Threshold voltage modulation in monolayer MoS₂ field-effect transistors via selective gallium ion beam irradiation

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ABSTRACT Electronic regulation of two-dimensional (2D) transition metal dichalcogenides (TMDCs) is a crucial step towards next-generation optoelectronics and electronics. Here, we demonstrate controllable and selective-area defect engineering in 2D molybdenum disulfide (MoS₂) using a focused ion beam with a low-energy gallium ion (Ga⁺) source. We find that the surface defects of MoS₂ can be tuned by the precise control of ion energy and dose. Furthermore, the field-effect transistors based on the monolayer MoS₂ show a significant threshold voltage modulation over 70 V after Ga⁺ irradiation. First-principles calculations reveal that the Ga impurities in the monolayer MoS₂ introduce a defect state near the Fermi level, leading to a shallow acceptor level of 0.25 eV above the valence band maximum. This defect engineering strategy enables direct writing of complex pattern at the atomic length scale in a controlled and facile manner, tailoring the electronic properties of 2D TMDCs for novel devices.

Keywords: two-dimensional transition metal dichalcogenides, field-effect transistors, defect engineering, Ga ion irradiation

INTRODUCTION

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDCs), such as molybdenum disulfide (MoS₂), are considered key candidates for next-generation optoelectronics and electronics owing to their atomically thin dimensions that can mitigate short-channel effects, layer-dependent bandgap and intriguing carrier transport properties [1–3]. Despite the promises, large variations in threshold voltages (V_{th}) for 2D TMDC field-effect transistors (FETs) hinder their implementation in future electronic devices [4–8]. The V_{th} variations of 2D FETs originate from the gate voltage induced by the alignment of energy states in the 2D channel with the Fermi level of the source/drain electrodes [9,10]. Therefore, reliable and controllable engineering of energy states in ultrathin 2D

TMDC FETs is necessary to tailor their V_{th} to a desired level [11]. Recent studies have demonstrated the V_{th} modulation of 2D TMDC FETs via a variety of approaches, which include (i) introducing interfacial dipoles [12–14], (ii) surface functionalization [15], and molecular doping [16]. But their limited tunability and incompatibility with high-temperature annealing process greatly hinder their practical applications. Among those approaches, ion implantation with the highest maturity level in conventional semiconductors (e.g., Si and III–V groups) stands out over other methods in terms of reliability, controllability, and site selectivity [17,18]. However, ion implantation applied to the emerging 2D materials has been a challenging issue. Undesirable side effects caused by structural transition from crystalline to amorphous or even etching of the entire film can readily occur as the dose increases, presenting challenges in the precise control of defects, especially for monolayer and few-layer TMDCs.

Encouraged by the efforts on the modelling of ion irradiation in graphene, along with our previous work on TMDC growth and surface engineering [5,19–22], we propose the optimization of the irradiation energy as well as the search for effective dopants, which hold great potential to address the above issues. It is well established that the ion irradiation power and time are the key factors to decouple the effects between chemical etching and defect states generation. However, low-energy ion irradiation for defects engineering of 2D TMDCs remains challenging, particularly for monolayers. In this work, we present a controllable and effective V_{th} modulation scheme for monolayer MoS₂ by using a focused ion beam (FIB) with low-energy gallium (Ga) source. First-principles calculations confirm that substitutional Ga atoms replace S atoms in MoS₂, achieving a shallow acceptor level at 0.25 eV above the valence band maximum (VBM). Importantly, we precisely tune the defect density in the monolayer MoS₂, resulting in a large threshold voltage modulation in the FET over 70 V. In addition, the FIB enables direct writing of spatially desired patterns with high resolution

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in atomically thin MoS₂ in a mask-free and resist-free manner.

EXPERIMENTAL AND THEORETICAL METHODS

Samples preparation

High-quality MoS₂ crystals purchased from HQ graphene were exfoliated onto SiO₂/Si substrates (300 nm SiO₂ and 500 μm p⁺⁺ Si). The ion beam irradiation of Ga was carried out in a dual beam FIB/FEI Helios NanoLab 450S. The MoS₂-substrate mounted on the sample stage was loaded to the FIB system. When the chamber was pumped down to 5×10^{-7} mbar (1 mbar = 100 Pa), a beam with the current of 12 pA, acceleration voltage of 1 keV and dwell time ranging from 2 to 60 s was used, creating a series of Ga⁺ dose variations.

