Indications of superconductivity at somewhat elevated temperatures in strontium titanate subjected to high electric fields

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Insulating single-crystal $SrTiO_3$ wafers have been rendered conductive below room temperature by subjecting them to electric fields. With moderate fields the process can be reversed by warming the substrates to room temperature or slightly above. At higher fields the process is not reversible. When substrates subjected to high fields are cooled to temperatures in the range of 2–6 K, they exhibit significant and sharp resistance drops that respond to magnetic field in a manner suggestive of the presence of superconductivity despite the fact that the resistance does not fall to zero. If these effects are indeed indications of superconductivity they are occurring at temperatures in excess of those found employing techniques previously used to induce superconductivity in $SrTiO_3$. The phenomenon is sample dependent and is not observed in every sample. We suggest that these effects are the result of static electric fields producing a redistribution of oxygen vacancies and possibly irreversible structural changes leading to channels that are sufficiently doped so as to be superconducting. The reason the onset temperatures for this effect are higher than those achieved using more conventional doping approaches is an open question.

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Strontium Titanate is a band insulator which can be rendered superconducting by introducing oxygen defects, by doping with Nb, Zr, La, or Ta,[1–6] through charge transfer processes resulting from the deposition of several layers of $LaAlO_3$,[7] or by electrostatic charging using an electronic double-layer transistor configuration.[8] In a recent article Szot *et al.*[9] demonstrated bistable switching of the conductance between nonmetallic and metallic behavior upon the application of a sufficiently large electric fields. Furthermore they demonstrated that this behavior was an intrinsic feature associated with extended defects such as dislocations, in single crystals of $SrTiO_3$. Specifically the oxygen content along a dislocation was modulated in such a manner as to produce a doping-induced insulator-metal transition along the defect, leading to conductive channels on a nanometer scale. They showed, using local conductivity atomic force microscopy as well as optical microscopy that the conductivity of undoped $SrTiO_3$ single crystals resulted from these filaments. The bistable switching was asserted to originate from oxygen transport along filaments associated with dislocations. The measurements were carried out using both planar and capacitor structures. In this Brief Report we describe metallic and possibly superconducting behavior in $SrTiO_3$ produced though a process also involving the application of high electric fields in both planar and capacitor geometries. In contrast with the work of Szot *et al.*[9] the insulator-to-metal transition leading to superconductivity was irreversible. The apparent superconducting transition temperatures were higher than the maximum value of 1.2 K achieved through Nb doping.[10] This procedure suggests a possible path toward inducing superconductivity in insulators, assuming that the breakdown process can be controlled.

Epi-polished (100) single-crystal $SrTiO_3$ samples in the form of flat plates, usually employed as substrates, were obtained from Princeton Scientific Corporation. Two different electrode configurations were employed in the charging and breakdown process. These were first a configuration with planar electrodes and second, an ordinary parallel plate capacitor configuration. In the planar configuration, the Pt or Ti/Au electrodes, which are not superconducting, were deposited on the epi-polished side of the sample. The electrodes were 10 μm apart and were patterned using photolithography in the configuration shown in Fig. 1(a). In the parallel plate capacitor configuration, the $SrTiO_3$ samples were thinned down to 60 μm on the unpolished side using a mechanical technique.[11] These samples were annealed for 6 h in an O_2/O_3 atmosphere at 725–775 °C to recover the oxygen lost during the micromachining thinning process. The Pt or Ti/Au electrodes were deposited on both sides, as shown in Fig. 1(b). Before applying high electric fields, the

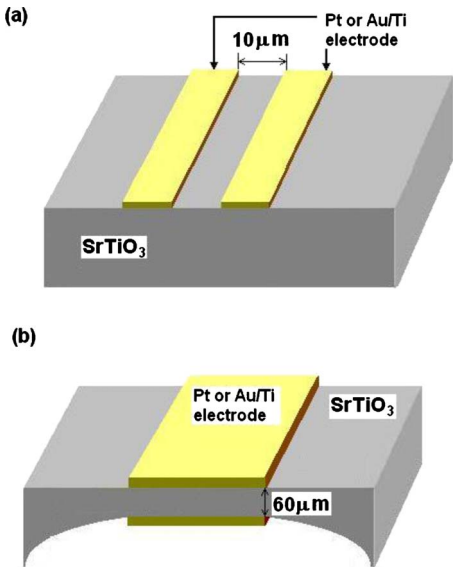

FIG. 1. (Color online) Schematics of the (a) planar capacitor configuration and the (b) normal capacitor configuration of the electrodes. Note that these drawings are not to scale.

