Discovery of superconductivity in KTaO$_3$ by electrostatic carrier doping

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Superconductivity at interfaces has been investigated since the first demonstration of electric-field-tunable superconductivity in ultrathin films in 1960$^1$. So far, research on interface superconductivity has focused on materials that are known to be superconductors in bulk$^{1-9}$. Here, we show that electrostatic carrier doping can induce superconductivity in KTaO$_3$, a material in which superconductivity has not been observed before$^{10,11}$. Taking advantage of the large capacitance of the self-organized electric double layer that forms at the interface between an ionic liquid and KTaO$_3$ (ref. 12), we achieve a charge carrier density that is an order of magnitude larger than the density that can be achieved with conventional chemical doping. Superconductivity emerges in KTaO$_3$ at $50 \text{ mK}$ for two-dimensional carrier densities in the range $2.3 \times 10^{14}$ to $3.7 \times 10^{14} \text{ cm}^{-2}$. The present result clearly shows that electrostatic carrier doping can lead to new states of matter at nanoscale interfaces.

Chemical doping is the process of introducing electrical conductivity in an insulator by replacing atoms of one of the constituent elements with atoms of another element with a different valence state. To convert a Mott insulator, such as a cuprate, into a superconductor$^{13}$, it is necessary to achieve a dopant concentration of $\sim 10\%$ or $1 \times 10^{21}$ dopant atoms per cm$^3$, but in many cases the chemical solubility of the insulator is too low to reach such concentrations. In addition, the replacement of some atoms during doping inevitably changes the crystalline structure and often introduces randomness into the system. Another way of donating charge carriers to an insulator is electrostatic doping by a field effect, as used in field-effect transistors (FETs). One can also accumulate mobile carriers at the surface of an insulator by applying a gate voltage $V_G$, but the gate dielectric breaks down when the electric field reaches a value of $1-10 \text{ MV cm}^{-1}$, which corresponds to a two-dimensional carrier density $n_{2D}$ of $\sim 1 \times 10^{13} \text{ cm}^{-2}$ (refs 3, 5, 14–16).

Recently, very high electric fields have been applied with an electric double-layer transistor, a device that uses a liquid electrolyte as a gate dielectric$^{17-19}$. When a solid sample is immersed in this liquid electrolyte, a Helmholtz electric double layer (EDL) self-organizes at the interface (Fig. 1). This double layer can be thought of as a capacitor composed of a sheet of ions in the electrolyte and another sheet of accumulated image charges on the surface of the solid. These two layers are separated by less than 1 nm, which allows the EDL transistor to achieve values of $n_{2D}$ as high as $8 \times 10^{14} \text{ cm}^{-2}$ within an electrostatic mechanism$^{12}$.

Figure 2a summarizes the relationship between the critical transition temperature $T_C$ and three-dimensional carrier density $n_{3D}$ for bulk superconductors that were converted from insulators by means of chemical or electrostatic doping. It is clear that the values of $n_{3D}$ achieved by electrostatic doping are well above those needed to reach a superconducting state in the cuprates, so the EDL transistor should be able to induce superconductivity in insulators that cannot be made superconducting by chemical doping.

KTaO$_3$ is a promising candidate for superconductivity induced by electrostatic doping because it is similar to the low-$n_{3D}$ superconductor SrTiO$_3$ in many ways: both have a perovskite structure, both have similar band structures, and both exhibit quantum paraelectricity$^{10,20}$. It has also been shown that metallic conductivity can be induced in KTaO$_3$ at temperatures of $\sim 10 \text{ K}$ in conventional FET structures$^{21,22}$, but searches to temperatures as low as $10 \text{ mK}$ have failed to find evidence for superconductivity in KTaO$_3$ (ref. 11). Insufficient carrier density is likely to be the reason why superconductivity has not yet been observed in KTaO$_3$; the tantalum ions in oxides have only one stable oxidation state ($5^+$), in contrast to the three stable states ($2^+, 3^+$ and $4^+$) of titanium ions. As a result, the chemical solubility limit of KTaO$_3$ gives a maximum value of $n_{3D} = 1.4 \times 10^{20} \text{ cm}^{-3}$ (ref. 23). However, there is scope for electrostatic doping reaching values of $n_{3D}$ that cannot be achieved with chemical doping.

