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# Electric field effect on insulating cuprate planes

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We have studied field effect doping of nearly insulating *p*-type $CuO_2$ planes in single crystal transistor heterostructures. By using a high $\varepsilon_r$ epitaxial $SrTiO_3$ dielectric layer, a wide range of doping control is obtained, from −0.40 to 0.15 carriers/Cu (or $\sim 10^{14}$ carriers/$cm^2$). While a considerable field effect is observed for carrier depletion, the induced holes are completely localized even up to carrier density levels far beyond the bulk insulator-to-superconductor transition value. This implies that large induced carrier density and single crystalline interface is not a sufficient condition for electric field induced insulator-to-superconductor transition for cuprates. We show that the induced carriers are almost confined to the top single $CuO_2$ plane and propose that two-dimensional confinement introduces this localization. Understanding and overcoming this localization behavior is a serious challenge to any attempt to use electric field to induce superconductivity in insulating cuprates.

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Soon after the discovery of high temperature superconductivity in cuprates, it was noted that the relatively low two-dimensional (2D) carrier density per molecular plane ($\sim 10^{14}$ carriers/$cm^2$) required for superconductivity opened the possibility of field effect induced superconductivity.[1] In spite of both technological and fundamental significance, this suggestion has evaded a conclusive answer and still remains an open question.[2] To evaluate the potential of this approach for doping, it is important to know whether induced charge will actually induce conductivity. For 2D materials, such as $CuO_2$ planes with a large density of states, field-induced carriers predominantly accumulate in the top molecular layer. We report using an electric field to reversibly induce charge in such a cuprate layer over a wide range, more than 0.5 charge/Cu site, in a single crystal heterostructure. We observe a considerable field effect for the case of carrier depletion. In contrast, field-induced hole carriers are found to be immobile, implying that field effect doped carriers form a localized phase in an isolated 2D $CuO_2$ layer that would be conducting in bulk.

Earlier field effect work on cuprate systems was mostly focused on superconducting films.[3–5] The transition temperature was lowered by depleting cuprate layers of charge[3,4] and ultrathin underdoped superconducting cuprate films were driven insulating using a switched ferroelectric gate.[5] On the other hand, studies on insulating cuprate layers attempting to make them superconducting, which would be even more interesting both fundamentally and technologically, were limited to small charging levels ($\sim$0.01 charge/Cu) by gate leakage current[6,7] and could not discover what happens when the induced charge density goes beyond the bulk insulator-superconductor transition value. In order to clarify the possibility of an electric field induced insulator-to-metal (or superconductor) transition in a cuprate system, two requirements can be identified. First, it should be possible to accumulate a 2D charge density greater than $\sim$0.05 charge/Cu, at which density occurs the bulk insulator-to-superconductor transition. There is no result available satisfying this requirement. In addition, the interface between the gate dielectric and the cuprate layer should be almost as defect free as the bulk of the cuprate system to rule out any extrinsic complication. This has also not been carefully addressed in any previous result. This paper reports the experiment satisfying both of these requirements. Another unique aspect of this work is that the induced carrier density dependence of the electric field effect is measured for the first time in a cuprate system. This was done by accurately measuring the induced carrier density using a capacitance vs gate voltage measurement. The gate voltage dependence, which is commonly reported instead,[3–7] cannot be considered equivalent to carrier density dependence since dielectric capacitance and leakage are generally sensitive functions of gate voltage.

