take into account the finite length of the one-dimensional channel and the finite temperature (2). The stability and reproducibility of the single channel is qualitatively different from the higher order conductance channels, most likely because of the increased disorder and fluctuations that can occur as the number of atoms making up the channel increases.

What is the size of the OPC junctions studied here? Comparison of the experimental behavior with the model of Tekman and Ciraci (2) shows that the width of the single conductance channel is less than  $\lambda_{\rm E}$  (0.52 nm for Au). Wider channels correspond to higher order channels. The Tekman and Ciraci model also suggests that the length of the QPC junctions measured here is less than  $\lambda_{\rm F}$ ; if the constriction were longer, the higher order conductance plateaus would be much more distinct than are observed experimentally [see figure 2 of (2)]. We therefore conclude that for the single quantized channel, which corresponds to the highconductance state of the QPC switch, the width is less than  $\lambda_{\rm F}$  and the length is probably also less than  $\lambda_{F}$ . Because the electronic diameter of a metallic atom is  $0.611\lambda_{\rm F}$ , the single-channel constriction probably corresponds to a single atom.

The application of the QPC for use as an analog signal switch is demonstrated in Fig. 4C. A sine-wave voltage with no dc component is applied to  $V_{\rm IN}$  and the current is monitored at  $V_{\rm OUT}$  while a 0.24-nm ramp (not shown) is applied to  $V_{\rm Z}$  (see Fig. 1A). This analog switch is functionally analogous to the field effect transistor (FET) switch shown in Fig. 1B, where the gate voltage is used to modulate the drain-source channel between high- and low-conductance states. The width of the conductance channel of the FET is controlled by an electric field, whereas the width of the conductance channel of the QPC is controlled by mechanical displacement of atoms in the junction. The QPC switch functions more precisely as an electromechanical relay. The interesting features are that on-off switching is accomplished by displacing the electrodes by only 2 Å and that the contact region is extremely small, perhaps only one atom in size.

Eigler *et al.* have shown that the motion of a single atom of Xe between a tungsten tip and a nickel surface can cause the tunneling conductance between the electrodes to change by a factor of between one and seven (1). The maximum high-conductance state corresponded to a resistance of 220 kilohms, and the device could only operate at very low temperatures because of the mobility of Xe. By comparison, the QPC switch demonstrated here has a conductance ratio of about 20 and a highconductance state with an impedance of 13 kilohms. Another important distinction is that the Xe switch is a two-terminal device that is toggled by applying a current pulse between the electrodes. In contrast, the OPC switch is a three-terminal device with an independent control input. An important disadvantage of a two-terminal device is the impossibility of power gain, that is, a large current is required to switch a smaller current. The OPC switch displays power gain and can be used to make an oscillator (by feeding the output signal back into the control input) or to drive a series of other QPC switches. Finally, QPC behavior has been observed at room temperature (8, 9). The angstrom size of the QPC conductance channel suggests that the QPC may be useful in exploring the physical and engineering issues surrounding atomic-scale electron devices.

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- 11. The work function was measured by addition of a *z*-modulation ( $\Delta z = 40 \text{ pm}$ ) to the piezoelectric transducer and detection of the modulation  $\Delta I$  in the tunneling current. Assuming  $I \propto \exp(-2\kappa z)$ , where  $\kappa$  is the electron wave number, then  $\Delta I/I = 2\kappa \Delta z$ ; the value of  $\kappa$  thus derived enables calculation of the work function  $\varphi = (\hbar \kappa)^2/2m_{\rm e}$ , where  $\hbar = h/2\pi$  and  $m_{\rm e}$  is the electron mass. Ratios of  $\Delta I/I$  between 0.75 and 0.9 were measured, which implied values of  $\varphi$  between 3.0 and 4.0 eV.
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- 13. It is possible to estimate the change in resistance in the tunnel regime as  $\rho = R_1/R_2 = \exp[2(\kappa_1 z_1 \kappa_2 z_2)]$ . Assume that the tunnel barrier maintains a constant value of  $\kappa = 10 \text{ nm}^{-1}$ , corresponding to  $\varphi = 4 \text{ eV}$ , until contact occurs (3, 4) and that  $\Delta z = 0.15$  nm, the approximate portion of the ramp in the tunnel regime. Then  $\rho = \exp(2\kappa\Delta z) = 20$ , in agreement with the observed switching behavior.
- W. H\u00e4berle assisted in the construction of the experimental apparatus and G. Binnig provided helpful criticism of the manuscript.

