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Superconductivity above 28 K in single unit cell FeSe films interfaced with GaO$_{2-\delta}$ layer on NdGaO$_3$(1 1 0)

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The discovery of high temperature superconductivity in single unit cell (UC) FeSe on TiO$_2$-terminated perovskite SrTiO$_3$(0 0 1) substrates$^{[1]}$ has attracted intensive attention on searching for new superconducting systems with engineered interfaces as well as understanding the mechanism of interface high temperature superconductivity. In stark contrast to bulk FeSe—a superconductor with transition temperature $T_c \sim 8$ K at ambient pressure$^{[2]}$, the single UC FeSe on SrTiO$_3$(0 0 1) becomes superconducting at $T_c \sim 65$ K$^{[3–5]}$ or higher$^{[6,7]}$, holding the record $T_c$ among all known Fe-based superconductors. The superconducting gap is enhanced by one order of magnitude compared to the value of bulk FeSe, i.e. 20 meV$^{[1]}$ vs. 2.2 meV$^{[8]}$. What is more interesting is that monolayer FeSe on several TiO$_2$-terminated substrates, such as BaTiO$_3$$^{[9]}$, SrTiO$_3$(0 0 1)$^{[10–12]}$ and TiO$_2$(1 1 0)$^{[13,14]}$, exhibit similarly high transition temperatures, despite the variation of lattice constant$^{[15,16]}$. The common features shared by all these 1-UC FeSe/TiO$_2$ systems are the enlarged electron pockets at the Brillouin zone (BZ) corners$^{[3,17,18]}$ and emergent replica bands 90–100 meV from the main bands$^{[11,14,18]}$. They indicate that FeSe is electron-doped and the electrons therein couple with Ti-O stretching phonons$^{[19,20]}$, respectively. On the other hand, electron-doped FeSe systems, such as K-coated multilayer FeSe, exhibit similar Fermi surfaces but universally lower $T_c$ (<45 K) and smaller superconducting gaps (<14 meV)$^{[21–24]}$. This difference indicates that interface electron-phonon interaction plays an important role in further enhancing superconductivity by cooperatively mediating the cooper pairing$^{[15,16,18,22,25]}$.

The FeSe/TiO$_2$–a interface bears sharp resemblance to the building blocks of cuprate and Fe-based high temperature superconductors. There, superconductivity emerges in the CuO$_2$ and FeAs layers, which are interfaced with oxide layers of BaO/SrO and LaO/SmO, respectively$^{[26–28]}$. The fact that a variety of oxide layers can act as the charge reservoir layer motivates us to look for an oxide layer that is different from TiO$_2$–a. One recent endeavour by interfacing FeSe with MgO(0 0 1) proved that the onset superconducting temperature can be raised to 18 K$^{[29]}$. Here, we report on the observation of superconductivity with an onset temperature of 28 K in single UC FeSe films epitaxially grown on perovskite NdGaO$_3$. Scanning transmission electron microscopy (STEM) reveals that FeSe sits on double GaO$_2$ layers in a striking similar manner as that of FeSe on TiO$_2$–a. Electron energy loss spectroscopy (EELS) further identifies the charge transfer across the FeSe/GaO$_2$ heterojunction.

NdGaO$_3$ has been commonly used as a substrate for thin-film deposition of high temperature cuprate superconductors due to the matching lattice constants and thermal expansion coefficients$^{[30,31]}$. NdGaO$_3$ has a distorted orthorhombic structure with lattice parameters: $a = 0.543$ nm, $b = 0.550$ nm and $c = 0.772$ nm$^{[32]}$. In order to achieve lattice matching between FeSe and NdGaO$_3$, we chose NdGaO$_3$(1 1 0). This crystal orientation corresponds to in-plane lattice constants: $a_{\text{GaO}_2} = 0.384$ nm and $b_{\text{GaO}_2} = 0.386$ nm (Fig. 1a), which are close to the in-plane lattice constant of FeSe: $a_{\text{FeSe}} = 0.379$ nm$^{[2]}$. To obtain single GaO$_2$-terminated surface, we pretreated NdGaO$_3$(1 1 0) substrates by...
rate annealing in a tube furnace at 930 °C under O2 flux for 3 h [33].

wet chemical etching in a 10%-HCl solution for 45 min before ther-

Fig. 1. Structure and morphologies of FeSe films on GaO2/C terminated NdGaO3(1 1 0) substrates. (a) Schematic structure of GaO2/C terminated NdGaO3(1 1 0) surface (top panel) and FeSe/NdGaO3 hetero-structure (bottom panel). (b) and (c) Typical STM images of FeSe films on GaO2/C and NdO co-existed (sample bias V = 2.8 V, tunneling current I = 310 pA) and single GaO2/C terminated NdGaO3(1 1 0) (V = 2.0 V, I = 350 pA) substrates, respectively. Line profiles (lower panels) correspond to the blue lines in the morphology images. The dashed lines represent the stepped surfaces of NdGaO3(1 1 0) substrates with red/green double arrows mark steps of 0.19/0.38 nm high. The blue double arrows indicate the height of single UC FeSe.

