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Electrostatic and electrochemical tuning of superconductivity in two-dimensional NbSe₂ crystals

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We report modulation of the superconducting critical temperature (T_c) of ultrathin niobium diselenide (NbSe₂) single crystals by gating an electric double-layer transistor. We realized reversible and irreversible changes of the T_c by adjusting the operating range of the voltage. The reversible and irreversible responses correspond to the electrostatic carrier doping and the electrochemical etching of the crystal, respectively. The results suggest that electric double-layer gating provides opportunities to control and functionalize collective electronic phenomena in two-dimensional crystals. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4950804>]

Two-dimensional (2D) crystals¹ belong to a new class of nanosystems, where the reduction of the thickness significantly modifies its electronic properties. When isolated in a monolayer, the change in the electronic band structure is drastic, as demonstrated in graphene² with the Dirac electronic band and in 2D semiconducting transition metal dichalcogenides that are direct band gap³ semiconductors hosting emergent valleytronics.^{4,5} Dimensionality is also important in layered compounds with correlated electrons.^{6–9} These layered compounds are constructed using isolated building blocks of monolayers, which interact weakly when they are stacked. 2H-type niobium diselenide (NbSe₂) is a well-studied layered superconductor with charge density wave (CDW) ordering.^{10–19} The superconducting critical temperature (T_c) of layered NbSe₂ single crystals (Fig. 1(a)) is suppressed as the thickness is reduced.^{11–16,18} Such a thickness-driven decrease of T_c is commonly observed in superconducting thin films, which is attributed mainly to the effect of disorder.²⁰ In the case of NbSe₂, modification of the band structure was experimentally confirmed in the single-layer system,¹⁷ which should also contribute to the thickness dependence of T_c . Therefore, NbSe₂ can be used to investigate the relationship between the collective electronic phenomena and the thickness-dependent electronic structure.

The atomically thin nature of 2D crystals enables us to effectively control their physical properties by manipulating the surface. The field effect transistor is a powerful device where electrostatic carrier accumulation occurs at the surface of the channel material. Recently, control of the surface has been significantly enhanced by introducing the electric double-layer (EDL) interface.^{21–26} Regardless of the choice of channel materials, EDL gating relies on a self-assembled channel/dielectric interface with a high capacitance using an

ionic liquid. Not only can large amounts of carriers be accumulated by gating electrostatically, the EDL transistor (EDLT) also provides opportunities to control the channel properties beyond the conventional field effect transistor carrier doping. An electrochemical process can take place at the EDL interface by setting the bias beyond the electrostatic doping range.^{27,28}

FIG. 1. (a) Crystal structure of 2H-NbSe₂. (b) The resistivity (ρ) versus temperature (T) characteristics of an NbSe₂ bulk single crystal. (c) Schematic of AFM imaging of an EDLT for an ultrathin NbSe₂ single crystal. (d) T dependence of the normalized sheet resistance (R_s) for bulk, 7-, and 3-nm-thick single crystals.

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To explore the layered nature of the materials and to engineer the superconductivity, we applied the EDL technique to ultrathin NbSe₂ single crystals. First, we checked the bulk properties of an NbSe₂ single crystal. Figure 1(b) shows the temperature (T) dependence of the resistivity (ρ) in the NbSe₂ bulk single crystal. A resistive anomaly appeared in the ρ - T curve, reflecting the phase transition from a normal metal to an incommensurate CDW phase. We defined the CDW transition temperature (T_{CDW}) as the temperature at which the derivative of the resistivity ($d\rho/dT$) had a local minimum, and T_{CDW} was 32 K. The superconducting transition appeared at 7.2 K. These successive transitions are consistent with the literature values, and the clear signal of the CDW transition originates from the high-quality pristine single crystal.