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# Ferroelectric Field Effect in Epitaxial Thin Film Oxide SrCuO<sub>2</sub>/Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> Heterostructures

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A ferroelectric field effect in epitaxial thin film SrCuO<sub>2</sub>/Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> heterostructures was observed. A 3.5 percent change in the resistance of a 40 angstrom SrCuO<sub>2</sub> layer (a parent high-temperature superconducting compound) was measured when the polarization field of the Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> layer was reversed by the application of a pulse of small voltage (<5 volts). This effect, both reversible and nonvolatile, is attributed to the electric field–induced charge at the interface of SrCuO<sub>2</sub> and Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub>. This completely epitaxial thin film approach shows the possibility of making nonvolatile, low-voltage ferroelectric field effect devices for both applications and fundamental studies of field-induced doping in novel compounds like SrCuO<sub>2</sub>.

**R**ecent developments in the physical vapor deposition of complex oxides, notably advances in magnetron sputtering, laser ablation, and reactive molecular beam epitaxy

(MBE), have permitted the growth of very high quality epitaxial oxide thin film structures, as demonstrated, for example, by the fabrication of thin film superlattices of the copper oxide superconductors (1, 2). Although in large part developed for the growth of high transition temperature (high- $T_c$ ) superconductors, these techniques have now been applied to other oxide materials, including ferromagnetic and ferroelectric perovskites (3, 4). These advances offer the possibility of growing

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epitaxial heterostructures consisting of materials that have very similar crystalline structures but possess remarkably different electronic and magnetic properties, ranging from insulators with high dielectric constants and ferroelectric compounds to metals, ferromagnets, and superconductors. Such structures are of interest from the point of view of both fundamental and applied science (5).

We studied the field effect at the interface of an all-epitaxial oxide heterostructure. To do this, we considered the interface between  $SrCuO_2$ , a material related to the high- $T_c$  superconductors (6), and Pb( $Zr_{0.52}Ti_{0.48}$ )O<sub>3</sub> (PZT), a ferroelectric compound that is a distorted perovskite. The field effect-induced changes in conductance we measured are sensitive tests of the quality of the SrCuO<sub>2</sub>-PZT interface. In principle, such a structure could lead to a superconductor-insulator field effect device, because SrCuO<sub>2</sub> when appropriately doped (for example, with Nd) is a high- $T_c$  superconductor (6). We chose  $SrCuO_2$  in its nominally undoped state to approach and investigate the field effect from the insulating side; all other such studies have been carried out on materials that were already doped well into the superconducting state (7, 8). Our approach also differs from other field effect studies of the cuprates in that we used the builtin, nonvolatile polarization field from a thin film ferroelectric compound, PZT, rather than the volatile polarization of a high dielectric constant compound. Finally, the epitaxial thin film approach used here allowed us to use electric fields that are an order of magnitude lower than those used before, corresponding in our case to switching voltages that are only a few volts (< 5 V).

Using a ferroelectric to produce a field effect is not a new idea; it was proposed in 1956 and has intrigued researchers since then because of the possibility of making a device with a nonvolatile gate supply (9). The difficulty has been in finding compatible materials that form good interfaces because traps at the interface can strongly screen and attenuate the applied electric field. In fact, for this reason the only semiconducting field effect devices mass-produced today are  ${\rm Si}{\rm -}{\rm Si}{\rm O}_2$  devices, which have nearly perfect interfaces. Recently, there have been reports of polycrystalline ferroelectric-Si field effect transistor (FET) structures (10) and thick YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (YBCO) films deposited on ferroelectric substrates (11).

To grow the  $SrCuO_2$ -PZT heterostructures, we used a combination of deposition techniques. The PZT was grown on metallic Nb-doped  $SrTiO_3$  (Nb- $SrTiO_3$ ) with offaxis radio frequency-reactive sputtering.

This technique allows the growth of very high quality thin films with excellent composition control (4, 12). X-ray analyses demonstrated the growth of exclusively c axis epitaxial grains with intense (001) and (002) reflections; the rocking curves for the (001) reflection had a 0.09° full width at half maximum (FWHM). For this orientation, the two polarization states were perpendicular to the Nb-SrTiO<sub>3</sub> surface, and we measured a remanent polarization on the order of 15 to 20  $\mu$ C cm<sup>-2</sup>, which corresponds to a surface charge density of  $\sim 10^{14}$  charges cm<sup>-2</sup>, and a coercive field of 70 kV cm<sup>-1</sup>. Atomic force microscopy showed that the surfaces had a root-meansquare roughness of less than 3 Å over an area 0.5 µm by 0.5 µm (12).

