**Project Title:** **Nanoscale Ferroelectric Control of Novel Electronic States in Layered Two-Dimensional Materials**

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**Principal Investigator:** Dr. Xia Hong, University of Nebraska-Lincoln

**Abstract:**

In this DOE Early Career project "Nanoscale Ferroelectric Control of Novel Electronic States in Layered Two-Dimensional Materials," the PI's group has combined ferroelectric field effect with nanoscale domain imaging and writing to design the electronic and optical properties of two-dimensional (2D) van der Waals materials, including graphene and transition metal dichalcogenides $MoS_2$ and $ReS_2$. The van der Waals materials have been prepared into field effect transistor (FET) devices with ferroelectric gates. Through domain patterning in a ferroelectric polymer PVDF-TrEF top-gate via conductive atomic force microscopy, the team has created programmable Schottky junctions in monolayer $MoS_2$, where both barrier height and *I-V* rectifying polarity can be reconfigured. The transport anisotropy of monolayer to few-layer $ReS_2$ has been mapped out by defining the entire channel into an insulating state and creating nanoscale conducting paths along different directions through domain writing in the ferroelectric top-gate. The result shows that the conductivity along and perpendicular to the Re-chain can differ by $>5.5x10^4$. Theoretical modeling points to the band origin of the transport anomaly and reveals the emergence of a flat band in few-layer $ReS_2$. The interfacial epitaxial relation between $ReS_2$ and PVDF-TrFE further promotes the formation of close-packed, highly ordered PVDF-TrFE nanowires with width of 35 nm and 10 nm. Nonvolatile modulation of quantum Hall effect has been achieved in graphene FETs with a ferroelectric oxide $Ba_{0.4}Sr_{0.6}TiO_3$ back-gate. Scattering from the remote surface optical phonon in $Ba_{0.4}Sr_{0.6}TiO_3$ limits the room temperature mobility of graphene to be about $3x10^4$ $cm^2/Vs$. Steep-slope switching has been achieved in $MoS_2$ FETs back-gated by polycrystalline $Pb(Zr,Ti)O_3$, which signals a static-state negative capacitance mode without involving an additional dielectric layer. Piezoresponse force microscopy studies show that the sub-threshold swing can be well correlated with the domain wall density in $Pb(Zr,Ti)O_3$. The team also observes an unconventional filtering effect of the second harmonic generation response at the $MoS_2/Pb(Zr,Ti)O_3$ heterointerface, which can be accounted for by the alignment between one of the polar axes of $MoS_2$ and the chiral dipole rotation at the surface of domain wall in $Pb(Zr,Ti)O_3$. The research supported by this DOE grant has significantly advanced the fundamental understanding and functional design of ferroelectric/2D van der Waals heterostructures for their implementation towards energy applications.

**Key Words:** van der Waals materials; ferroelectrics; piezoresponse force microscopy; field effect transistors; domain wall; magnetotransport; second harmonic generation

## Final Report

## 1. Scientific Accomplishments

### 1.1 Ferroelectric Field Effect in Monolayer $MoS_2$

We have examined the effect of ferroelectric polarization on the mobility of monolayer (lL) $MoS_2$ field effect transistor (FET) devices sandwiched between a $SiO_2$ bottom-gate and a ferroelectric copolymer poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) top-gate. Employing the conductive probe atomic force microscopy (AFM) approach to control the polarization in P(VDF-TrFE), we have induced reversible modulation of the conduction and transfer characteristics of the $MoS_2$ FET. By modeling the back-gate voltage $V_{bg}$ dependence of the channel conduction, we have identified the critical role of the midgap impurity states in determining the total carrier density $n_{total}$ and free carrier density $n_{free}$ in the channel when the ferroelectric top-gate is uniformly written into the polarization up ($P_{up}$) and down ($P_{down}$) domains. By patterning a ferroelectric domain wall (DW) in the top-gate, we have created programmable Schottky-junction states in the $MoS_2$ channel.

