<table>
<thead>
<tr>
<th><strong>Journal:</strong></th>
<th>Materials Horizons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manuscript ID:</strong></td>
<td>MH-COM-11-2018-001499</td>
</tr>
<tr>
<td><strong>Article Type:</strong></td>
<td>Communication</td>
</tr>
<tr>
<td><strong>Date Submitted by the Author:</strong></td>
<td>23-Nov-2018</td>
</tr>
</tbody>
</table>
| **Complete List of Authors:** | Hu, Guangliang; Xi'an Jiaotong University  
Wu, Jingying; Xi'an Jiaotong University  
Ma, Chunrui; Xi'an Jiaotong University,  
Liang, Zhongshuai; Xi'an Jiaotong University  
Liu, Weihua; Department of Microelectronics, Xi'an Jiaotong University  
Liu, Ming; Xi'an Jiaotong University, School of Electronic and Information Engineering  
Wu, Judy; University of Kansas, Department of Physics and Astronomy  
Jia, Chun-Lin; School of Microelectronics; Peter Grünberg Institute and Ernst Ruska Center for Microscopy and Spectroscopy with Electrons |
Conceptual Insights

Graphene has been widely used in various electronic devices and controlling the doping state or Dirac point voltage ($V_{\text{Dirac}}$) of graphene is essential for its practical applications. Different from traditional methods to modulate the doping in graphene, such as UV radiation in different gas environments, absorption of ionic liquid/ionic gel or gas molecules, here, we proposed a new method by applying mechanical bending stress on an all-inorganic flexible graphene-field effect transistor (GFET). Compared to other methods, the mechanical stress/strain designed graphene doping has three advantages: (i) it does not involve the absorption from secondary substances like gas molecules or ionic liquids; (ii) it is recoverable without any change on graphene; (iii) the doping operation is simple and reliable. The GFET with ferroelectric gate ($\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin film) exhibits a linear shift of Dirac point with increasing the bending stress due to the flexoelectric effect of ferroelectric gate. These phenomena indicate that it can be used to both tune the graphene doping state through adjusting curvature and detect bending curvature by monitoring the variability of its $V_{\text{Dirac}}$. This makes it enormously useful in the flexible electronic devices and flexible deformation sensors.
Designable Dirac Point Voltage of Graphene by Mechanical Bending Ferroelectric gate of Graphene Field Effect Transistor and Its Multifunctional Application

Guangliang Hua, Jingying Wua, Chunrui Maab, Zhongshuai Lianga, Weihua Liub, Ming Liub, Judy Z. Wu, Chun-Lin Jiab

Control of Dirac point voltage of graphene is essential for various practical applications of graphene. Here, a designable doping effect is achieved in flexible graphene field effect transistors (GFETs) by mechanical bending stress. By gradually increasing the bending strain (the decrease of upward/downward bending radius), the Dirac point ($V_{\text{Dirac}}$) linearly shifts to left/right, which is induced by the flexoelectric effect of the ferroelectric Pb$_{0.2}$La$_{0.8}$Zr$_{0.52}$Ti$_{0.48}$O$_{3}$ (PLZT) gate. In addition, a superior mechanical antifatigue character is obtained in the flexible GFETs, and the doping effect is recoverable. The sensitive characteristics to strain and high bending stability not only offers an easy, controllable and nonintrusive method to obtain a specific doping graphene for flexible electric device, but also promote the flexible ferroelectric PLZT-gated GFETs enormous potential applications as wearable sensors.