We fabricated field effect transistors from a multilayer structure, grown by ozone assisted atomic layer-by-layer molecular beam epitaxy on a $SrTiO_3$ (001) substrate,[8] starting with a semi-insulating base film of 30 molecular layers of $Bi_2Sr_{1.5}La_{0.5}CaCu_2O_{8+\delta}$. The growth temperature ranged between 690 °C–720 °C. The La substitution on the Sr site compensates for holes usually present and results in a net density of about 0.04 holes/Cu inferred from transport.[9] This doping level is intentionally chosen for an important technical reason, which we will describe later in the paper. The interface between the cuprate film and the insulating dielectric was structured as shown in Fig. 1(b). This stacking sequence was chosen since all of the neighboring plane sequences are found in thermodynamically stable phases. Reflection high-energy electron diffraction (RHEED) in Fig. 1(a) shows how the interfacial layers evolved. While it is difficult to interpret all of the RHEED intensity pattern, the specular reflection provides a quantitative measure of surface flatness. Moreover, the dynamics of RHEED patterns obtained during the layered growth of related phases provide a reference to which patterns observed at specific planes during the growth of these device structures can be compared. In the top cuprate unit cell, after two $CuO_2$ planes separated by

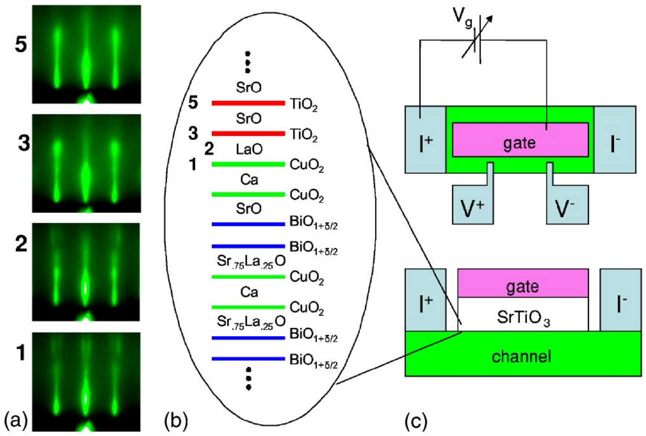

FIG. 1. (Color online) (a) RHEED images: note the abrupt change of the image symmetry at the interface. There is no second phase or deterioration of the RHEED through the interface, which indicates almost defectless nature of the interface. The horizontal spacing between the lines is $2.5 \times 10^9$ m$^{-1}$ in $k$ space and the beam is incident at an angle $\sim 1°$. (b) Layering order of atomic oxide planes in vicinity of the top cuprate layer. Note that the sequence is made to be a part of the known stable compound. (c) Top and side schematic views of the device structure.

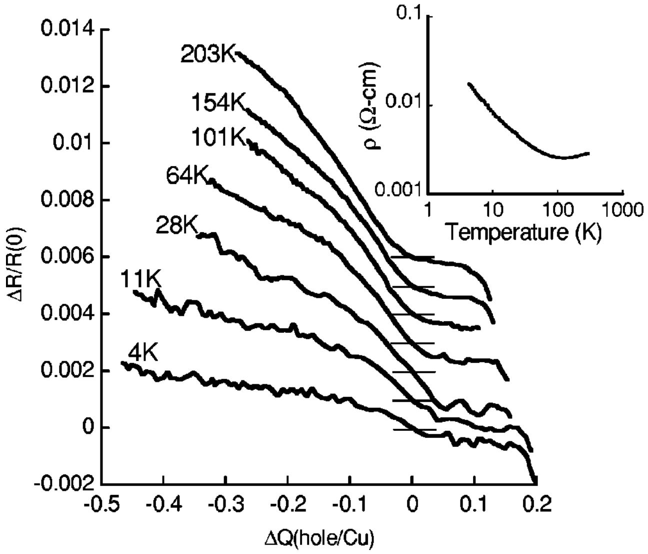

FIG. 2. Fractional change in channel resistance as a function of gate charge. Curves are displaced upward by 0.001. The drop in $R$ at the positive limit of the curves is due to leakage current. Inset, channel transport vs temperature.