Since NdGaO3 is highly insulating, we attached carbon nanotubes (tens of turns, ~2 nm wide) at one end of the substrate before loading the substrate to UHV chamber. This method guarantees in-situ room temperature scanning tunneling microscopy (STM) characterization of the overlaid FeSe film, indicating that carbon nanotubes electrically bridge the FeSe film and the contacting bar of the sample holder. Samples for ex-situ transport and STEM measurements were further capped by 10 UC FeTe films. The FeTe films were grown by co-evaporating Fe and Te from standard Knudsen cells at a substrate temperature of 430 °C. The Fe/Se flux ratio was ~1:10 and the growth rate ~0.10 UC per minute. Then the samples were in-situ post-annealed at 450 °C to remove extra Se.

In stark contrast, the intensity peaks of Fe L23-edges in the first UC of FeSe that is directly interfaced with GaO2/C do not show clear relative shift (the top four curves). From the fifth to the second Fe layers, the intensity peaks of Fe L23-edges do not show clear relative shift (the top four curves). In stark contrast, the intensity peaks of Fe L23-edges in the first UC of FeSe that is directly interfaced with GaO2/C layer consistently get broadened and shift (0.4 ± 0.1) eV to higher energy, indicating that Fe ions therein accept electrons from the GaO2/C layer. Notably, such an Fe L23-edge blue shift is observed at room temperature, whereas a blue shift of (~0.7 ± 0.1) eV was observed in 8 UC FeSe/SrTiO3 only at 10 K [35]. This contrast may stem from the distinctly different temperature dependent properties of SrTiO3.
and NdGaO$_3$ substrates. For example, the dielectric constant of SrTiO$_3$ increases by two orders of magnitude as the temperature decreases from room temperature to about 4 K, which does not happen in NdGaO$_3$ [36]. From the energy band perspective, NdGaO$_3$ has a larger band gap (3.8 eV) than SrTiO$_3$ and the band bending in NdGaO$_3$/SrTiO$_3$ heterostructure happens in a similar manner to that in LaAlO$_3$/SrTiO$_3$ [37]. These facts indicate that the electron affinity of NdGaO$_3$ is smaller than that of SrTiO$_3$. Therefore, the band bending in FeSe/NdGaO$_3$, which drives the charge transfer, is weaker than that in FeSe/SrTiO$_3$ [38].

Our most important finding is the observation of enhanced superconductivity with an onset temperature of 28 K in single UC FeSe on NdGaO$_3$(110). Displayed in Fig. 3 are the temperature dependent resistances of 1 UC, 3 UC, and 4 UC FeSe samples. The schematic setup for transport measurements is shown in the inset. Freshly cut indium cubes were cold pressed onto the samples as contacts. Samples were measured in a four-terminal configuration by employing the standard lock-in technique (1 μA at 13 Hz). All these ultrathin FeSe films on NdGaO$_3$(110) substrates undergo superconducting transitions at 25–35 K. For the 1 UC sample, the resistance starts to drop at ~35 K, and for the 4 UC sample, the resistance starts to drop at ~30 K and reaches zero at 11 K. We define the onset superconducting temperature as the crossing point of the extrapolated lines from the normal state and the transition regime (gray lines). The upper inset panel in Fig. 3 summarizes the onset temperatures: $\gamma_{\text{UC}}^{\text{onset}} = 28.0$ K, $\gamma_{\text{UC}}^{\text{onset}} = 25.3$ K and $\gamma_{\text{onset}}^{\text{onset}} = 24.7$ K, all of which are more than three times the $T_c$ for bulk FeSe (8 K) [2]. Notably, the superconducting transition shifts to lower temperatures and widens considerably with increasing FeSe thickness – a typical feature of interface enhanced superconductivity. For conventional metal superconductors, however, a thicker film usually has a higher $T_c$ with a sharper transition. The opposite behavior seen here reflects the decaying influence from the substrate. Previous transport measurements have revealed that thicker FeSe films on SrTiO$_3$ also exhibit lower transition temperatures as well as wider transition temperature regions, suggesting that only the first UC of FeSe at the interface is superconducting [35,39]. The same thickness dependence seen in FeSe/NdGaO$_3$(110) system, therefore, indicates here also only the first UC FeSe becomes superconducting.

