff}} \approx 10^{-7}\ \mathrm{C/cm}^2 \times \pi (5\ \mathrm{nm})^2 \approx 7.9 \times 10^{-20}$ C. Due to the limited resolution of the current apparatus, a more quantitative account of polarization on the SEC effect was not attempted. Nonetheless, we point out that the anomalous widening of ΔV_0 observed here should be carefully taken into account when inferring gap information directly from the Coulomb staircase structures as adopted by McGreer *et al.*[3]

In summary, we have unambiguously shown that the SEC effect is playing a prominent role in the tunneling characteristics of both YBCO and Tl-1223 superconducting thin films at room temperature. The sole dependence of ΔV_n on V_t found in both types of film studied indicates that the SEC effect should be ubiquitous to mesoscopic systems with nanoscale granularity regardless of the electrode materials probed. The anomalous widening of ΔV_0 turned out to be unique to YBCO films only. Preliminary polarization experiments suggest that it might be intimately related to the degraded top layers of YBCO films.

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