Characterizations

The thickness of MoS₂ samples were determined by the optical microscopy, atomic force microscopy (AFM) and Raman characterizations. Optical images were captured with a Leica DM750M microscope. AFM images were captured with a Park NX200 model in tapping mode. And X-ray photoelectron microscopy (XPS) measurements were performed in a VG ESCALAB 220i-XL system using a monochromatic Al Kα source at the pass energy of 10 eV for high measurement resolution. Raman characterizations were obtained by using a Thermo Scientific DXR confocal Raman system with a 514 nm laser excitation. The laser power was kept below 1 mW to avoid any heating damage to the sample. The Si Raman peak at 520.7 cm⁻¹ was used to calibrate the Raman and photoluminescence (PL) signal. The elemental mapping was obtained by using time-of-flight secondary ion mass spectrometry (TOF SIMS) (ION-TOF GmbH, Muenster, Germany), equipped with a liquid metal ion gun at an angle of 45° to the surface normal and using an ion-beam with kinetic energy of 25 keV. Few-layered MoS₂ flakes were used in SIMS characterization.

Device fabrication

Back-gated MoS₂ FETs were fabricated by a standard fabrication process of 2D material FETs. Electron beam lithography, followed by electron beam evaporation and a lift-off process were used to define the source and drain contacts. Ti/Au was used as the contact metal, following the same metallization process for MoS₂ FET devices [21]. Electrical measurements were carried out in a vacuum probe station. Prior to the electrical measurement, vacuum annealing of the devices at 200°C for 2 h was carried out to remove surface contamination and improve the contact properties.

Calculations

The geometric and electronic properties of the pristine MoS₂ and Ga-doped MoS₂ were evaluated using first-principles calculations by employing the Vienna *ab initio* simulation package (VASP) [23,24]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was applied to the density functional theory (DFT) analysis [25]. The electron wave functions were expanded in plane waves with a cutoff energy of 500 eV. A 6 × 6 supercell containing 108 atoms was employed. In order to avoid interlayer interactions, the distance between monolayers was set to be larger than 20 Å. A 5 × 5 × 1 Monkhorst-Pack *k*-point mesh was used to calculate the Brillouin zone integration [26]. Good convergence was obtained with these parameters, and the

total energy was converged to 1.0×10^{-5} eV per atom. To further explore the Ga concentration-dependent band structure, we increase the number of Ga adatoms which substitute S atoms (denoted as Ga_S) in the supercell model. Note that we denote the one, two, and three Ga_S defects in each 108-atom supercell model as 1Ga_S, 2Ga_S, and 3Ga_S, corresponding to the Ga concentration of ~1%, 2%, and 3%, respectively. As a benchmark, the electronic properties of the pristine MoS₂ monolayer were also reproduced.