Afterward, the PZT was transferred to an ultrahigh vacuum MBE chamber, where the PZT surface was cleaned at 600°C for ~10 min in a flux of atomic oxygen, which created very clean, crystalline, metallic YBCO surfaces (13). The PZT surface quality was checked by reflection high-energy electron diffraction (RHEED), and after adjustment of the PZT temperature to 570°C, the SrCuO<sub>2</sub> was deposited at ~1.5 Å s<sup>-1</sup> with reactive electron beam coevaporation. The film thicknesses were varied from 40 to 450 Å, with the stoichiometry of Cu and Sr being controlled to within 2%, which is the uncertainty in the Rutherford backscattering spectrometry (RBS) composition analysis. The electron beam MBE system and the growth of both *a*- and *c* axis-oriented  $SrCuO_2$  films are described elsewhere (14, 15).

In Fig. 1A, we plotted an x-ray diffraction scan of a 450 Å SrCuO<sub>2</sub>-2500 Å PZT-Nb-SrTiO<sub>3</sub> heterostructure. Only the PZT(001) and SrCuO<sub>2</sub>(001) reflections were seen (along with substrate and Cu K $\beta$ reflections), which shows that the SrCuO<sub>2</sub> grew with its c axis perpendicular to the Nb-SrTiO<sub>2</sub> substrate. The FWHM of the rocking curve for the (001) peak of SrCuO<sub>2</sub> is 0.4° to 0.5°. Figure 1B is a  $\phi$  scan (angle around the normal to the film) of the (101) reflections of SrCuO<sub>2</sub>, demonstrating the in-plane epitaxial growth of SrCuO2 on PZT, with SrCuO<sub>2</sub>[100] PZT[100] Nb-SrTiO<sub>3</sub>[100]. We also characterized the surface crystallinity of these films with in situ low-energy electron diffraction (LEED) and RHEED (Fig. 2, A and B). The LEED pattern, taken at a beam voltage of 80 eV to achieve greater surface sensitivity, reveals the square symmetry of the a-b plane of SrCuO<sub>2</sub>, whereas the streaky RHEED pattern, taken along a [100] direction, shows that the film is smooth. When we grew SrCuO<sub>2</sub> directly on SrTiO<sub>3</sub>, the LEED and RHEED patterns were sharper and the FWHM of the SrCuO<sub>2</sub> rocking curve was  $\sim$ 0.2°, which was limited by the instrumen-



**Fig. 1.** (**A**) Log scale x-ray diffraction pattern (intensity versus 20) of a 450 Å SrCuO<sub>2</sub>-PZT film deposited on Nb-SrTiO<sub>3</sub>. (**B**) A typical  $\phi$  scan of the (101) reflection of SrCuO<sub>2</sub>, showing cube-oncube epitaxy, with SrCuO<sub>2</sub>[100] || PZT[100] || Nb-SrTiO<sub>3</sub>[100].

SCIENCE • VOL. 269 • 21 JULY 1995



**Fig. 2.** (**A**) LEED pattern taken at 80 eV of a 40 Å  $SrCuO_2$ -PZT film deposited on Nb-SrTiO<sub>3</sub>. At this energy, the elastic mean free path of an electron in the material is nearly minimized, resulting in greater surface sensitivity. (**B**) RHEED pattern of this film taken at 20 keV along a [100] direction.

tal resolution (16). Two possible reasons for these differences are that there is a larger lattice mismatch between  $SrCuO_2$  and PZT (3%) than there is between  $SrCuO_2$  and  $SrTiO_3$  (1%) and that the in-plane reflections of PZT are broader than those of single-crystal  $SrTiO_3$ . We have also observed broadened rocking curves (~1.2°) for YBCO-PZT heterostructures (12, 17).

In addition to confirming both the bulk and surface crystallinity of the SrCuO<sub>2</sub> film, we examined the electronic structure at the upper surface using in situ ultraviolet photoelectron spectroscopy (UPS). An angleintegrated spectrum of a SrCuO<sub>2</sub> film 40 Å thick and grown on PZT with He I radiation is shown in Fig. 3. The Cu 3d peak is clearly defined, and there is no 9-eV impurity feature, which is often observed on the surfaces of high-T<sub>c</sub> superconductors that have absorbed small amounts of gaseous impurities from the vacuum chamber (13). Also, there is some spectral weight at the Fermi level, comparable to that measured on clean YBCO films (18), which indicates that the material is at least marginally doped.