EDL transistor devices were fabricated on KTaO$_3$ (001) single crystals with an ionic liquid as the electrolyte with a planar device configuration (Fig. 1; see Methods). Excellent transistor characteristics were obtained at room temperature (shown in Supplementary Fig. S1). We observed an abrupt increase in drain current for values of $V_G$ above $2.7 \text{ V}$ (and up to $5 \text{ V}$), yielding an on/off ratio as high as $1 \times 10^5$. When $V_G$ was too high, a large leakage Faradaic current flowed between the channel and the gate electrode owing to an electrochemical reaction in the ionic liquid. A leakage current larger than $1 \mu\text{A}$ was observed for $V_G$ above $8 \text{ V}$ (Supplementary Fig. S2). Therefore, $V_G$ was limited to below $6 \text{ V}$ for all of the experiments shown in this Letter.

Figure 2b,c shows the temperature dependence of transport properties. The channel maintained a metallic state down to $2 \text{ K}$ for $V_G$ larger than $2.75 \text{ V}$, whereas the channel was insulating at $V_G = 2.5 \text{ V}$. We observed a sharp increase in mobility towards low temperatures, as observed in chemically doped crystals$^{10}$. The two-dimensional carrier density $n_{2D}$ was temperature-independent above $140 \text{ K}$ and monotonically increased with $V_G$. However, a peculiar decrease in $n_{2D}$ was observed with decreasing temperature for $V_G > 3.5 \text{ V}$, saturating below $10 \text{ K}$. Similar temperature dependence was reproducibly observed for all samples. Such
Figure 2 | Characterization of EDL transistors. a, Superconducting critical temperature $T_c$ as a function of three-dimensional charge carrier density for chemically doped superconductivity in 11 different material systems (filled symbols), and electrostatically induced superconductivity in two of these (open symbols). The lower panel shows the electronic phases appearing in KTaO$_3$ as a function of carrier density up to the maximum density that can be achieved with chemical doping; much higher densities are possible with EDL transistors (dashed red vertical line). b, Sheet resistance $R_s$ (on a logarithmic scale) versus temperature $T$ at six different gate voltages $V_G$ for an EDL transistor in which the channel is a single crystal of KTaO$_3$. The channel shows metallic behaviour for values of $V_G$ higher than a threshold of 2.75 V. c, Two-dimensional charge carrier density $n_{2D}$ (top) and carrier mobility (bottom) versus $T$ for five values of $V_G$; both $n_{2D}$ and mobility were evaluated by Hall measurements.

behaviour was previously reported for two-dimensional conductive layers in SrTiO$_3$, such as niobium-doped thin films, delta-doped heterostructures, LaAlO$_3$/SrTiO$_3$ heterostructures and electric-field-induced accumulation layers. Takahashi et al. compared the change in the Hall coefficient at various temperatures and electrostatic charging, and concluded that the Hall coefficient above 100 K yields a correct estimate of the carrier density. This phenomenon may be related to the quantum paraelectricity and ferroelectricity induced upon the electric field in these systems. In the following part of this Letter, we use $n_{2D}$ at 100 K as a representative value for the discussion of transport and superconducting properties unless otherwise specified.

The two-dimensional carrier density showed a nearly proportional increase with $V_G$ above a threshold voltage (Fig. 3a). The mobility was as high as 7,000 cm$^2$ V$^{-1}$ s$^{-1}$ at a low $n_{2D}$ of $2.4 \times 10^{13}$ cm$^{-2}$ (Fig. 3b), which is the highest value recorded in two-dimensional systems formed of transition metal oxides. Mobility decreases as a function of $n_{2D}$. To compare this behaviour with the case of bulk chemical doping, we need to estimate three-dimensional carrier density $n_{3D}$. For this purpose, we
performed a sub-band calculation by using reported values of dielectric constant and effective mass. (More details are given in the Supplementary Information and ref. 7.) Figure 3c shows $n_{\text{3D}}$ dependence of the mobility for EDL transistors and chemical doping. For EDL transistors, the mobility versus $n_{\text{3D}}$ relation agrees well for measurements taken at 100 K (solid symbols, Fig. 3c) and 2 K (open symbols, Fig. 3c). Mobility commonly decreases with increasing $n_{\text{3D}}$, but in convex and concave manners for the chemical doping and EDL transistors, respectively, possibly reflecting the difference in the carrier scattering mechanism: impurity scattering and surface scattering are thought to be dominant in the chemically doped crystals and the EDL transistor, respectively. Here, it should be stressed that $n_{\text{3D}}$ obtained by the EDL transistor exceeds the chemical doping limit by an order of magnitude. Although the quantitative accuracy of $n_{\text{3D}}$ estimated by means of the sub-band calculation should be re-examined in the future by experimental studies, Fig. 3c strongly indicates that electrostatic doping by the EDL transistor has an ability to go beyond the limit of conventional chemical doping.