We have also achieved programmable 1L $MoS_2$-metal Schottky junction by contact engineering via local ferroelectric domain patterning. Imposing different domain configurations onto the ferroelectric polymer at the contact area modulates the contact potential between $MoS_2$ and the metal contact (Ti/Au). For symmetric contact domains in the up-poled, $P_{up}$ and $P_{down}$ states, the source-drain current-voltage ($I_{DS}$-$V_{DS}$) characteristics of the device show linear, ohmic behavior. We have achieved nonvolatile modulation of the channel current by a factor of more than 150 times between the $P_{down}$ and $P_{up}$ states of contact doping. In sharp contrast, asymmetric contact doping can lead to programmable junction state in $MoS_2$. Fitting the diode-like $I_{DS}$-$V_{DS}$ relationship to the thermionic emission model yields a room temperature Schottky barrier height $\phi_B^{eff}$ of about 530 meV, while the polarity of current rectification has been reversed by reversing the polarization at both contact areas. This study provides a well-controlled, reconfigurable strategy to design 2D semiconductor diodes with tunable barrier height through the ferroelectric domain patterning.

### 1.2 Exploring Transport Anisotropy in $ReS_2$ via Nanoscale Ferroelectric Domain Gating

We have exploited nanoscale domain patterning combined with ferroelectric field effect to examine the transport anisotropy in layered 2D direct band gap semiconductor 1T'-$ReS_2$. We fabricated lL to few-layer $ReS_2$ FET devices sandwiched by $SiO_2$-backgates and ferroelectric copolymer PVDF-TrFE top-gates. Switching the polarization of PVDF-TrFE has led to a nonvolatile current switching ratio of $>10^7$ in the bilayer $ReS_2$ channel and change the channel from *n*-type to *p*-type. We have then polarized the entire channel to the highly insulating, depletion state, and written nanowires along different orientations to define directional conducting paths. The sample shows highly anisotropic transport along and perpendicular to the Re chain (*b*-axis), with the conductivity difference exceeding $5.5 \times 10^4$ in the 1L sample. The observation can be well explained by the band anisotropy combined with the anisotropic electron-phonon scattering, as revealed by density functional theory calculations.

### 1.3 Formation of Ordered Crystalline PVDF-TrFE Nanowires on $ReS_2$

We prepared 1 to 9 monolayers (1-9L) of PVDF-TrFE films on $ReS_2$ via the Langmuir–Blodgett (LB) method. Upon thermal annealing, the samples transition to thin films of close-packed, single crystalline nanowires (P-NWs) with 10 nm and 35 nm width that are aligned perpendicular to the *b*-axis of $ReS_2$. *In situ* AFM measurements show that the transition occurs in two stages. The initially uniform, unstructured film first becomes textured with short segments at moderate temperature, which then rotate and merge to form longer, well ordered P-NWs when the sample is heated close to the melting temperature. Compared with conventional PVDF-TrFE films prepared using LB and spin-coating methods, which are polymorphous, the P-NWs are single crystalline with the polar axis aligned to the out-of-plane direction. As a result, the switching voltage can be as low as 0.1 V, corresponding to a coercive field of $E_c$ ~0.01 V/nm, which is orders of magnitude lower than that of LB films ($E_c$ ~0.5 V/nm). Our study thus solves a major material limitation, *i.e.*, high switching voltage, for the ferroelectric polymer for low power nanoelectronic applications.

### 1.4 Domain Wall Facilitated Steep-Slope Switching in $MoS_2$ Transistors

A negative capacitance (NC) FET takes advantages of the negative curvature in the free energy profile of a ferroelectric gate to achieve steep slope switching in a semiconductor channel that transcends the 60 mV/dec classic Boltzmann limit for the sub-threshold swing (*SS*), which shows great potential for developing energy efficient logic applications that can outperform the conventional information technology. Previous studies have focused on the ferroelectric/dielectric stack gate to stabilize the NC mode, which involves high switching field close to $E_c$ and possible existence of hysteresis. We have demonstrated that steep slope switching can be realized in bilayer and few-layer $MoS_2$ FETs gated by a single layer polycrystalline $PbZr_{0.35}Ti_{0.65}O_3$ film, with current switching ratio of $>10^6$ achieved within a record low gate voltage ($V_g$) range of ±0.25 V and a minimum *SS* ($SS_{min}$) as low as 9.7 mV/dec at room temperature. This effect can be attributed to the high density of DWs hosted in the polycrystalline film, as characterized by piezoresponse force microscopy. We have investigated a series of bilayer $MoS_2$ FETs with progressively higher gate voltage $V_g$ sweeping range below $E_c$ and found that $SS_{min}$ increases with increasing $V_g$ range, which can be well correlated with the diminishing DW density, clearly ruling out the contribution of polarization switching to the steep slope switching. Theoretical modeling shows that poling the metastable polar states within the DW can yield a *SS* that is in quantitative agreement with the experimental data at a field well below $E_c$. Our study thus provides a simple yet effective material strategy for achieving quasi-static NC mode at substantially lower electric field that is promising for hysteresis-free operation.