Fig. 4 shows transport results of 1 UC and 4 UC FeSe samples under a perpendicular magnetic field. The transition broadens and shifts to lower temperatures at higher magnetic fields. For a 2D superconductor, its response to an external magnetic field normal to the 2D plane is expected to follow the linear Ginzburg-Landau formula [40].
Fabricating multi-layers of FeSe/GaO$_2$ could be grown at lower temperature, for Ga has higher saturated vapour pressure than Ti. Fabricating multi-layers of FeSe/GaO$_2$ may be a feasible way to further enhance superconductivity. The insets show the upper critical field as a function of temperature (blue dots) and the corresponding linear fittings (red lines).

![FeTe/1 UC-FeSe/NdGaO$_3$(1 1 0) hetero-structures](image)

**Fig. 4.** Magneto-transport of FeTe/FeSe/NdGaO$_3$(1 1 0) hetero-structures. (a) and (b) The temperature dependent resistance under various perpendicular magnetic fields for FeTe/FeSe/NdGaO$_3$(1 1 0) hetero-structures that consist of 1 UC and 4 UC FeSe films, respectively. The insets show the upper critical field as a function of temperature (blue dots) and the corresponding linear fittings (red lines). (c) and (d) The corresponding Arrhenius plots of (a) and (b), respectively. Gray dashed lines show linear fits in the low-temperature regime, reflecting the thermal activation behavior. The insets show the activation energy $\frac{U_0}{k_B}$ as a function of the perpendicular magnetic field (blue dots) with linear fittings (red lines).

$$\frac{d}{\eta H} = \frac{\xi_0^2}{2 \pi^3 \lambda^2},$$

where $\lambda$ the London penetration depth. By assuming $d = 0.55$ nm (only interfacial single UC FeSe is superconducting), we obtain London penetration depths: $A_1$ UC = 84 nm and $A_4$ UC = 126 nm. The Ginzburg-Landau parameter $\kappa = \frac{\lambda}{c}$ is therefore larger than 20, indicating a type II superconductor.

NdGaO$_3$ is the third type of oxides, after TiO$_2$-family (including SrTiO$_3$, BaTiO$_3$, TiO$_2$ etc.) and MgO layers, that can enhance superconductivity in single UC FeSe films. The $T_c$ ranks between the two previous ones [4,29]. Similarly, interface charge transfer is identified from EELS. In comparison to FeSe on SrTiO$_3$(0 0 1), FeSe on NdGaO$_3$ possesses smaller in-plane lattice constants and larger out-of-plane Fe-Se distance. The band bending and screening effect are also weaker (estimated from work functions and dielectric constants, respectively). They correlate with the observed lower $T_c$, suggesting that superconductivity in FeSe indeed depends on the in-plane stretching [42] and band bending [21–24]. Our work also hints at a universal method to enhance superconductivity in single UC FeSe films on NdGaO$_3$ substrates. Similar to FeSe/TiO$_2$ heterostructures, the Ginzburg-Landau parameter $\kappa = A/\xi$ is indeed higher than 20, indicating a type II superconductor.

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In this work, we observed interface enhanced superconductivity in single UC FeSe films grown on GaO$_2$-terminated NdGaO$_3$(1 1 0) substrates. Similar to FeSe/TiO$_2$ interface, interface charge transfer was identified. Our finding suggests that FeSe/GaO$_2$ is a new platform for investigating the mechanism of interface high temperature superconductivity. This work could also facilitate fabrication of sandwiched oxide/FeSe/oxide heterostructures to achieve higher $T_c$.

**Conflict of interest**

The authors declare that they have no conflict of interest.

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**Author contributions**

Qi-Kun Xue and Lili Wang conceived and designed the experiments. Haohao Yang, Guanyu Zhou, Yuying Zhu, Guan-Ming Gong, Qinghua Zhang, and Menghan Liao performed the experiments. Haohao Yang, Yuying Zhu, Guan-Ming Gong, and Lili Wang helped perform the analysis with constructive discussions. Haohao Yang, Ding Zhang, and Lili Wang wrote the paper.
References


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