We investigated the transport properties of vacancy-doped  $Sr_1$ ,  $CuO_2$  (x = 0, 0.1, 0.15, 0.2, and 0.3) layers by measuring the temperature dependence of the resistivity using standard four-point transport measurements and by measuring the Hall effect to determine the sign of the carriers. We found that for nominally undoped films (x= 0, within the uncertainty of the RBS analysis), the room temperature resistivity was on the order of a few hundred milliohm centimeter. Given this finite resistivity, it is likely that these films have a small percentage of Sr vacancies. The resistivity of these films increases rapidly with decreasing temperature, although it cannot be fit to simple exponential, semiconducting behavior. Rather, it is more consistent with three-dimensional, variable-range hopping behavior {resistivity  $\rho(T)$  $\exp[(T_0/T)^{1/4}]$ . If we assume a reasonable tunneling length of 10 to 50 Å, we infer a



**Fig. 3.** Angle-integrated He I photoemission spectrum of a 40 Å SrCuO<sub>2</sub>-PZT film deposited on Nb-SrTiO<sub>3</sub>. The arrow indicates the Fermi energy.

density of localized states of  ${\sim}2\times10^{18}$  to 2  $\times$  10<sup>20</sup> cm<sup>-3</sup> eV<sup>-1</sup> using the theory of variable-range hopping (19). Although this density is rather large and raises questions about the strict validity of this analysis, it does confirm a high density of states at the Fermi level, consistent with the magnitude of the resistivity and the UPS spectra. For samples that were intentionally grown to be Sr-deficient (ranging from 10 to 30%), the resistivity dropped to  $\sim 5$  mohm·cm and became essentially independent of temperature, with no superconducting transition observed for these vacancy-doped films. Understanding how vacancy doping influences the degree of disorder in these films will allow a better understanding of the absence of superconductivity. Finally, the results of the Hall effect measurements show that the addition of Sr vacancies induces p-type conductivity in  $Sr_{1,r}CuO_2$ , which is consistent with simple chemical arguments.

We plotted the resistivity of a lightly doped 40 Å SrCuO<sub>2</sub> film deposited on PZT (2500 Å thick) as a function of the PZT polarization (Fig. 4). To polarize the PZT, we applied 5-V, 100-ms rectangular pulses between the SrCuO<sub>2</sub> layer and the metallic Nb-SrTiO<sub>3</sub> substrate, which was held at 0 V. After each pulse, the resistivity of the SrCuO<sub>2</sub> layer was determined by currentvoltage (*I*-V) measurements with standard four-point contacts. Although it is difficult to discuss the resistivity of a film for a field effect–induced change in the doping profile, here we define resistivity as

### resistance $\times$ total cross-sectional area/

distance between the voltage leads

As can be seen on the graph, the resistivity of the  $SrCuO_2$  changes by as much as 3.5%, corresponding to a change in resistance of

3000 ohms as the polarization of the PZT is reversed. In contrast to conventional field effect experiments, this change is nonvolatile (that is, no voltage is required to maintain either resistivity state) with no noticeable change in the resistivity for up to 10 min, which was the longest period we waited. We also observed a ~1% change on a film of SrCuO<sub>2</sub> (450 Å thick), and an earlier experiment with a Au–5000 Å PZT– 150 Å DyBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> structure also displayed a resistivity change of ~1% (17).

The ferroelectric field effect shown in Fig. 4 also demonstrates that the Sr-deficient  $SrCuO_2$  films exhibit *p*-type conductivity. When a -5-V pulse was applied to the structure, negative charges were brought into the  $SrCuO_2$  layer to screen the positive surface charge induced on the top PZT surface. As a result, the net hole concentration decreased, thereby increasing the resistivity of the  $SrCuO_2$ . Such a measurement provides a convenient determination of the carrier sign in these materials.

Another series of measurements used a periodic pulse train whose basic unit consisted of three negative pulses followed by three positive pulses (Fig. 4, inset). Additional pulses of the same polarity did not alter the resistivity state because the PZT polarization did not change sign. We believe that the weak changes in resistivity we observed may be related to incomplete polarization of the PZT, because the SrCuO<sub>2</sub> layer with high resistivity may not form an equipotential surface when the poling voltage is applied. To verify the field effect, we performed various tests, including applying aperiodic pulse trains and checking for stray voltages and capacitances from the poling and transport leads; these checks were all consistent with a field-induced change in the resistivity of the SrCuO<sub>2</sub>.