a Ca layer were grown, an LaO layer was deposited. This is the same stacking sequence above the CuO$_2$ plane as found in La$_2$CaCu$_2$O$_6$, and electron charge transfer from the LaO$^+$ layer to the top CuO$_2$ layer results in that layer having no holes. RHEED shows that this layer grows two dimensionally and exhibits a reduced amplitude of the incommensurate structural modulation found in bulk Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (compare image 1 and 2). A TiO$_2$ plane was then deposited. This stacking sequence is the same as found in LaTiO$_3$. The RHEED pattern shown in image 3 has a reduced specular intensity, similar to what is seen during the growth of LaTiO$_3$ films. The specular intensity is recovered after the next TiO$_2$ plane (image 5) is grown. Then 100 unit cells of high dielectric constant SrTiO$_3$, $200 < \varepsilon_r < 500$, were grown to form the gate dielectric. On top of that, 10 layers of optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ were grown to form the gate electrode, which was followed by in-situ and sputtered ex-situ gold for electrical contact. Optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ was chosen as the gate electrode in order to minimize the work function difference[10] between the base layer and the gate, which is known to produce asymmetric dielectric response.[3,4] Using standard microprocessing techniques, the film was processed to make devices shown schematically in Fig. 1(c), with a gated area of 30 $\mu$m $\times$ 240 $\mu$m. The total transport channel from source ($I^+$) to drain ($I^-$) is the top CuO$_2$ layer, which is charge modulated by the gate voltage, in parallel with the semi-insulating base film, which we argue below is not charge modulated by the gate.

The semi-insulating character of the base film is shown in the inset of Fig. 2. At low temperatures transport is via variable range hopping. The conductivity and temperature dependence corresponds to a doping level $\sim 0.04$ hole/Cu.[9] Such a doping level is low enough not to support superconductivity in the base layer but high enough to make the base layer adequately conductive to remain at the same potential as the $I^+$ source contact. Such a level of doping for the base layer is one of the key technical requirements for this kind of experiment. When we tried a similar experiment using a CaCuO$_2$ film as the base layer, the channel was so insulating at low temperatures that the gate to source potential primarily dropped in the cuprate film between the gate and source contacts and not across the titanate dielectric.

To induce hole carriers in the top CuO$_2$ layer, labeled 1 in Fig. 1(b), a negative voltage was applied to the gate relative to the $I^+$ electrode. In this situation the induced holes are confined only to the top CuO$_2$ layer, which can be seen by considering a simple electrostatic model. If we assume that the field induced free carriers only reside on the CuO$_2$ layers with areal carrier density $\sigma_i$, where $i$ is the layer index starting at zero, and the carrier density is given by the potential of the layer times a 2D density of states within a rigid band picture, a discrete version of the Poisson equation reduces to $\sigma_i - [2 + (gd/\varepsilon_0\varepsilon_r)]\sigma_{i-1} + \sigma_{i-2} = 0$, where $g$ is the 2D density of states in C/m$^2$V, $d$= average distance between CuO$_2$ planes, and $\varepsilon_r$=dielectric constant between the CuO$_2$ planes. If $gd/\varepsilon_0\varepsilon_r \gg 2$, which we argue it is, the solution for this is approximately given by $\sigma_i = \sigma_0[2 + (gd/\varepsilon_0\varepsilon_r)]^{-i}$. This means that the induced charge distribution exponentially decreases away from the dielectric-cuprate interface. With $g \approx 2$ C/m$^2$,[11] $d \approx 3$ Å, and $\varepsilon_r = 4$, we get $\sigma_i \approx \sigma_0/18^i$, which means that more than 90% of the induced carriers reside on the top most CuO$_2$ layer. Therefore, to a good approximation we may assume that all the induced holes are confined only to the top most single CuO$_2$ layer.