Now we show the results measured in a dilution refrigerator for device D with $V_G = 5 \text{ V}$. Figure 4a shows the temperature dependence of four-terminal sheet resistance $R_S$, indicating a superconducting transition with an onset at 70 mK and zero resistance at 35 mK. The mid-point critical temperature $T_{\text{c}}^{\text{mid}}$ was 47 mK, where $R_S(T_{\text{c}}^{\text{mid}}) = 0.5R_S(0.2 \text{ K})$. The zero-resistance state was suppressed by application of a small magnetic field above 5 Oe normal to the surface, and $R_S$ returned to the normal state value above 30 Oe, as shown in Fig. 4b.

Figure 3 | Transport properties. a, Two-dimensional charge carrier density $n_{\text{2D}}$, deduced from the Hall coefficient at 100 K, versus gate voltage $V_G$ for four different EDL transistors in which the channel is a layer of KTaO$_3$. b, Mobility at 2 K versus $n_{\text{2D}}$ for the same four samples. c, Mobility versus three-dimensional carrier density $n_{\text{3D}}$, deduced from the estimated depth distribution of carriers (see Supplementary Information) for the same four samples: note that both axes are logarithmic. Solid and open symbols correspond to the data deduced from the three-dimensional carrier density $n_{\text{3D}}$ determined by the Hall coefficient measured at 100 K and 2 K, respectively. Data for chemically doped bulk KTaO$_3$ crystals from ref. 10 are also shown. Chemical doping in KTaO$_3$ cannot access values of $n_{\text{3D}}$ in the shaded area.

Figure 4 | Superconducting properties. a, Sheet resistance $R_S$ versus temperature $T$ at gate voltage $V_G = 5 \text{ V}$ in an EDL transistor in which the channel is a layer of KTaO$_3$. The solid line denotes the mid-point of the superconducting transition. b, $R_S$ versus magnetic field $\mu_0H$ at 20 mK. c, Current $I$ versus differential voltage $V$ at 20 mK, measured in a four-terminal geometry.
chemical doping, which could lead to the discovery of more superconducting compounds.

Methods

Devices were fabricated on KTaO$_3$ (001) single crystals, which had atomically flat surfaces as delivered from the vendor (Furuuchi Chemical Co. Ltd). We used a planar device configuration as shown in Fig. 1. In the previous study, we used a platinum wire as a gate and all the components, including substrate, gold wirings to the substrate and the platinum wire, were immersed in an electrolyte$^7$. As a result, large leakage current was observed owing to electrochemical reactions between the platinum wire and the gold wirings. In the planar configuration, the gate electrode was fabricated on the substrate and placed near the channel (Fig. 1a). A drop of an ionic liquid (electrolyte) covered only the area between the channel and the gate electrode, and did not contact other electrodes or wirings (Fig. 1b). The leakage current was therefore greatly reduced in comparison with the previous configuration with a platinum wire. Ohmic contact electrodes with a Hall bar geometry were fabricated by electron-beam evaporation of a gold/titanium film, which enabled measurement of the four-terminal resistance and Hall coefficient of the channel. Hard baked photoresist was used for the separator layer between the single crystal and the electrolyte. We selected a sputtered platinum film and an ionic liquid N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium tetrafluoroborate (DEME-BF$_4$) as the gate electrode and the electrolyte, respectively, owing to their electrochemical stability$^{25,26}$.

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References


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Author contributions

Additional information
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