RESULTS AND DISCUSSION

In a typical experimental procedure of FIB irradiation on MoS₂ samples, the Ga⁺ ion source is accelerated and directly focused onto the monolayer and few-layer MoS₂ samples at room temperature as schematically depicted in Fig. 1a. The Ga FIB systems can deliver currents ranging from tens of nanoamperes down to tens of picoamperes with a spot size on the order of a few nanometers, which allows us to achieve a desired doping density with minimum surface damage. At a low implant energy of 1 keV, an exposure time of 10 s and a current of 12 pA, the Ga⁺ exhibits an ultra-shallow diffusion depth of ~2 nm, highlighting the potential of the FIB for controlled doping of atomically thin 2D TMDCs (Fig. 1b). According to the SIMS results, when the applied irradiation energy increases from 1 to 5 keV, the diffusion depth increases dramatically from 2 to 8 nm (Fig. 1c), accompanied by partial surface etching (Fig. S1). Therefore, for monolayer MoS₂, an implant energy of 1 keV was used to avoid over doping or even etching of the 2D materials. Furthermore, the Ga⁺ FIB enables the direct writing of spatially complex doping pattern with high resolution. By using the imaging function of the FIB system, the Ga⁺ can be positioned to the designed regions and thus it can be used to draw sophisticated patterns with nanoscale precision. As shown in Fig. 1d, e, the gallium ions were selectively implanted into MoS₂, spatially defining the 100th anniversary logo of Xiamen University. High-resolution SIMS elemental mapping was used to identify the patterns. The SIMS signal of Ga⁺ shows a uniform distribution of the logo pattern drawn by the Ga⁺ FIB with beam energy of 2 keV for 120 s. The reduced intensity of Mo in the elemental mapping suggests the slight etching of the MoS₂ layer after Ga FIB irradiation (Fig. 1d). By decreasing the Ga⁺ implantation time, the SIMS mapping of Mo signal shows negligible change before and after implantation, revealing that the etching effect is almost eliminated (Fig. 1e). In our SIMS mapping, a minimum line width of ~1 μm can be clearly defined from the logo pattern, indicating the ability of high spatial resolution.

In order to achieve a controllable and quantifiable defect density, the ion beam was rastered over the monolayer MoS₂ surface. The ion dose concentration (σ) was calculated as $\sigma = I \times t / (Ae)$, where *t* is the exposure time, *I* is the ion current and *A* is the rastered area. A series of implantation experiments with a dose concentration between 1×10^{11} and 1×10^{14} Ga⁺ cm⁻² were performed by varying *t* and *A* (see Table S1 for the dosage parameters). As a high-throughput and non-destructive technique, Raman spectroscopy was used to probe the structural disorder and charge doping effect after Ga⁺ implantation in MoS₂. The Raman spectra of the monolayer MoS₂ were characterized by two prominent peaks, namely, in-plane E_{2g}¹ and out-of-plane A_{1g} phonon modes. Fig. 2a shows the Raman spectra of the exfoliated MoS₂ flakes on SiO₂/Si substrate under different concentrations of Ga ions. The bottom spectrum in Fig. 2a

Figure 1 (a) Schematic diagram of the gallium ion implantation system. (b) SIMS depth profile of Ga, Mo in MoS₂ layer using 1 keV gallium ions for 10 s. (c) Dependence of ion diffusion depth in MoS₂ on the irradiation energy. Selective Ga-implanted pattern (the 100th anniversary logo of Xiamen University) mapped by TOF SIMS signal for gallium 69 and Mo 98 with 2 keV gallium ions for 120 s (d) and 50 s (e).

Figure 2 (a) Raman spectra of the monolayer MoS₂ at different dose concentrations. The spectrum of the pristine monolayer MoS₂ is presented for comparison. The unit for the dose concentration is Ga⁺ cm⁻². (b) The relationship between Ga⁺ dose concentration and the Raman shift for E_{2g}¹ and A_{1g} phonon modes extracted from (a). (c) Optical microscopy image (left) and the corresponding AFM image (right) of the monolayer MoS₂ flake. AFM step profile before (left) and after (right) Ga ion implantation. XPS spectra for (d) Ga 2p, (e) Mo 3d and (f) S 2p of MoS₂ with various Ga implantation doses.

represents the Raman spectrum of the pristine MoS₂ for comparison. The peak separation between E_{2g}¹ and A_{1g} phonon modes for the pristine MoS₂ is 17.8 cm⁻¹, which is consistent with the reported exfoliated monolayer MoS₂ [27]. Notably, as shown in Fig. 2b, the Raman spectrum gradually evolves as a function of σ . This evolution involves the red shift in the frequency of E_{2g}¹ phonon, and blue shift in that of A_{1g} phonon. According to previous report, E_{2g}¹ peak is a structural indicator that is closely related to the defect induced by lattice distortions, while A_{1g} phonon is very sensitive to the electron level due to strong electron-phonon coupling of the A_{1g} mode [28–30]. Therefore, the blue shift in the E_{2g}¹ phonon mode with respect to the pristine MoS₂ indicates that compressive strain is introduced after Ga ion implantation. A similar effect of compressive strain has been observed in the nitrogen doping of MoS₂ [31]. Apart from the strain effect, the charge effect induced by ion implantation is reflected in the evolution of A_{1g} phonon modes. The increase in σ leads to a gradual blue shift in the frequency of A_{1g} phonon modes (Fig. 2b) of MoS₂ by Ga⁺ implantation. Furthermore, the radiation damage caused by the Ga implantation was examined by AFM (Fig. 2c and Fig. S2), with a slight decrease in MoS₂ thickness before and after implantation at $\sigma = 1.5 \times 10^{13}$ Ga⁺ cm⁻². Meanwhile, its thickness remains unchanged when the dose concentration reduces to 9.0×10^{12} Ga⁺ cm⁻². This confirms that the observed Raman peak shift is a result of defect engineering instead of surface etching.