**Fig. 4.** Plot of the room-temperature resistivity of a 40 Å  $SrCuO_2$ -PZT film deposited on Nb-SrTiO<sub>3</sub> as a function of the polarization of the PZT. The pulse train shown is used to change the polarization of the PZT. The arrows indicate changes of sign of the voltage pulse train. The graph demonstrates that the change in resistivity is nonvolatile. (**Inset**) Repeated pulses of the same polarity do not alter the resistivity state of the material. To the right of the graph is a schematic of the heterostructure and the measurement geometry.

Our results show that the ferroelectric field effect can be achieved in high-quality epitaxial heterostructures. The main advantage of this integrated thin film approach is that the electric field necessary to switch the thin epitaxial PZT layer is only of the order of  $10^5$  V cm<sup>-1</sup>, which is an order of magnitude lower than what has been used for other field effect experiments performed on high- $T_c$  superconductors (7, 8). As a result, the corresponding voltages are only a few volts (1 V per 1000 Å of PZT). Furthermore, the use of the nonvolatile polarization field from PZT allows us to rule out various concerns that have been raised with regard to field effect experiments on high- $T_c$  materials with ordinary dielectric insulators. For example, whereas such experiments attest to high-quality interfaces, the large fields that must be supplied across the dielectric during the measurement have caused concern about leakage current during measurement, heating effects, and electrostriction. Here, there was no voltage applied across the ferroelectric during transport measurements and hence no possibility of leakage currents through the ferroelectric compound or spurious resistive heating effects. Also, because the PZT has the same tetragonal crystal structure in its two polarization states, it is unlikely that strain is the source of the observed resistance change. Finally, we note that the choice of YBCO as the conductor in previous field effect experiments has raised the possibility that the effect is related to the motion of mobile O ions in the CuO chains, rather than to the response of the hole carriers to the applied electric field (20). In SrCuO<sub>2</sub>, all the atoms are strongly bonded, and thus the observed resistance changes with applied electric field can arise only from changes in the free charge carrier density in the material.

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# Luminescence Enhancement by the Introduction of Disorder into Poly(*p*-phenylene vinylene)

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A method is described for increasing luminescence in poly(*p*-phenylene vinylene) (PPV) light-emitting diodes. Cis linkages were engineered into the PPV chain. These linkages interrupt conjugation and interfere with the packing of the polymer chains, which results in the formation of amorphous PPV. Large-area electroluminescent devices were prepared from this polymer. Devices made of an aluminum electrode, PPV as the luminescent layer, and an electron-transporting layer have internal quantum efficiencies of 2 percent, a turn-on voltage of 20 volts, and can carry current densities of 2000 milliamperes per square centimeter. The current density is at least an order of magnitude higher than previously obtained.

The potential for making large-area displays from easily processable polymers has driven much of the recent research in the area of polymeric light-emitting diodes (LEDs). Of all the polymers evaluated for LEDs, PPV has attracted the most interest. It is used in devices more than any other polymer as either the light-emitting layer (1, 2) or the hole-transporting layer (3). PPV is commonly prepared by the Wessling precursor method that was developed some 30 years ago (4). We have previously shown that this method is laden with problems (5,6). The polyelectrolyte nature of the precursor leads to dramatic increases in viscosity during polymerization, which in turn limits yield. In addition, the polyelectrolyte is only soluble in polar solvents such as water or methanol, which are both poor solvents for spinning high-quality films. Large-area pinhole-free films necessary for displays are difficult to obtain by this method. The fact that the tetrahydrothiophenium group, used in the Wessling method, is an excellent leaving group further complicates this approach. This group is readily substituted with methoxy (7) and hydroxy

(8) groups during polymerization and dialysis of the precursor. The hydroxy groups are then oxidized to carbonyls, which limit electroluminescence, when the precursor is thermally converted to PPV (6). Also, the extent of substitution can vary considerably with minor changes in the handling or storing of the precursor, resulting in dramatic differences in polymer performance. This extreme sensitivity to process variables makes the Wessling route to PPV unsatisfactory for manufacturing real devices. Another problem with the PPV produced by Wessling's method is that it is predominately trans and, therefore, is also highly crystalline.

Work by Yan *et al.* (9) indicates that photoluminescence efficiency can be increased in a polymer by separating the polymer chains. Reasoning that amorphous PPV would have better chain separation than crystalline PPV would, we devised a method to synthesize PPV in a way that would overcome most of the problems encountered in the Wessling route. Specifically, we wanted an organic soluble precursor to improve film quality and a leaving group that would not undergo nucleophilic substitution by hydroxyl groups and would be eliminated to produce a

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