Capacitance vs voltage (C-V) measurements, where the capacitance was almost frequency independent between 5 Hz up to 100 KHz, were performed using lock-in technique and integrated to obtain actual charge accumulation per Cu atom, $\Delta Q$, as a function of gate bias for each measurement temperature (Fig. 3). In order to determine the de-

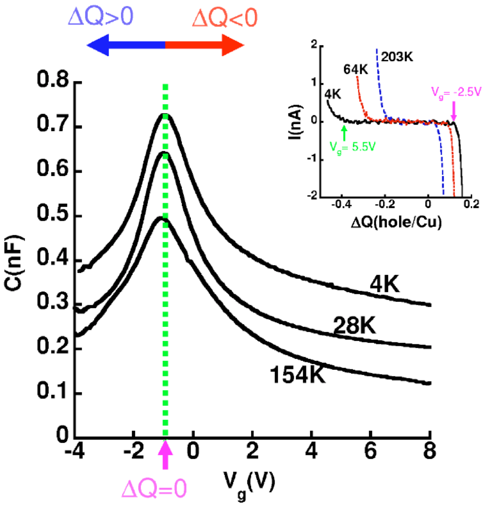

FIG. 3. (Color online) Capacitance vs Gate voltage plots. Note that there exists nonzero built-in polarizations. The integration of these plots gives charge density. This built-in polarizations should be considered when charge density is estimated. Inset, leakage current vs induced charge density, where breakdown voltages are specified for 4 K.

pendence of transport properties of the top layer on the charge carrier concentration of the top layer, it is necessary to determine under what conditions the top layer has no holes. Based on the charge transfer engineered at the interface by using the stacking sequence shown in Fig. 1(b), we expect the top layer to have no holes as long as the polarization of the dielectric is zero. Figure 3, however, shows that the dielectric susceptibility has a maximum value when a negative voltage of almost a Volt is applied. This indicates that the dielectric is imprinted with a polarization, perhaps by the asymmetry of the base layer and the gate. In order to obtain zero hole doping, it is necessary to apply an electric field to cancel out the built-in polarization. By integrating the capacitance from zero bias to the voltage corresponding to the peak in the dielectric constant we obtain a two-dimensional charge density offset caused by the built-in polarization. This is included in calculating the value of the horizontal axis for each data point in Fig. 2. $\Delta Q$ in Fig. 2 is equal to the raw $\Delta Q$ deduced from the C-V data minus $\sim$0.07 hole/Cu, which accounts for the charge accumulated by the built-in polarization of the dielectric. The gate dielectric remained insulating ($>10^{12}$ $\Omega$ cm) over a large voltage range, allowing us to continuously tune the induced charge from +0.15 to −0.4 charge/Cu site, before the leakage current suddenly turned on.

In Fig. 2, the fractional change in channel resistance is plotted vs $\Delta Q$ for different temperatures. The resistance was measured by the standard four-probe method with bipolar averaging to eliminate any built-in offset voltage, while the gate leakage current was monitored using a high input impedance electrometer (Keithley 617) as shown in the inset to Fig. 3. The probe current was 10 $\mu$A. The horizontal line for each curve identifies the point where zero holes are in the top layer. A positive surface charge can be accumulated to a level of 0.1–0.15 charges per Cu site (in addition to $\sim$0.07/Cu needed to compensate for the offset in C-V measurement mentioned above) before leakage current suddenly turns on and influences the channel resistance reading. On the other hand, a negative surface charge of $\sim$0.4 charge/Cu is obtained before leakage occurs. A striking asymmetry to the consequences of plus and minus charge accumulation is evident. The mobility of the charge induced by field effect doping is proportional to the slope of the curves $\mu_{\text{induced}} \propto d(\Delta R/R)/dQ$. Since the base electrode is a lightly hole doped semi-insulating cuprate, the accumulation of positive charge implies the accumulation of holes. Focusing first on these induced holes, we see that the mobility is essentially zero up to $\sim$0.15 holes/Cu(or $\sim 10^{14}$ holes/cm$^2$), even though an epitaxial and 2D interface, similar in quality to those obtained in the growth of known stable phases, was obtained. This implies that, even when the induced hole density in the top cuprate layer is substantially higher than the insulator-to-superconductor transition level in the bulk, the top layer remains completely insulating, even more insulating than the semi-insulating base layer. In other words, a large induced carrier density and a single crystalline interface are not a sufficient condition to convert insulating cuprates into superconductors.