1. Introduction

Graphene, a monolayered carbon material with a hexagonal structure, has been considered as a promising material for high-performance nanoelectronics due to its superior chemical stability, high electron mobility, mechanical flexibility and high transmittance\textsuperscript{1-3}. Especially, the ambipolar characteristics of graphene based on field effect transistors (GFETs) make them highly competitive with the present electronic devices, since the graphene can behave as n-type or p-type by doping. Until now, great efforts have been performed to modulate the doping in graphene, such as UV radiation in different gas environments, absorption of ionic liquid/ionic gel or gas molecules\textsuperscript{4-6}. Actually, graphene doping by these methods are realized through surface-transfer doping, which involves electron exchange between graphene and dopants. It is known that a mechanical stress/strain can break centrosymmetry and hence generate a spontaneous electrical polarization (electric charge) in a dielectric material. Therefore, graphene can be tuned by applying a mechanical stress/strain to the gate (dielectric material) of flexible GFETs in principle. Compared to other methods, the mechanical stress/strain tunable has three advantages: (i) it does not involve the absorption from secondary substances like gas molecules or ionic liquids; (ii) it is recoverable without any change on graphene; (iii) the doping operation is simple and reliable. Based on the above advantages, the mechanical stress/strain is ideally suitable for tuning graphene doping. Unfortunately, the research of mechanical stress/strain tunable GFETs is lacking presently.

Moreover, the rapidly increasing demands for human-machine interfacing have driven flexible devices become one of the greatest technological and societal challenges nowadays\textsuperscript{7-12}. Flexible thin film is a key component of wearable sensors. Recently, some inorganic functional oxide thin films, such as CuFe$_2$O$_4$ and LiFe$_2$O$_3$, have been made flexible by directly fabricating the desired thin film on flexible Mica substrate or transferring the desired thin film from rigid substrates to flexible substrate through etching a buffer layer between the desired thin film and rigid substrate\textsuperscript{13, 14}. It is known that the inorganic ferroelectric thin films as the gate of GFETs can significantly low down the operating voltage, compared with the conventional gate materials (SiO$_2$/Al$_2$O$_3$) or the organic flexible ferroelectric gate. For example, the popular organic ferroelectric gate made of poly(vinylidenefluoride-co-trifluoroethylene) (P(VDF-TrFE)) requires operating voltage of at least ±5 V, but typically at ±40 V. While these are among the lowest reported on the organic ferroelectric gates, the operating voltage on organic gates is significant greater than that for the inorganic ferroelectric gates, such as Pb$_{0.92}$La$_{0.08}$Zr$_{0.52}$Ti$_{0.48}$O$_3$ (PLZT) or Pb$_{0.7}$Zr$_{0.3}$Ti$_{0.8}$O$_3$ with operation voltage typically less than ±2 V\textsuperscript{12, 15-17}. In addition, GFETs provide a unique platform to design various sensors since the conductance of GFET channel is sensitive to...
interfacial electrical charges with high bipolar electrical susceptibility\textsuperscript{1, 18}. Using PLZT-gated GFETs, we have demonstrated detection of the dynamic self-assembly of monolayer molecular ions on graphene\textsuperscript{19}, and the high sensitivity is anticipated from the high gate efficiency of the ferroelectric PLZT gate\textsuperscript{6, 16}. Herein, we design an all-inorganic flexible ferroelectric-gated GFET based on the PLZT gate on Fluorophlogopite (F-Mica) substrate. Remarkably, the GFET Dirac point ($V_{\text{Dirac}}$) can be tuned by mechanical bending linearly. Based on the change of the Dirac point, this kind flexible GFETs have broad application prospect. Through the tuning of curvature, we can obtain a specific Dirac point that we need, which can be used in the flexible electronic or optoelectronic devices requiring a controllable doping graphene. Furthermore, by monitoring the variability of source-drain current ($I_D$) and gate voltage ($V_G$), the curvature variation can be detected, which can be used in field of flexible deformation sensors, such as the motion of soft robotics and human.

2. Results

Multilayer films of PLZT/La$_0$Sr$_{0.33}$MnO$_3$/SrTiO$_3$ (PLZT/LSMO/STO) were fabricated by Pulse Laser Deposition (PLD) on F-mica. The crystallinity of the films has been characterized using x-ray diffraction (XRD) as shown in Fig. S1(a). It can be seen only (111) peak can be seen for both STO buffer layer and LSMO electrode layer on (001) F-mica substrate. Combined with the φ scans performed around from the (002) reflections of the LSMO/STO and the (202) reflections of the F-mica substrate shown in Fig. S1(b), the LSMO/STO is most probably form an epitaxial relationship of (111)$_{\text{LSMO}}$/[111]$_{\text{STO}}$/[001]$_{\text{F-Mica}}$ and [100]$_{\text{LSMO}}$/[110]$_{\text{STO}}$/[010]$_{\text{F-Mica}}$. The PLZT film fabricated on LSMO/STO is also highly oriented. Only a minor peak of (101) was detectable besides the main (111) PLZT peak.