### 1.5 Effect of Remote Surface Optical Phonon Scattering in Ferroelectric-Gated Graphene

We have investigated the effect of remote surface optical phonon (RSO) scattering on the high temperature transport properties of 1L graphene gated by ferroelectric $Ba_{0.6}Sr_{0.4}TiO_3$ (BSTO) thin films. The graphene FETs exhibit high field effect mobility up to $\mu_{FE}$ ~23,000 $cm^2$/Vs. Switching the polarization of BSTO yields nonvolatile hysteresis in the resistance state and quantum Hall effect. The BSTO films possess high dielectric constant, with $\kappa$ varies from 60 to 140 depending on temperature, which allows for highly efficient electron/hole doping. We have examined the temperature dependence of the sheet resistance ($R_s$) at a wide range of carrier density and fitted the data considering the scattering from the charge impurity, intrinsic longitudinal acoustic phonon of graphene, and RSO phonon modes from BSTO. The *T*-dependence of $R_s$ at a wide range of sheet charge densities ($n_s$) can be well described by considering dominant RSO phonon mode at 35.8 meV from the interface with BSTO, which imposes a room temperature mobility limit of about 30,000 $cm^2$/Vs for graphene. Our result can be used to assess the high temperature mobility limit in graphene imposed by a ferroelectric oxide gate, thus relevant to developing room temperature electronic applications based on ferroelectric-gated 2D materials.

### 1.6 Probing Ferroelectric/$MoS_2$ Interfacial Polar Coupling via Second Harmonic Generation

Like the ferroelectrics, monolayer transition metal dichalcogenides such as $MoS_2$ are non-centrosymmetric and possess polar axes. We have exploited the second harmonic generation (SHG) technique to probe such polar symmetry coupling at the interface between 1L $MoS_2$ and ferroelectric $Pb(Zr,Ti)O_3$. We have created a series of square domain structures with opposite polarization directions on

50 nm epitaxial $Pb(Zr,Ti)O_3$ thin films and transferred mechanically exfoliated 1L $MoS_2$ flakes on top, with the zigzag axis aligned with the horizontal DWs. The heterostructure exhibits either strong enhancement or substantial quenching of the reflected SHG response at the horizontal DWs. In sharp contrast, no appreciable SHG contrast has been observed at the vertical DW. Theoretical modeling shows that the unconventional light filtering effect originates from the polar coupling between the chiral rotation of the surface dipole at the DWs and one of the polar axis of $MoS_2$. Our study points to a new strategy for designing nanoscale electrically programmable optical applications.

## 2. Products and Dissemination

The results have been disseminated through journal publications, conference presentations, and research seminars. Our efforts have resulted in 17 journal publications and 1 Ph.D. dissertation. Below is a detailed publication list.

1. Jingfeng Song, Yubo Qi, Zhiyong Xiao, Seung-Hyun Kim, Angus. I. Kingon, Andrew M. Rappe, and Xia Hong*, "Domain Wall Enabled Hysteresis-Free Steep Slope Switching in $MoS_2$ Transistors", *npj 2D Materials and Applications* **6**, 77 (2002).
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**3. Opportunities for Training and Professional Development**

Two postdoctoral researchers and six graduate students (one female) have worked on this project. They have been trained on the state-of-the-art research facility and have carried out nanolithography, structural and surface characterizations, electrical characterizations, scanning probe microscopy/spectroscopy, optical microscopy/spectroscopy, and magnetotransport measurements. They have also developed skills in data analysis, scientific communication, paper writing, and presentation, which are essential for their career development.

Six undergraduate students (two females, one minority) have participated in this project. They have been teamed with the graduate students in the research group. These experiences motivate the undergraduate students to pursue a science/engineering career. The teamwork also helps the graduate students to develop skills in leadership and mentorship.