The effect of the Ga irradiation on the electronic structure and surface chemistry of monolayer MoS₂ was validated by XPS (Fig. 2d–f). At the dose of $\sigma = 1.5 \times 10^{12}$ Ga⁺ cm⁻², the doublets located at binding energies (BEs) of 1118.3 and 1144.8 eV corresponding to Ga 2p_{1/2} and Ga 2p_{3/2}, respectively, were observed in the Ga 2p region, indicating the presence of Ga in MoS₂ (Fig. 2d). Notably, in the Ga-irradiated MoS₂, the BE of Ga 2p_{3/2} peak is higher than that at the elemental state (~1116.7 eV). This suggests that the chemical state of Ga in MoS₂ is at its oxidation state, implying the formation of chemical bonds between Ga and MoS₂. The Mo 3d and S 2p peaks from the pristine MoS₂ with different Ga doses are shown in Fig. 2e, f, respectively. For the pristine MoS₂, the Mo 3d spectrum contains one main doublet at the BE of 230.0 eV with 3d_{5/2}:3d_{3/2} ratio of 0.6 and a spin-orbit

splitting of 3.1 eV associated with Mo⁴⁺ in a sulfur environment [32]. In S 2p spectrum of the pristine MoS₂, the doublets present at the BEs of 163.8 eV (S 2p_{1/2}) and 162.6 eV (S 2p_{3/2}), respectively, as expected for divalent sulphide species in MoS₂. After exposure to Ga⁺ irradiation, the core level peaks of Mo 3d and S 2p show a downshift in the BEs (Fig. 2e, f) with respect to the pristine MoS₂, implying that the Fermi level shifts towards the valance band edge [5,9,32]. Additionally, the full width at half-maximum of both Mo 3d and S 2p peaks increases after Ga ion irradiation, indicating that the increased bond diversity is generated at the MoS₂ surface. The stoichiometry of MoS₂ with respect to the Ga⁺ dose is shown in Fig. S3. Prior to Ga⁺ irradiation, the stoichiometry of MoS₂ appears at ~1.98 (S/Mo) as determined by XPS, representing MoS₂ lattice with intrinsic sulfur deficiency [33,34]. Subsequently, the ratio decreases gradually with the increase of σ . The transition suggests the preferential removal of sulfur atoms from MoS₂ due to the lower formation energy of sulfur vacancies and the low implantation energy.

To further investigate the Ga irradiation effect on the electrical properties of the MoS₂, back-gated monolayer MoS₂ FETs were fabricated. The post treatment of Ga⁺ irradiation was carried out upon the as-fabricated MoS₂ FETs, so that the MoS₂ layer underneath the contact region remains intrinsic and only the channel region is exposed to Ga⁺ irradiation. This can rule out the influence of the contact resistance and enable us to investigate the evolutions of the electrical properties of the channel region irradiated by Ga⁺. Indeed, the contact resistance remains almost unchanged before and after irradiation (Fig. S4). The devices were measured in high vacuum (~1 × 10⁻⁵ Torr, 1 Torr = 133.3 Pa) in order to reduce the hysteresis. Fig. 3a shows the transfer characteristics of the FET devices with increasing dose concentration. For each dose concentration, four MoS₂ FET devices were measured and their transfer curves are shown in Fig. S5. Here the back-gate voltages were scanned from ON state to OFF state at a fixed positive drain voltage in all measurements. As a result, the extraction of threshold voltage (V_{th}) is immune to the hysteresis effect. And thus the comparisons are reasonable. As expected, the pristine MoS₂ FET exhibits strong electron conduction with a negative V_{th} and a high on/off ratio