A structure of the flexible GFET was designed and its fabrication process is schematically shown in Fig. 1(a). The LSMO film layer is used as the back-gate electrode and the Pt layer parts are used as the source drain electrode. The GFET channel is about 30 µm in length and 50 µm in width. Fig. 1(b) shows the Raman spectrum of the graphene channel. The intensity of the 2D peak is around twice of that of G peak, which is anticipated on the single-layer graphene. The GFET sample was annealed in vacuum below 10\textsuperscript{-6} Pa for about 24 hours before the electrical transport measurement to remove the residual adsorbates attached to the GFET channel in the GFET fabrication process\textsuperscript{16}. The source-drain current ($I_D$) on a representative PLZT-gated GFET (black) is depicted in Fig. 1c as function of gate voltage ($V_G$) with a fixed source-drain bias ($V_D$)=20 mV. The leakage current through the PLZT gate (blue) is less than 50 nA as shown in the same figure. The Dirac point $V_{\text{Dirac}}$ is 0.72 V. The positive $V_{\text{Dirac}}$ indicates the graphene is p-doped, which is attributed to the polarization of PLZT ferroelectric gate\textsuperscript{16, 20}.

The differential transconductance $g_m$ of the PLZT-gated GFET can be obtained from the $I_D$-$V_G$ characteristic by the formula:

$$g_m = \frac{dI_D}{dV_G}.$$  

(1)

It is shown in Fig. 1(d) in the $V_G$ range of ±2 V. The field effect mobility of holes and electrons can be calculated from the peak transconductance using the formula\textsuperscript{21, 22}:

$$\mu = \frac{g_m}{WC_D}.$$  

(2)

Where, $L$ is the channel length, $W$ is the channel width, $V_D$ is the drain voltage and $C_D$ is the specific capacitance of gate. The calculated field effect mobility of holes and electrons are $\mu_{h,b}=54.8$ cm$^2$V$^{-1}$s$^{-1}$ and $\mu_{e,b}=58.7$ cm$^2$V$^{-1}$s$^{-1}$, respectively, which are comparable to the results of our previous work for the PLZT-gated GFET on Nb:STO substrate\textsuperscript{18}. The reason for the low graphene mobility is complex, the defects of graphene (such as cracks or folding by transfer procedure), the screening effect at the graphene/PLZT interface and nanoscale scattering mechanisms may play an important role\textsuperscript{16, 22, 23}.

In order to investigate the tuning effect by mechanical strain on the transfer characteristic of GFET with the PLZT gate, the F-Mica substrate was mechanically exfoliated down to few tens of micrometers to obtain a good flexibility and then the GFET device was transferred on a Polyimide tape for bending test. Firstly, the strain is introduced by upward bending. The strain was changed by bending the Polyimide tape at various curvature radii of 12 mm, 10 mm, 8 mm and 6 mm, respectively. The $I_D$-$V_G$ characteristics of the flexible PLZT-gated GFET at different curvature radii are shown in Fig. 2(a) and the inset is a photo of the bending measurement. Despite a little change in $I_D$ at the $V_{\text{Dirac}}$, which may be caused by the effect of air atmosphere, the mobilities of hole and electron are almost the same with increasing bending ratio from no bending to 6 mm bending radius. The $V_{\text{Dirac}}$ exhibits a consistent shift from 0.72 V in flat state to 0.4 V at the 6 mm bending radius. Interestingly, the $V_{\text{Dirac}}$ shift is almost linear with the decreasing bending radius as shown in Fig. 2(b) (fitted by the red line). Secondly, a strain is introduced by downward bending. As shown in Fig. S2(a), a similar linear shift of $I_D$-$V_{BG}$ curves with decreasing bending radius can be obtained. However, the $V_{\text{Dirac}}$ shifts toward positive value. The details are shown in Fig. 2(c), a linear increase of $V_{\text{Dirac}}$ can be seen as bending radius decreases, and the total right shift is about 0.31 V. In fact, this response is highly reproducible, suggesting the all-inorganic flexible GFET exhibits excellent flexural fatigue as shown in Fig. S2(b). Basically, the $I_D$-$V_G$ curves of the GFET bending cycle between 1 and 1000 under bending radius (downward bending) of 6 mm coincide well. The $V_{\text{Dirac}}$ of these curves are extracted and summarized in Fig. 2(d). Although the $V_{\text{Dirac}}$ shows a slight increase of 0.04 V when the bending cycling is above 500, no further changes are observed, suggesting that the PLZT-gated flexible GFET has a
stable flexural fatigue characteristic. The similar flexural fatigue property for upward bending can be seen in Fig. S3.