Next, we fabricated EDLTs for ultrathin NbSe₂ single crystals. Ultrathin NbSe₂ single crystals were obtained by mechanical exfoliation of the bulk single crystal. We transferred the ultrathin crystals onto a 300-nm-thick silicon/silicon dioxide (SiO₂) substrate. Four-probe electrodes were patterned using electron-beam lithography, followed by the sequential deposition of titanium (5 nm) and gold (60 nm). An insulating SiO₂ layer (30 nm) was deposited on the electrodes to avoid exposing the metal electrodes to ionic liquids. We also prepared a gold gate electrode as shown in Fig. 1(c). Just before the gating experiment, we put an organic ionic liquid, *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis-trifluoromethylsulfonyl-imide, between the channel and the gate electrode to complete the EDLT structure.

Figure 1(d) shows the temperature dependence of the normalized sheet resistance (R_s) for the bulk, 7-nm-thick, and 3-nm-thick single crystals. The thickness was confirmed using atomic force microscope. There are approximately 12 and 5 layers for the 7- and 3-nm-thick samples, respectively. For the thin crystals, we measured R_s as a function of T before putting the ionic liquid on the channel. There was a systematic decrease in the superconducting transition temperature (T_c) as the thickness was reduced as shown in Fig. 1(d). We also observed a broadening of the R_s - T curve at the onset of superconductivity in the thin samples, indicating enhancement of the thermal fluctuations in two dimensions. The observed relationship between T_c and thickness is qualitatively consistent with literature.^{11–16,18}

After confirming the thickness-controlled superconductivity in NbSe₂, we put the ionic liquid onto the crystals to tune the T_c through gating. We applied a relatively low gate voltage (V_G) to the 3- and 7-nm-thick crystals at $T = 210$ K under high vacuum. Figure 2(a) shows the V_G dependence of the normalized change of R_s , calculated using

$$\Delta R_s(V_G)/R_s(0 \text{ V}) = [R_s(V_G) - R_s(0 \text{ V})]/R_s(0 \text{ V}). \quad (1)$$

Within $|V_G| \leq 1$ V, both the crystals had reversible changes in the R_s , indicating electrostatic electron and hole doping by applying positive and negative V_G , respectively. It is also shown in Fig. 2(a) that the change in R_s upon application of V_G is greater in the 3-nm-thick crystal than in the 7-nm-thick crystal. This result is an evidence of the occurrence of electrostatic carrier doping; because of screening by the large number of carriers in the metallic NbSe₂ system, the effect of surface carrier doping is more apparent in thinner samples.

FIG. 2. (a) Gate voltage (V_G) dependence of the normalized change in R_s [$\Delta R_s(V_G)/R_s(0 \text{ V})$] for the 3- (the red curve) and 7-nm-thick single crystals (the cyan curve) measured at $T = 210$ K. (b) T dependence of R_s for the gated 3-nm-thick single crystal. (c) V_G dependence of R_s for the 7-nm-thick single crystal measured at $T = 210$ K for different cycles.

After applying V_G at $T = 210$ K under high vacuum, we cooled the sample down to $T = 170$ K, and purged the sample with helium. The sample was then cooled to $T = 1.8$ K. Figure 2(b) shows the R_s versus T curves in the 3-nm-thick crystal at low temperatures. There was a decrease in T_c by gating at $V_G = 1$ V. The observed suppression of superconductivity through electron doping is consistent with the results reported in solid-gated^{12,13} and intercalated NbSe₂ systems.¹⁴ Figure 2(b) also shows a decrease in T_c just by applying the ionic liquid. It is probable that band bending occurred and electrons were effectively doped when the channel/liquid interface was realized.²⁹

In contrast to the small electrostatic modulation of R_s shown in Figs. 2(a) and 2(b), we observed a large change in R_s by applying a higher V_G . The purple curve shown at the bottom of Fig. 2(c) is the evolution of R_s in the 7-nm-thick crystal upon decreasing V_G from 0 V to -2 V under high vacuum. There was a steep increase in R_s at $V_G = -1.6$ V, which was absent in Fig. 2(a). After applying $V_G = -2$ V, we cooled the sample down to $T = 1.8$ K through purging at $T = 170$ K. We then released V_G at 1.8 K, warmed up the sample to 210 K, and applied V_G again from 0 V to -3 V. The resulting R_s versus V_G curve is the violet curve on the second row from the bottom in Fig. 2(c). Because the first purple and second violet R_s - V_G curves are not identical, the gating operation is irreversible and is no longer electrostatic. We repeated the procedure 10 times to gate and cool/warm the sample so that R_s increased by an order of magnitude as shown in Fig. 2(c). The irreversible monotonic increase in R_s indicates the occurrence of an electrochemical process at $V_G < -1$ V. The voltage range $-3 \text{ V} < V_G < -1 \text{ V}$ is within

