High-Mobility Few-Layer Graphene Field Effect Transistors Fabricated on Epitaxial Ferroelectric Gate Oxides

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1. Characterizations of Pb(Zr0.2Ti0.8)O3 films

The crystalline quality of the PZT thin films is characterized with x-ray diffraction (XRD). Figure S1 shows the $\theta$-2$\theta$ measurement of a typical 300 nm Pb(Zr,Ti)O$_3$ (PZT) film grown epitaxially on SrTiO$_3$ (STO) substrate. Only 00$n$ ($n$ =1, 2, etc.) peaks for PZT and STO are detected, showing a c-axis oriented film growth, with the polarization $P$ pointing normal to the surface (characterized with piezoresponse force microscopy, see below). The c-axis lattice constant is $\sim$4.15 Å, consistent with the value of a partially relaxed film. The rocking curve of the 001 peak has a full-width-half-maximum of 0.04°, close to the instrumental resolution, reflecting very high crystallinity.

![Fig. S1 X-ray $\theta$-2$\theta$ measurement of a 300 nm PZT film grown on a SrTiO$_3$ substrate. The double-peak feature is due to the $k_{\alpha 1}$ and $k_{\alpha 2}$ x-rays.]

We have chosen film thickness of $d$ = 300 and 400 nm to enhance the optical visibility of graphene through modeling described in Ref. [1]. AC voltages and voltage pulses of different polarity and magnitude are applied to the AFM tip scanning in contact with the PZT surface to perform piezoresponse force microscopy (PFM) [2]. Negative voltage pulses $> 8$ V are needed to switch the polarization of 400 nm as-grown films. We conclude that $P$ uniformly points into the surface, as expected from the growth procedure. The direction of $P$ remained unchanged throughout the current study.

2. Substrate preparation before the exfoliation of graphene

Prior to graphene exfoliation, PZT and SiO$_2$ substrates are sonicated in acetone for 20 minutes followed by an IPA rinse (1 min) and drying under a stream of dry N$_2$ gas. They are subsequently baked at 120°C for 5 minutes before the exfoliation of graphene.
3. The band structure of FLG

We employ a simply two-band model to estimate the band overlap energy $\delta \varepsilon$ and the densities of electrons and holes in the two-carrier regime near the charge neutrality point of our device, using band parameters determined by Novoselov et al. for FLG in Ref. [3] and supporting materials. Measurements there indicate a single electron band with an effective mass $m^*_{e} = 0.06m_0$ and two hole bands with a heavy hole mass $m^*_{h} = 0.1m_0$ and a light hole mass $m^*_{l} = 0.03m_0$. Note these effective mass values are close to those found in bulk graphite: $m^*_{e} = (0.056\pm0.003)m_0$ and $m^*_{h} = (0.084\pm0.005)m_0$ as well [4]. Without knowing the exact offset between the two hole bands, we simplify the estimate by ignoring the light holes, which likely account for less than 25% of the hole population due to the mass ratio. The densities of states of electrons and holes are then given by $\frac{2m^*_{e,h}}{\pi\hbar^2}$, where we have included the 4-fold degeneracy due to valley and spin [3].

The density of electrons and holes in the band overlap regime of the FLG is calculated as follows:

$$n_{e,h} = n^0_{e,h} \pm \frac{\alpha V \frac{m^*_{e,h}}{m^*_e + m^*_h}}{m^*_e + m^*_h} \quad \text{("+" for electron and "+" for hole)} \quad \text{(S1)},$$

where $n^0_{e,h}$ represents the electron/hole density at the charge neutrality point. At the threshold voltage $V^T_g = 1.1$ V (Fig. 2(b)) where the hole band is completely filled, $n_e = 1.5\times10^{12}/\text{cm}^2$ and $n_h = 0$. Using Eq. S1, we estimate that $n^0_e = n^0_h \sim 9\times10^{11}/\text{cm}^2$ at the charge neutrality point. This translates into a band overlap of $\delta \varepsilon \sim 30$ meV between the electron and hole bands. Alternatively, we determine $\delta \varepsilon$ by fitting $\rho(T)$ at the charge neutrality point to the thermal excitation model described in Ref. [3] and obtain $\delta \varepsilon \sim 27$
meV. The good agreement between these two methods and with theory [5] gave us confidence in these estimates. However we emphasize that the central results of our paper are derived from the electron-only regime ($V_g > V_T$) and do not rely on an accurate knowledge of the band structure in the two-carrier regime.

4. Dielectric constant measurements of PZT

We deduce the dielectric constant $\kappa$ of PZT substrate by Hall and low-frequency capacitance measurements independently. Figure S2 shows hole densities extracted from Hall measurements as a function of the backgate voltage $V_g$ in three different devices placed on the same PZT substrate, including the device shown in Fig. 2. We determine the charge injection rate $\alpha = (1.35\pm0.05) \times 10^{12} \text{ cm}^{-2}/V_g(V)$ using Eq. (2) in the single carrier (hole) regime, and calculate $\kappa \approx 100$ using a parallel-plate capacitor model.

![Fig. S2 Hole density $n$ vs. backgate voltage $V_g$ taken on three devices (squares, circles and triangles) on the same PZT substrate. The fit (blue dashed line) corresponds to a charge injection rate of $1.35\times10^{12} \text{ cm}^{-2}/V$. $V_g$ is shifted to align the charge neutrality point at $V_g = 0$ V as described in the text. Inset: Hall resistance $R_{xy}$ vs. perpendicular magnetic field for $n = 4.6\times10^{12}/\text{cm}^2$.]