The linear shift of $V_{\text{Dirac}}$ with the increasing bending curvature (or decreasing bending radius) can be understood based on two factors. One is the GFET channel and the other one is the characteristics of the gate, in response to the clamped dielectric susceptibility $\chi$. This journal is © The Royal Society of Chemistry 20xx

The first term describes the dielectric response with the clamped dielectric susceptibility $\chi$, and the second term describes the flexoelectric response with the flexoelectric coefficient $\mu$. $E$ and $\partial u/\partial x$ are applied electric field and strain gradient, respectively. As shown in Fig. 4(a), the polarization ($P_0$) induced by the upward bending is up (middle figure), while the polarization induced by the downward bending is down (right figure). From the Equ. 3 and the strain gradient calculation shown in Fig. S4, it can be derived that the polarization induced by strain gradient increases as the bending curvature increases. For upward bending case (Fig 4(b)) when a positive voltage ($V+$) applied to the bottom electrode, the direction of polarization induced by applied electric field ($P_d$) is parallel to $P_0$. When a negative voltage ($V-$) applied to the bottom electrode, the direction of $P_d$ is antiparallel to $P_0$. Therefore, the $P$-$V$ loops will take a upward shift, which is consistent with the measured $P$-$V$ loops (Fig. 3(c)). The downward bending (Fig.4(c)) generate an opposite behavior, that is the polarization induced by $V+$ is antiparallel to $P_0$, and the polarization induced by $V-$ is parallel to $P_0$, and will make the $P$-$V$ loops shift downward (Fig. 3(e)). The upward polarization generated by the upward bending contributes positive charges at the surface of the PLZT thin film. For compensation of the positive charges, negative charges are accumulated in graphene, as depicted in Fig. 4(d), leading to a negative-charge-doping effect and a left shift of the $V_{\text{Dirac}}$. With increasing the bending curvature, more positive charges are generated and hence induce the $V_{\text{Dirac}}$ left shift further. Conversely, the polarization induced by downward bending results in a positive-charge-doping effect in graphene, as shown in Fig. 4(e), and a right shift of $V_{\text{Dirac}}$.

In order to quantitatively analyze the effect of the mechanical bending on the doping of graphene, we calculated the change of charge carrier ($\Delta Q$) in graphene under bending state. As we known, the charge carrier change is related to the Dirac point shift ($\Delta V_{\text{Dirac}}$) by $\Delta Q=C_g \Delta V_{\text{Dirac}}$, where $C_g$ is back gate capacitance. From Fig. 2, it can be seen that the total change of $V_{\text{Dirac}}$ under upward bending and downward bending are about 0.32 V and 0.31 V, respectively, when the device is bent from 6mm to 2 mm bending radius. As shown in Fig. S5, the capacitance of back-gate is 0.6 uF/cm², which leads to the charge carrier change of around 0.192 µC/cm² and 0.186 µC/cm² in graphene for upward bending and downward bending, respectively. They are comparable to the polarization change of $\Delta P$, as shown in Fig. 3(d) and 3(f). Based on the experiment results and above discussions, the change of polarization of PLZT and $V_{\text{Dirac}}$ of GFET is mainly caused by the flexoelectric effect of PLZT thin film. Moreover, the good characteristic in flexural fatigue of PLZT thin film, as shown in Fig. S6, provides the stability for the flexible GFET device. These phenomena suggest that the mechanical bending can be used to tune the graphene doping state according to the change of $I_{V_g}$ characteristics ($V_{\text{Dirac}}$), which provide great opportunities for wearable mechanics-electronic sensors and flexible electronic devices, as shown in Fig. 5. By monitoring the change of $I_{V_g}$ characteristics (Dirac point voltage), the curvature variation can be detected (process 1 in Fig. 5), which
can be used in the field of flexible deformation sensor to detect the mechanical movement state, such as the human or robot bending action. On the other hand, we can get specific graphene doping state (Dirac point voltage) that we need through tuning the mechanical bending stress (curvature), which can be used in the flexible GFETs and other flexible electronic devices (process 2 in Fig. 5).