the electrochemical potential window of the ionic liquid, *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methyammonium bis-trifluoromethylsulfonyl-imide, even at room temperature.²⁷ The observed voltage range of $-1\text{ V} < V_G < 0\text{ V}$ for electrostatic hole doping reflects the sensitive nature of the surface of NbSe₂.

Figure 3(a) shows the temperature dependence of R_s after each application of V_G . As the number of cycles increased, R_s increased and the residual resistivity ratio decreased. We show the temperature dependence for each cycle of the normalized R_s at low temperature in Fig. 3(b). Figure 3(b) shows a systematic decrease in both the onset transition temperature and the sample temperature to realize a zero resistance state as the number of cycles increased. We define T_c as the temperature at which the sheet resistance falls to $R_s(8\text{ K})/2$, where we assume that the crystal is in the normal state at $T = 8\text{ K}$. Figure 3(c) shows the systematic decrease in T_c as a function of the cycle number. Figure 3(d) shows the evolution of R_s at $T = 8\text{ K}$, where there is a monotonic increase in the normal resistance. After repeating the gating process 10 times, the R_s in the normal state was still smaller than the quantum resistance, $R_Q = h/4e^2 = 6.45\text{ k}\Omega$, which explains the absence of a superconductor–insulator transition in Fig. 3(a).

There was a striking similarity between the gate-controlled superconductivity shown in Fig. 3 and the thickness-controlled superconductivity in Fig. 1(d). By either reducing the thickness or repeating the gating process, the system shows an increase

in R_s , a decrease in residual resistivity ratio and T_c , and broadening at the onset of superconducting transition. Such similarity reminds us of the recently reported monolayer iron selenide films made by electrochemical etching with ionic liquid gating, suggesting that etching occurs in a layer-by-layer manner.³⁰ We presume that a similar electrochemical etching process takes place in the NbSe₂ ultrathin crystal under the application of a high V_G and that the thickness of the ultrathin crystal kept decreasing as the number of gating cycles increased. However, the electrochemical etching process does not seem to be sufficiently controlled. There are multiple superconducting transitions visible in Fig. 3(b) for the sample that was gated many times. The transition also broadened. Such broadening may be attributed to the inhomogeneity of the gated sample. These results suggest that repeating the gating cycles not only promoted the etching but also increased the disorder at the surface, which is another way to effectively reduce the thickness of the superconducting layers. Further optimization of the electrochemical process is needed to achieve layer-by-layer etching with minimal disorder. Nevertheless, the present results indicate that we can, in principle, systematically reduce the thickness of the superconducting layers by controlling the voltage bias.

In conclusion, we realized modulation of the superconducting transition temperature (T_c) in ultrathin NbSe₂ single crystals by ionic liquid gating. We achieved reversible and irreversible gating operation by applying a low and high V_G , respectively. The reversible tuning of T_c was attributed to electrostatic carrier doping. The irreversible change in T_c indicates electrochemical etching of the ultrathin crystal, reflecting the thickness-dependent nature of the superconductivity in 2D NbSe₂ crystals. The results imply that the ionic liquid gating enables transformation of any layered superconductor into an ultrathin two-dimensional superconductor, providing more opportunities to control and engineer its peculiar properties.

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FIG. 3. (a) R_s versus T curves for the gated 7-nm-thick single crystal for different cycles. (b) T dependence of the normalized R_s . (c) The evolution of the superconducting phase transition temperature (T_c) as a function of cycle number. T_c is the temperature at which half the resistance disappeared. (d) Dependence of the R_s on cycle number at $T = 8\text{ K}$. The dashed line represents the quantum resistance, $R_Q = h/4e^2 = 6.45\text{ k}\Omega$.

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