Figure 3 (a) Transfer characteristics of the MoS₂ and Ga-doped MoS₂ FET at various Ga⁺ dose concentrations. (b) Dose concentration dependence of the FET's threshold voltage (V_{th}) extracted at a drain current of 1 nA. The inset in (b) shows the optical image of the FET device.

($\sim 10^5$) due to the intrinsic sulfur vacancies which act as electron donors [35]. However, we observe a positive V_{th} shift towards higher gate voltage together with a slight reduction in the ON-state current after Ga^+ irradiation. The decrease in the ON-state current with the Ga^+ implantation can be attributed to enhanced scattering due to the presence of Ga. The change of V_{th} , on/off ratio, subthreshold swing (SS) and mobility with respect to σ are summarized in Fig. 3b and Fig. S6. Specifically, the V_{th} gradually increases from -39 V in the pristine MoS_2 FET to 32.9 V (over 70 V) in the Ga^+ -implanted MoS_2 FET at $\sigma = 9.0 \times 10^{12} Ga^+ cm^{-2}$. The positive shift of the threshold voltage indicates that there is a lower electron density in the semiconductor channels with Ga^+ irradiation. A relatively high on/off ratio of 1.0×10^5 has been maintained at the high dose concentration, which indicates a good gate modulation of the channel (Fig. S5a). At $\sigma = 1.5 \times 10^{13} Ga^+ cm^{-2}$, the on/off ratio of MoS_2 FET degrades to less than 10 at 60 V gate voltage due to surface etching of the monolayer MoS_2 (Fig. S7).

The SS values of MoS_2 FETs are positively correlated with the dose concentration due to the increased defect density by Ga^+ ions (Fig. S6b). Moreover, the field-effect mobility for electrons of the Ga^+ -implanted FET at a low supply voltage of 0.5 V was calculated using $\mu = g_m L / (W V_{DS} C_{OX})$, where L is the channel length, W is the channel width, C_{OX} is the dielectric capacitance per unit area, and g_m is the transconductance. As shown in Fig. S6c, the mobility deteriorates with increasing dose concentration, indicating that there is a trade-off between the mobility and V_{th} modulation. Post implantation annealing of MoS_2 FETs in sulfur atmosphere may recover the mobility. Note that the p-type conduction behavior is not observed after the Ga^+ irradiation. The n type conversion and the mobility degra-

dation after the Ga^+ irradiation may be ascribed to the Fermi level pinning due to the increased defect density.

To shed light on the underlying mechanism of Ga implantation, DFT calculations were further performed to explore the electronic properties of the Ga-implanted MoS_2 (Fig. 4). In order to suppress the interaction between adjacent defects, we expanded the unit cell to a $6 \times 6 \times 1$ supercell with 36 Mo and 72 S atoms for defect formation calculations. We considered four possible Ga-related defect configurations, namely one Ga_S defect (Ga adatom in S vacancies), two Ga_S defects, three Ga_S defects and one Ga_{Mo} defect (one Ga adatom in Mo vacancies) (Fig. S8). We calculated the formation energies for different defect configurations by using

$$E_f = E_{doped} - E_{pure} - n_{Ga}\mu_{Ga} + n_{Mo}\mu_{Mo} + n_S\mu_S,$$

where E_{doped} is the total energy of the Ga-implanted MoS_2 , and E_{pure} is the total energy of the pure MoS_2 supercell. μ_{Mo} , μ_{Ga} , μ_S are chemical potentials for the Mo atom, Ga atom and S atom, respectively. n_{Ga} , n_{Mo} and n_S represent the number of Ga, Mo and S atoms in the superlattice, respectively. The formation energies are presented in Fig. S9. It should be noted that, the Ga irradiation experiment was conducted under S-poor condition. Obviously, the substitution of Ga at the S site (Ga_S) has the lowest formation energy among the four possible defects (Fig. S9). Therefore, the formation of Ga_S defects is the most energetically favorable and stable.