3. Conclusions

In summary, a tunable Dirac point voltage have been achieved in an all-inorganic flexible GFET by mechanical bending stress. The $I_D$-$V_G$ characteristics exhibits a continuous change in the Dirac point voltage under the mechanical strain (both upward and downward bending). It is exciting that the change of Dirac point voltage with the mechanical bending strain is linear resulting from the fact that the flexoelectric effect of ferroelectric PLZT gate generates additional positive (negative) charges at the surface of PLZT thin film with upward (downward) mechanical bending and induces electron-doping (hole-doping) effect into graphene. This provides great opportunities for the wearable mechanical sensors and flexible electric devices requiring a specific doping graphene. What’s more important, the PLZT-gated GFET devices exhibit excellent stability against flexural fatigue with negligible degradation after 1000 bending cycles. Therefore, the flexible all-inorganic GFET device are promising for widely applications in flexible sensing systems.

4. Experimental Method

Fabrication of thin Film

A buffer layer of ~30 nm SrTiO$_3$ (STO) was first epitaxially growth on the F-mica substrate by KrF excimer pulsed laser deposition system with a wavelength 248 nm at 800 °C and 50 mTorr oxygen pressure. On the buffer layer the electrode LSMO (about 45 nm) was epitaxially grown at 700 °C in oxygen atmosphere with a pressure of 50 mTorr. Then, the LSMO/STO double layers were annealed at 700 °C for 15 mins under 400 Torr oxygen atmospheres and cooled down to room temperature at the rate of 5 °C/min. Afterwards, a PLZT thin film was deposited on the LSMO/STO films with a thickness of 500 nm. The PLZT growth condition was selected under an oxygen pressure of 150 mTorr at 650 °C. After the growth, the PLZT thin films were annealed at the growth temperature for 15 min in pure oxygen (350 Torr) and then naturally cooled down to room temperature. The laser energy density was about 2.0 J·cm$^{-2}$ with laser repetition rate of 5 Hz for LSMO and PLZT film and 3 Hz for STO film, respectively.

Graphene Transfer

A layer of Poly-methyl methacrylate (PMMA) was spin-coated on a commercial graphene/Cu sheet with typically 1×1 cm$^2$ in dimension (Muke Nano, Nanjing) and baked in air at 60 °C for 10 mins. Before removing the Cu sheet by immersing the graphene sample into a copper etchant (solution of ammonium persulfate stabilization), it was cut into a small sheet of 0.2×0.6 cm$^2$ in dimension to expose the edge of the copper for etching. The PMMA/graphene was rinsed with deionized (DI) water for multiple times after the copper was fully dissolved. The graphene sample was then transferred onto the PLZT with a pre-fabricated Pt source and drain electrodes and baked in air at 150 °C for one hour to eliminate moisture. The PMMA on graphene was removed by acetone, then the sample was rinsed by isopropyl alcohol to remove residues on the graphene surface.