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original resistance between the two electrodes was typically larger than 100 GΩ at room temperature.

The typical breakdown processes were carried out in a vacuum of 10^{-6} Torr and in the temperature range between 2 or 6 K, where the dielectric constant κ of $SrTiO_3$ can exceed 10 000. This work was originally directed at learning the maximum gate voltage that could be applied to mechanically thinned $SrTiO_3$ membranes used simultaneously as substrates and gate insulators in electrostatic charging studies.[11] When a high voltage was applied between the two electrodes, the charge density accumulating on the electrodes was extremely high due to the large areal capacitance. Under these conditions, the breakdown of $SrTiO_3$ could be brought about through the use of one of two processes, which differ in the rate of ramping of the electric field. When the voltage across the electrodes was increased slowly, the current increased in a nonlinear fashion. In this incremental charging process, a breakdown voltage was reached at which point the current dramatically increased and reached the current limit of the power supply, which was 10 mA. The precise values of breakdown voltages varied from sample to sample but they were typically greater than 200 V. The two terminal resistance $R=V/I$ was then about 10–100 kΩ after the breakdown voltage was achieved. After the applied voltage was reduced to a value smaller than 1 V, the resistance could recover to values the order of several gigaohms (GΩ). This process was reversible. Upon further thermal cycling between low temperature and room temperature further recovery of the resistance back to 100 GΩ was achieved.

On the other hand, sudden, subsequent application of high voltages exceeding the breakdown voltage caused irreversible changes in resistance. The irreversible breakdown resulted in possible superconductivity at elevated temperatures, which is the subject of this report. In this case, reducing the voltage or thermal cycling back to room temperature did not result in the recovery of high resistance. The two-terminal resistance value at temperatures of the order 10 K after this type of breakdown can be several 100 Ω to several 100 kΩ. The resistance can be further reduced down to 10 Ω to 1 kΩ by performing this process of breakdown more than once.

Due to limitations in the current-carrying capacity of wiring these breakdown processes were carried out in the ^{4}He cryostat of the Quantum Design physical property measurement system (PPMS), whose base temperature is 2 K. Some of the $R(T)$ measurements were carried out using the ^{3}He insert of the PPMS, which can be cooled to 400 mK. However the resistances of samples subjected only to reversible breakdown processes would recover if warmed and switched between the two systems. Therefore, there are no $R(T)$ measurements below 2 K on samples subjected only to reversible breakdown using moderate electric fields. The experimental results reported in this Brief Report are thus limited to two-terminal measurements of $R(T)$ on samples subjected to irreversible breakdown.

The transport properties of $SrTiO_3$ varied, depending upon the number of times a sample was subjected to irreversible breakdown. The resistance in the high-temperature regime typically decreased with the number of breakdowns to which a sample was subjected. This resulted in very unusual

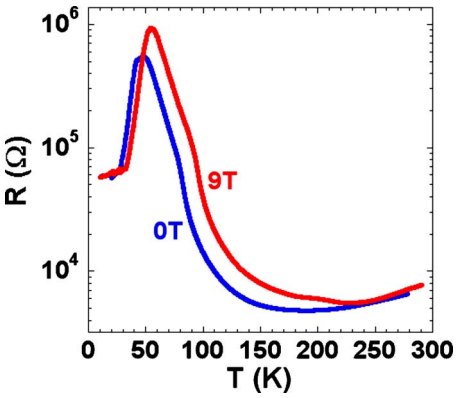

FIG. 2. (Color online) Resistance of a planar capacitor configuration of $SrTiO_3$ versus temperature in zero field and in a field of 9 T. This sample was subjected to irreversible breakdown only once. The resistance measurements were carried out in a two-terminal configuration.

behavior of $R(T)$ at temperatures lower than 150 K. Figure 2 shows $R(T)$ of a sample in a planar capacitor configuration after being subjected to a single irreversible breakdown process. It exhibits nonmonotonic behavior in $R(T)$, i.e., a resistance peak at 48 K. Furthermore, the position and magnitude of the peak vary with external magnetic field. The origin of this feature is unknown.

