

## Gates using mysterious 'Ionic Liquids' to achieve high surface charge density and superconductivity on an atomically flat film

*Liquid gated interface superconductivity on an atomically flat film*

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**Recommended with a Commentary by Atsushi Fujimori, University of Tokyo**

Chemical doping methods utilize atomic substitution or off-stoichiometry control and are versatile, but inevitably introduce randomly distributed charged impurities which strongly scatter charge carriers. As an alternative, "cleaner" route, carrier doping by electric field using field-effect-transistor (FET) structures has been attempted by many groups. Conventional gates consisting of an electrode and a channel sandwiching a dielectric oxide, however, (not withstanding the infamous work by Schoen) are not able to dope the host materials with a sufficient number of carriers. Using an organic polymer as the gate dielectrics, 2D carrier densities as high as  $n_{2D} > 10^{12} \text{ cm}^{-2}$  could be achieved at the dielectrics-SrTiO<sub>3</sub> interface and metallic transport of doped electrons in SrTiO<sub>3</sub> was realized [1]. Subsequently, utilizing electric double layers (EDL) induced at the electrolyte-SrTiO<sub>3</sub> or electrolyte-ZnO interfaces, 2D carrier densities as high as  $n_{2D} \sim 10^{14} \text{ cm}^{-2}$  were realized, leading to superconductivity in SrTiO<sub>3</sub> [2] and an insulator-to-metal transition in ZnO [3]. If the field-doped carriers are confined within several monolayers of the interface, the 3D carrier density would become  $n_{3D} \sim 10^{20} \text{ cm}^{-3}$ , which is sufficient to induce superconductivity in bulk SrTiO<sub>3</sub>, the superconductor with the lowest carrier density. For the field doping to be practical in a wider class of materials and other important applications, an order of magnitude increase of the carrier density (corresponding to several % carrier concentration) is necessary. Since the field-induced 2D carrier density is proportional to the electric field at the interface with the dielectrics and hence to the gate capacitance, dielectric materials with higher polarizability than electrolytes are required.

Recently, ionic liquids or room-temperature molten salts, which are ionic solids above the melting point but below room temperature, turned out to be useful materials as the gate dielectrics, as first demonstrated by Misra *et al.* [4]. In the recommended paper, Ye *et al.* used an ionic liquid (of the organic salt DEME-TFSI) and could increase the carrier density close to  $n_{2D} \sim 10^{15} \text{ cm}^{-2}$ , and could induce superconductivity in ZrNCl. ZrNCl is a layered compound, a band insulator like SrTiO<sub>3</sub> rather than a Mott insulator like the parent compounds of the cuprate superconductors, and its chemically doped materials such as Li<sub>x</sub>ZrNCl become superconductors for electron doping greater than 5%. The achieved  $T_c$  by the field-doping was 15.2 K, equal to the optimum  $T_c$  of the chemically doped  $x = 0.05$  samples, just at the insulator-superconductor boundary. Ionic liquids consist of only positive and negative ions of organic molecules and no solvent is needed unlike electrolytes. The Coulomb

interaction in ionic liquids is weak because of the large sizes of the ions, making the solid phase unstable. Ionic liquids have such remarkable properties as high dielectric constants, high chemical stability, and low vapor pressure (even compatible with ultra-high vacuum so that they can be studied by photoemission spectroscopy!) [5]. When an ionic liquid is used as the gate dielectrics, it forms an extremely thin EDL at the interface and hence has an extremely high dielectric constant. AC gate operation is possible up to the 1 to 10 kHz range depending on the ionic conductivity [6]. The polarized state can be frozen by reducing the temperature across the melting point and, therefore, superconductivity can be conveniently studied.

While the observation of the field-induced superconductivity in ZrNCl is remarkable by itself, various properties of the ionic liquids remain unclear. For example, although the 2D carrier density increased linearly with the gate voltage, the increase of  $T_c$  with the voltage was quite different from the  $T_c$  versus  $x$  relationship of the bulk materials: In the electric field gating, the  $T_c$  gradually increases with voltage up to 15.2 K, while in the bulk it suddenly jumps from 0 to 15.2 K at  $x = 0.05$  and then slowly decreases with  $x$ . This indicates that the field gating is not a simple, linear process. Theoretical studies using a simple model have indeed indicated that the EDL at the ionic liquid-metal interface involve image charges and thus effectively become thinner than the sizes of the constituent ions [7]! Further understanding of the EDL of ionic liquids would be necessary to understand the phenomena more properly. Also, extension of field doping using ionic liquids to other interesting materials is highly anticipated.

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