Characterization

The crystallinity of the PLZT, STO and LSMO thin films was characterized using a high-resolution X-ray diffraction system (HRXRD, PANalytical X’Pert MRD). For measurement of properties, Pt quadrates with 200 µm in length and 70 nm in thickness were deposited on the PLZT samples by sputtering through a shadow mask. The P-E loops were measured by TF Analyzer 2000E with FE-Module at a frequency of 1 kHz. The structure of graphene was characterized by Laser Raman Spectrometer (LabRAM HR Evolution, HORIBA Scientific), and the instrument is equipped with a standard 633 and 532 nm laser. For the electrical transport property measurement in air, a layer of PMMA was casted on the graphene channel for passivation. In addition, vacuum cleaning (≤ 2×10$^{-6}$ Torr) was applied to the GFET samples for further removal of the residues on graphene channel$^{16,29}$. The transport properties of the flexible ferroelectric-gated GFETs were characterized using an Agilent B4155C semiconductor analyzer. Half-cylinders with different diameter were used for the bending measurement.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

G.H., J.W., Z.L., C.M., M.L. and C.-L.J acknowledge the supports by National Science Foundation of China (No. 51702255 and 61631166004) and National “973” projects of China (No. 2015CB654903). M.L and C.M acknowledge the supports by Fundamental Research Funds for the Central Universities and China Postdoctoral Science Foundation (No. 2015M582649). W.L acknowledges the support National Science Foundation of China (No. 61671368). J.Z.W acknowledges support in part by US ARO contract W911NF-16-1-0029, and US NSF contracts NSF-DMR-1337737 and NSF-DMR1508494.

Notes and references

5. L. P. Wu, L. Qin, Y. Zhang, M. Alamri, M. G. Gong, W.

6 C. Ma, R. Lu, G. Hu, J. Han, M. Liu, J. Li, J. Wu, ACS Appl. Mater. Interfaces 2017, 9, 4244-4252.


16 C. Ma, Y. Gong, R. Lu, E. Brown, B. Ma, J. Li, J. Wu, Nanoscale 2015, 7, 18489-18497.


27 F. Ahmadpoor, P. Sharma, Nanoscale 2015, 7, 16555-16570.


The linearly $V_{\text{Dirac}}$ shift of the flexible GFET caused by flexoelectric effect of PLZT gate makes it enormously useful to both tune the graphene doping state and detect bending curvature.
Fig. 1 (a) Fabrication process of the flexible GFET. (b) The Raman spectrum of the graphene transferred on the PLZT thin film gate. (c) The transfer characteristic of PLZT ferroelectric gate GFET, measured with a fixed drain bias $V_D=10$ mV. (d) The transfer conduction ($g_m$) of the PLZT gate GFET corresponding to the $I_D-V_G$ curve in (c).

160x182mm (300 x 300 DPI)
Fig. 2 (a) $I_D$-$V_G$ curves measured under different upward bending state. The inset is a schematic diagram of the structure for measurement. (b) $V_{Dirac}$ obtained from (a). The inset is the schematic diagram of the structure for measurement of transfer characteristics under upward bending state. (c) $V_{Dirac}$ obtained under different downward bending state. The inset is the schematic diagram of the structure for measurement. (d) The $V_{Dirac}$ as function of the cycle number obtained from the $I_D$-$V_G$ characters for the flexible PLZT-gate GFET under 6 mm downward bending radius.
Fig. 3 (a) Typical P-E loops of the PLZT thin film with LSMO bottom electrode and Pt top electrode on F-Mica. (b) Leakage current density of the sample. (c) P-E loops under different upward bending radii at 2 V gate voltage. The inset is schematic of the measurement. (d) $V_c$ and $P_r$ of the loops in (c). (e) P-E loops under different downward bending radii at 2 V gate voltage. The inset is schematic of the measurement. (f) $V_c$ and $P_r$ of the loops in (e).
Fig. 4 (a) Schematic diagram of the curvature-induced polarization in PLZT. (b) The polarization in PLZT when positive $V^+$ and negative $V^-$ are applied on the bottom electrode under upward bending state. (c) The polarization in PLZT when positive $V^+$ and negative $V^-$ are applied on the bottom electrode under upward bending state. (d) Negative charge doping in graphene under the upward bending state. (e) Positive charge doping in graphene under the downward bending state.

160x130mm (300 x 300 DPI)
Fig. 5 Schematic illustration of the flexible mechanics-electronic sensing system for the inorganic PLZT-gated PLZT GFET.

1. Graphene doping state → detect bending curvature
2. Bending curvature → obtain graphene doping state