Since the induced carriers are almost completely confined to the top single $CuO_2$ plane as shown earlier, it is reasonable to expect that the transport property of the induced carriers would be very sensitive to the atomic structure of the interface. This is in contrast to the case in semiconductor field effect devices, where induced carriers extend in many molecular layers and the role of the single interfacial layer is less significant. Since the mechanism of HTCS is still unknown, a complete explanation for absence of insulator-to-superconductor transition in this field induced cuprate structure may not be possible. However, we can still suggest a couple of mechanisms which must be important.

The first thing to consider is the possibility of large density of interfacial point defects which may work as trapping centers in a conventional way. Although it is clear that point defects would reduce the carrier mobility, it is not likely that their density is as large as the maximum induced carrier density $\sim 10^{14}$ cm$^{-2}$ (or $\sim$0.15/Cu), which is orders of magnitude bigger than what is typically achieved in semiconductor field effect devices; such high level of interfacial defects would make the interfacial RHEED images diffuse unlike what is observed in Fig. 1. Alternatively, we suggest a slightly different picture regarding the role of defects. We think that even small density of defects could localize more carriers in a strongly confined electronic system. For example, a line defect, which is easily avoided in bulk transport, would seriously block the current flow if the carriers are confined only to the top $CuO_2$ plane. Confinement driven superconductor-to-insulator transition is an intensively studied subject; if a superconducting film is made very thin, the effective disorder increases and eventually the otherwise superconducting film turns into an insulator.[12,13] If a similar mechanism applies to the field induced carriers, which are almost confined to the top $CuO_2$ layer, even with minimal level of defects, the effective disorder may become large enough to localize all the induced carriers.

Another related factor, which also has to be considered, is the effect of screening by adjacent free carriers. Experimentally, a single $CuO_2$ plane has never been found to be superconducting, and the minimum number of $CuO_2$ planes which were found to superconduct is two,[14] which happens only when they are sandwiched by structurally similar and marginally conducting materials. In superlattice structures such as $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$, $T_c$ decreases when the distance between bilayer $CuO_2$ planes is increased[15] until it saturates at a minimum value. The saturated $T_c$ in such superlattices also tends to be higher with conducting barriers[16,17] and decreases substantially with more insulating barriers,[14] which indicates the importance of free carrier screening from adjacent layers for superconductivity to occur.[18] In the field effect structures we have studied, the induced holes are not only confined to a single $CuO_2$ plane, but are also adjacent to a highly insulating gate dielectric. If charge screening from free carriers is important for obtaining mobile carriers, then the absence of such screening in our samples may also foster the localization we observe.

In such a field effect structure it is also necessary to have the molecular structure containing the hole carriers be in close proximity to the molecular orbitals of the insulator. In this case the pyramidal cuprate states share an apical oxygen with the adjacent titanate octahedra. Such modification of the molecular orbital structure at the interface is unavoidable and will lead to changes in the electronic structure of the interfacial cuprate plane which is where the field effect doped holes reside. Earlier work on $SrTiO_3$/Bi-cuprate superlattices[8] showed that such an interfacial effect can destroy superconductivity and drive the system into an insulating state.

Turning to Fig. 4, we see that there are four distinct regions in the resistive response to the charging induced by the electric field. We have already discussed region C, where the induced holes become completely immobile, and region D, where the leakage current starts to affect the reading. Biasing with opposite polarity, as in region B, obtains the accumulation of negative charges. Since the resistance increases with increasing negative charge, we conclude that this bias depletes mobile holes, presumably from the second and then the third $CuO_2$ layers, increasing the channel resistance. Until inversion starts on the topmost $CuO_2$ layer, linear increase of the depletion depth appears as linear increase of the channel resistance as seen in region B. Once inversion occurs on the top $CuO_2$ layer, part of the induced carriers accumulates in the inversion layer and so the depletion depth increase rate is slowed down, which shows up as a reduced slope in region A of the resistance vs charge density curve, Fig. 4. The point when inversion starts to occur on the top most $CuO_2$ layer and electrons are accumulated in the upper Hubbard band can be estimated in the following way. Using the same discrete layer model we used earlier and the same rigid band DOS, we get a simple formula for the inversion condition,