For samples subjected to more than one irreversible breakdown process, the resistance could be decreased to values as low as few tens of ohms. The two-terminal resistance can exhibit sharp drops at temperatures below 10 K. Moreover, these drops can be eliminated by applying an external magnetic field. In Fig. 3(a), $R(T)$ of a sample in a planar capacitor configuration that was subjected to several irreversible breakdown processes is seen to exhibit a 20% resistance drop from 65 Ω at a temperature of 6.4 K. Fixing the temperature at 4 K, a 2 T magnetic field restores the resistance to 65 Ω. Another example of the result of subjecting a planar capacitor to irreversible breakdown is shown in Fig. 4. There are several resistance dips at different temperatures (6.5, 1.5, and 0.6 K) in zero field. These dips shift to lower temperature upon the application of increasing magnetic fields and disappear when a 1.5 T field is achieved.

In an ordinary parallel plate capacitor configuration, the same irreversible breakdown process can also be performed to lower the resistance. Figure 5(a) shows $R(T)$ of a sample in different magnetic fields. One can clearly see that the resistance begins to fall significantly at a temperature of 3 K in zero field. The application of an external magnetic field reduces the magnitude of the resistance drop and eventually removes the drop in a 2.5 T field. In Fig. 5(b), $R(H)$ at 2 K shows two different slopes below and above a 2 T field. A high excitation current at a temperature of 2 K and in zero field can also drive the resistance back up to 168 Ω, which was its value at the onset of the original resistance drop. The response to external magnetic fields and to high excitation currents suggest that it is possible that the observations are caused by superconductivity. The fact that the critical magnetic field is as high as 2 T suggests that the superconductivity is in a confined geometry and is perhaps filamentary.

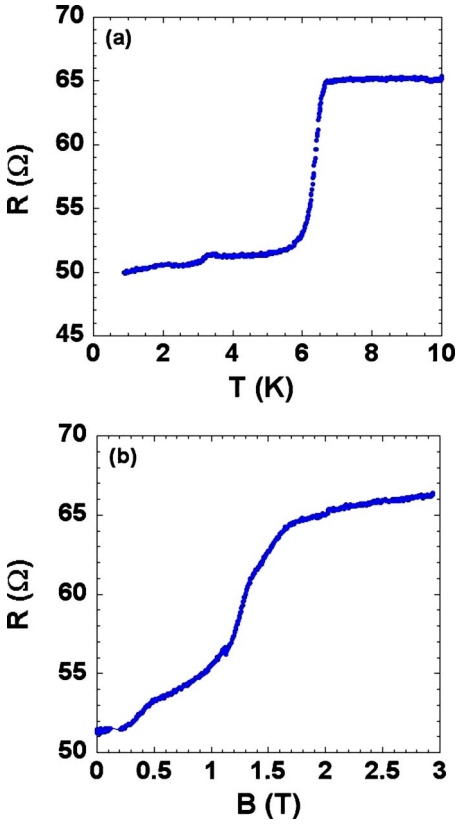

FIG. 3. (Color online) $R(T)$ of a planar capacitor configuration of $SrTiO_3$ subjected to irreversible breakdown processes in (a) zero field and in (b) magnetic field at 4K. Note this sample is the same as the one shown in Fig. 2 but after several additional irreversible breakdown processes to bring the resistance down below 100 Ω.

Although not precisely reproducible, the breakdown process may be a path to inducing superconducting behavior at somewhat elevated temperatures relative to what has been found in chemically or electrostatically doped $SrTiO_3$. Since the electrodes are formed from nonsuperconducting metals, the resistance drops cannot be associated with the onset of superconductivity in metallic filaments of the electrode materials. Another issue is whether the breakdown process results in filaments of Ti and Sr, or their alloys, whose superconductivity could be responsible for the observed effects. This possibility cannot be categorically ruled out but is unlikely. The bulk transition temperature of Ti is about 0.42 K.[12] To the best of our knowledge Sr is not a superconductor and there are no other reports of measured higher transition temperatures (up to 6 K) of Ti or its alloys with the electrode materials used in this work.[12,13]

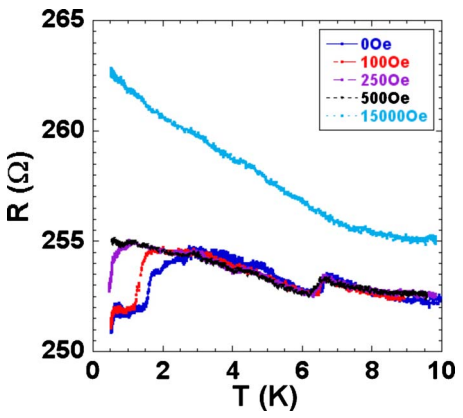

FIG. 4. (Color online) $R(T)$ of a planar capacitor configuration of $SrTiO_3$ subjected to irreversible breakdown in fields of 0, 10^{-2}, 2×10^{-2}, 5×10^{-2}, and 1.5 T