We also determine $\kappa$ directly through low-frequency (20-1000 Hz) capacitance measurements. Capacitors with varying areas are measured to eliminate the effect of parasitic capacitances. We calculate the area of a capacitor from the mask design and estimate $\kappa \approx 120$ from these measurements.
5. $\rho(V_g)$ fitting inside the band overlap regime

We fit our low-$T\rho(V_g)$ data to Eqs. (1) and (3) within the band overlap regime, using effective masses of $m^*_e = 0.06m_0$ and $m^*_h = 0.1m_0$. A different set of mass values may lead to a different band overlap $\delta \varepsilon$ and affects the value of the exponent $\beta$ in Eq. (3). For example, $\delta \varepsilon \sim 32$ meV and $\beta \sim 1.0$, or $\delta \varepsilon \sim 27$ meV and $\beta \sim 0.8$ can fit the same data equally well as the values used in the text ($\delta \varepsilon \sim 30$ meV and $\beta \sim 0.9$). Beyond this energy range of $\delta \varepsilon$ (27-32 meV), a power-law $n$-dependence of mobility no longer describes the data well. The above analysis shows that although the precise value of $\beta$ depends on $\delta \varepsilon$ and hence the detailed understanding of the band structure of FLG, the power-law $n$-dependence seems to be robust.

This $n$-dependence of mobility is also supported by the measurements of the Hall coefficient $R_H$. Within the band overlap regime, $R_H$ exhibits the characteristics of a two-carrier system described by Eq. S2:

$$R_H = \frac{n_h\mu_h^2 - n_e\mu_e^2}{e(n_h\mu_h + n_e\mu_e)^2}$$

(S2).

At high $|V_g|$, the system becomes a purely electron or hole gas and $R_H$ reads:

$$R_H = \frac{1}{en_{e,h}} = \frac{1}{e\alpha(V_g - V_g^0)}$$

(S3),

Where for PZT-gated samples $\alpha = 1.35\times10^{12}$ cm$^2$/V and $V_g^0$ is offset to 0 V. Figure S3 plots $R_H$ vs. $V_g$ of the FLG shown in Fig. 2, together with three fitting curves. $R_H$ calculated using Eq. (S2) with $n_{e,h}$ given by Eq. (S1) and $\mu_{e,h}$ given by Eq. (3) with $\beta = 0.9$ and $r = 0.6$ (red) produce an excellent agreement with the data. Calculations based on a
constant mobility $\mu_h = \mu_e = \text{const.}$ (green), or an $n$-dependent but symmetric electron and hole mobility $\mu_h = \mu_e \sim n^{0.9}$ (blue) clearly do not fit the data.

Fig. S3 Hall coefficient $R_H$ vs. $V_g$ at 10 K with three calculated curves. Curve A (red): $\mu_{e,h} \sim n_{e,h}^{0.9}$, $\mu_h/\mu_e = 0.6$ (Eq. 3 of text). Curve B (green): $\mu_h = \mu_e = \text{const.}$ Curve C (blue): $\mu_h = \mu_e \sim n^{0.9}$. The charge injection rate $\alpha = 1.35 \times 10^{12} \text{cm}^{-2}/\text{V}$.

6. The deformation potential of LA phonons in graphene

In Eq. (4), we assume an unscreened deformation potential $D$ for LA phonons. Studies in GaAs show that neglecting the dielectric screening may result in an underestimate of the deformation potential [6]. The detailed $T$-dependence in the BG regime from a sample of yet higher mobility is required to determine the effect of screening. This analysis is beyond the scope of the present paper.

7. Resistivity and Hall measurements of a SiO$_2$-gated FLG

To compare the performance of PZT and SiO$_2$ substrates, we fabricate a FLG-FET of the same thickness (2.4 nm) on 300 nm SiO$_2$ following identical preparation steps. Figure S4 shows $\rho(V_g)$ of the SiO$_2$-gated FLG at selected temperatures. The charge neutrality point occurs at $V_0^g = -15.5$ V due to unintentional chemical doping. We find the charge injection rate of the backgate to be $\alpha = 7.0 \times 10^{10} \text{cm}^2/\text{V}$, in excellent agreement with calculations and experimental values from other graphene FETs made from the same set
of wafers. We determine $\mu(T)$ using Eq. (2) at electron density $n = 2.4 \times 10^{12}$ cm$^{-2}$ ($V_g = 19$ V). The results are plotted in Fig. 4 as open triangles. The mobility $\mu$ is approximately 14,000 cm$^2$/Vs and shows a very weak $T$-dependence. These findings are in good agreement with what has been reported in the literature [3].

![Figure S5](image)

Figure S5 shows $R_H$ vs. $V_g$ in this FLG. The band overlap, electron-only and hole-only regimes are all clearly visible. Red solid lines are calculated from Eq. (S3) using $\alpha = 7.0 \times 10^{10}$ cm$^{-2}$/V and $V_g^0 = -15.5$ V. The transition voltage to the electron-only regime ($\sim 2$ V) is in good agreement with that of the PZT-gated FLG, indicated by an arrow.

![Figure S5](image)

Fig. S5 Hall coefficient $R_H$ vs. $V_g$ ($T = 4$ K) of the SiO$_2$-gated FLG. Red solid lines are calculated using Eq. S3 and correspond to electron- and hole-only regime, respectively. The blue arrow indicates the equivalent voltage of the band edge observed in the PZT-gated FLG of the same thickness. The cross marks (-15.5V, 0 $\Omega$/T).
References:

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