$$U_H = \frac{ed\sigma_{\mathrm{in}}}{\varepsilon_0\varepsilon_r}\frac{i_{\mathrm{inv}}(i_{\mathrm{inv}}+1)}{2},$$

where $U_H \approx 1-2$ eV is the Hubbard gap, $\sigma_{\mathrm{in}} \approx 0.04$ hole/Cu is the intrinsic carrier density inside the channel controlled by the La doping, and $i_{\mathrm{inv}}+1$ is the number of depleted $CuO_2$ layers when the inversion occurs on the top $CuO_2$ layer. By using the same material parameters, we find that approximately 2–3 depleted $CuO_2$ layers corresponding to ~0.1 depleted charge/Cu is the point where inversion occurs at the top $CuO_2$ layer. This is consistent with our result shown in Fig. 4, and in region A this inversion occurs in the top $CuO_2$ layer. More quantitative analysis for each part of the curve would require a theoretical model going beyond the rigid band picture and include interlayer coupling.

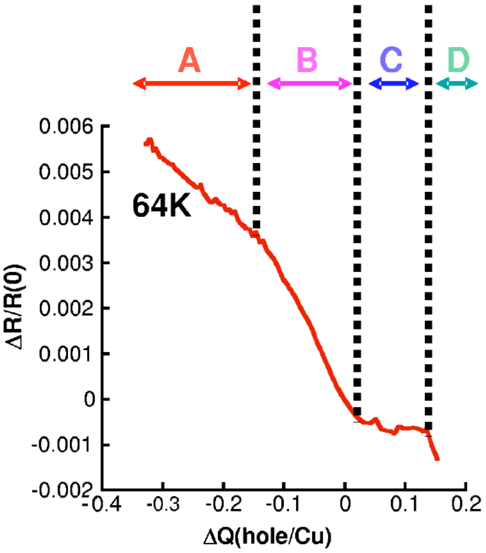

FIG. 4. (Color online) Detailed view of the field effect. Four distinct regions are clearly discernible. (A) Carriers in the top $CuO_2$ layer is inverted to electrons. (B) Depletion occurs in the top few $CuO_2$ layers. (C) Holes are introduced into the top $CuO_2$ layer but completely frozen. (D) Leakage current affects the data. Sharp drop is just an artifact due to the leakage current shown in the inset of Fig. 3.

In summary, by combining fine control of doping, the selection of the right gate electrode, a low leakage single crystal high $\varepsilon_r$ dielectric and high quality epitaxial control of the interface, we have investigated the possibility of electric field induced insulator-superconductor transition. For the first time, a hole carrier density larger than that required for the bulk insulator-superconductor transition was induced into an insulating cuprate system. While hole depletion shows considerable field effect in transport, induced holes are immobile and hence exhibit no insulator-to-superconductor transition even with a very high density of carriers and a single crystalline interface. This is in striking contrast to what happens when holes are chemically doped into cuprate planes in bulk samples where the physics is represented by the well-known phase diagram. It implies that large induced carrier density and a single crystal interface is not a sufficient condition for electric field induced insulator-to-superconductor transition. Although a conventional localization mechanism, such as large number of point defects, cannot be completely ruled out, the required defect density for such a mechanism seems too large for a single crystalline interface. Instead, we propose that extreme confinement of the induced carriers can make them susceptible to various other localization mechanisms. Whatever the physical origin may be behind the localization behavior, this is a serious challenge to any attempt to use electric field to induce superconductivity in an insulating cuprate system.

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