In order to reveal the origin of the V_{th} shift, we calculated the Ga-concentration-dependent band structure. For the pristine MoS_2 , no impurity states exist in the bandgap, and the bandgap is calculated to be 1.67 eV (Fig. 4a). For the MoS_2 with one Ga_S , the bandgap of MoS_2 was measured to be about 1.70 eV, almost

Figure 4 Band structures and the corresponding density of states of (a) the pristine MoS_2 and MoS_2 doped with (b) one Ga, (c) two Ga and (d) three Ga atoms. Asterisk (*) denotes shallow acceptor levels in monolayer Ga- MoS_2 , with an energy level of 0.25 eV above VBM.

the same as that of the pristine MoS₂. However, there are three new impurity states in the bandgap with the Fermi level passing through these impurity states. Furthermore, the energy distances between these impurity states and the VBM were further calculated to be 0.29, 0.44, and 0.98 eV, respectively. Therefore, Ga_s tends to form the multi-level impurity with one shallow acceptor level of 0.29 eV above the VBM in the monolayer MoS₂ and two deep levels. Furthermore, by increasing the Ga concentration in MoS₂, more impurity states appear in the bandgap of the monolayer MoS₂, with the lowest impurity state decreasing to 0.25 eV above the VBM. Density of states (DOS) and partial density of states (PDOS, Fig. 4 and Fig. S10) further reveal that the lower impurity state originates mainly from the hybridization of Ga 4p and Mo 4d orbitals, while the higher impurity state originates mainly from Ga 4p, Ga 4s and Mo 4d orbitals.

CONCLUSIONS

In summary, a controllable threshold voltage modulation of 2D MoS₂ FETs was demonstrated by selective-area ion irradiation with low-energy gallium. Surface damage can be eliminated by reducing the implantation energy and dose concentration, which is critical for the defect engineering of atomically thin 2D semiconductors. Both Raman and XPS characterizations show that the gallium atoms act as dopant defects in MoS₂. Further electrical characterization of the FETs based on monolayer MoS₂ reveals that a significant modulation of the threshold voltage can be achieved by Ga⁺ irradiation. First-principles calculations attribute the effective threshold voltage modulation to the substitutional replacement of sulfur atoms with gallium atoms, resulting in a shallow acceptor level at 0.25 eV above the VBM. The gallium ion irradiation technique can be adopted for the direct writing of complex patterns in 2D semiconductors, presenting a promising strategy for tailoring the electronic properties of 2D semiconductors for novel devices.

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Author contributions Tang B and Yang W conceived the concept and designed the experiments. Tang B and Leong JF performed the device fabrication, optimizations and characterizations. Tang B, Zhao Y and Yang W together analyzed the data, wrote and revised the manuscript. Zhou C and Zhu H designed and performed the DFT calculations. Zhang M and Shuai H contributed to the SIMS and FIB analyses. All authors were involved in the data analysis and discussion. All authors have given approval to the final version of the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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通过镓离子束辐照调控单层MoS₂晶体管的阈值电压

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摘要 对原子层厚度二维(2D)过渡金属硫化物(TMDCs)电子属性的调控是实现其新型光电和电子器件应用的关键。本文采用聚焦低能量镓离子束辐照超薄二硫化钼, 通过缺陷工程实现了原子层级的位点缺陷调控。研究发现二硫化钼表面缺陷可以通过精确控制镓离子束的能量和剂量来实现低损伤的镓掺杂。此外, 在镓离子注入后, 单层二硫化钼晶体管的阈值电压实现了超过70 V的迁移。第一性原理计算证实镓杂质离子在单层二硫化钼的费米能级附近引入一个位于价带顶0.25 eV的浅缺陷能级。这种可控和便捷的缺陷工程方法实现了原子层深度的复杂图样区域性掺杂, 进而调控超薄二维半导体的电学性能, 为实现高性能的新一代光电和电子器件奠定了基础。