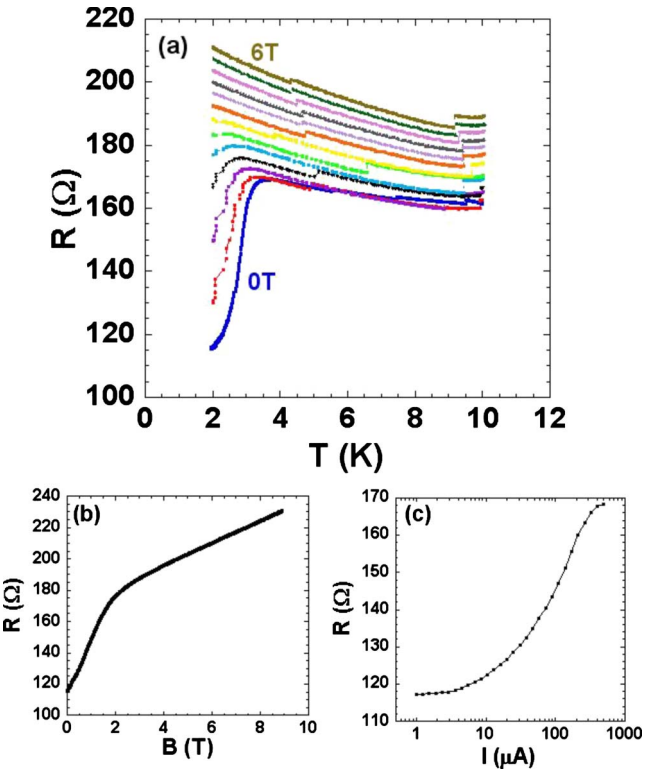

FIG. 5. (Color online) (a) $R(T)$ of a parallel plate capacitor configuration of $SrTiO_3$ subjected to irreversible breakdown steps in magnetic fields of (bottom to top) 0–6 T, in increments of 0.5 T. The small dips at approximately 9 and 4.5 K are instrumental (b) $R(H)$ at a fixed temperature of 2 K. The resistance is measured by applying an excitation current of 1 μA (c) Resistance vs excitation current at a fixed temperature of 2 K in zero magnetic field.

With moderate breakdown electric fields the switching between insulating and metallic behavior is reversible but there is no sign of superconductivity at temperatures down to about 2 K. Stronger fields, leading to irreversible switching to metallic behavior result in the appearance of large drops in the resistance in some samples. These changes respond to magnetic fields in a manner reminiscent of superconductivity. The temperatures at which these effects are seen, as well as the magnitudes of the resistance drops vary from sample to sample, and are not realized in some samples.

The study of breakdown in single-crystal $SrTiO_3$ as well as the response to electric fields has a long history. Barrrett pointed out that the field is dependent on sample shape and temperature.[14] He concluded that electrostrictive strain increases the breakdown field with an upper limit set by mechanical failure. It has become well known that the application of static electric fields to strontium titanate crystals result in a redistribution of oxygen vacancies and as a con-

sequence structural changes. Oxygen vacancies gain enhanced diffusion coefficients when transported along dislocation lines or planar defects.[9] X-ray absorption near-edge structure (Xanes) studies have been carried out and demonstrated that Ti *K* absorption edge energies shift under applied dc electric fields. These have been interpreted as a shift in the Ti valence state in a volume associated by the diffusion of oxygen ions and vacancies.[15] Also documented is electric field mediated switching of mechanical properties of $SrTiO_3$.[16] Again diffusion of oxygen vacancies resulting in a distortion of the perovskite structure in the near-surface layer was proposed as an explanation. Finally there are groups that have concluded that extrinsic defects in the form of oxygen vacancies are the source of the conductivity at the interface between $SrTiO_3$ and $LaAlO_3$.[17] It is thus highly likely, but not absolutely certain, that our observations are the result of irreversible creation of channels of oxygen defects, which become superconducting, but do no completely span the space between the electrodes. Control of the process would likely require crystals whose dislocation patterns are optimized for the creation of oxygen defects along the direction of the electric field. The process may of course be applicable to other oxides where the doping and resultant conductivity and superconductivity depend upon oxygen stoichiometry.

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