Irradiation Effects of High-Energy Proton Beams on MoS₂ Field Effect Transistors

Tae-Young Kim,[†] Kyungjune Cho,[†] Woanseo Park,[†] Juhun Park,[†] Younggul Song,[†] Seunghun Hong,^{†,‡} Woong-Ki Hong,[§] and Takhee Lee^{†,*}

[†]Department of Physics and Astronomy and Institute of Applied Physics, Seoul National University, Seoul 151-747, Korea, [‡]Department of Biophysics and Chemical Biology, Seoul National University, Seoul 151-747, Korea, and [§]Jeonju Center, Korea Basic Science Institute, Jeonju, Jeollabuk-do 561-180, Korea

ABSTRACT We investigated the effect of irradiation on molybdenum disulfide (MoS₂) field effect transistors with 10 MeV high-energy proton beams. The electrical characteristics of the devices were measured before and after proton irradiation with fluence conditions of 10^{12} , 10^{13} , and 10^{14} cm⁻². For a low proton beam fluence condition of 10^{12} cm⁻², the electrical properties of the devices were nearly unchanged in response to proton irradiation. In contrast, for proton beam fluence conditions of 10^{13} or 10^{14} cm⁻², the current level and conductance of the devices significantly decreased following proton irradiation. The electrical changes



originated from proton-irradiation-induced traps, including positive oxide-charge traps in the SiO₂ layer and trap states at the interface between the MoS₂ channel and the SiO₂ layer. Our study will enhance the understanding of the influence of high-energy particles on MoS₂-based nanoelectronic devices.

KEYWORDS: molybdenum disulfide (MoS₂) · field effect transistors · proton beam · electronic transport properties

ecently, two-dimensional (2D) transition-metal dichalcogenide (TMD) materials have gained significant attention due to their potential applications in atomic-film devices.^{1–4} Graphene, one of the most popular of these 2D materials, has been widely studied but has limited utility as a semiconductor because it lacks an energy band gap.⁵ Unlike graphene, TMD materials such as MoS₂, MoSe₂, and WSe₂ possess a band gap and semiconducting properties.⁶⁻⁸ In particular, molybdenum disulfide (MoS₂) has an indirect band gap of 1.2 eV as a bulk material and a direct band gap of 1.8 eV as a single layer.^{4,8} Numerous studies have explored the application of 2D TMD materials in nanoelectronic devices because of their semiconducting properties.^{9–14} For example, researchers have demonstrated that MoS₂based field effect transistor (FET) devices have outstanding electrical characteristics; a single-layer MoS₂ device exhibits a high mobility (\sim 200 cm²/(V s)) with a near-ideal subthreshold swing down to 74 mV/decade and a high on/off ratio ($\sim 10^8$).¹⁵

The ability to tailor the electrical properties of MoS₂ FETs would provide numerous advantages. In particular, to prepare a logic circuit using MoS₂, it is necessary to control the operation voltage. When trap states are introduced at the MoS₂ active layer and dielectric layer, the electrical properties of the device, such as the current and threshold voltage, are affected by charge trapping to these trap states. Attempts to tailor the electrical properties of FET devices made with carbon nanotubes^{16,17} or semiconducting nanowires¹⁸⁻²⁰ have been made using irradiation with high-energy particles. Originally, high-energy particle beams of protons, electrons, or ions were used to impact siliconbased metal-oxide-semiconductor (MOS) devices in order to modify the electrical properties of the devices or investigate the properties under outer space conditions.^{21–24}

A few theoretical and experimental studies have investigated the irradiation of MoS_2 materials with electrons, protons, or heavy ions. Komsa *et al.* studied the effects of electron beam irradiation on 2D

* Address correspondence to tlee@snu.ac.kr.

Received for review December 18, 2013 and accepted February 23, 2014.

Published online February 24, 2014 10.1021/nn4064924

© 2014 American Chemical Society

VOL.8 • NO.3 • 2774-2781 • 2014



TMD materials using first-principle simulations and experimental studies of single-layer MoS_2 devices irradiated by electron beams in a transmission electron microscope (TEM) operating at 20 keV.²⁵ Ochedowski *et al.* demonstrated the deterioration of MoS_2 FETs following 1.14 GeV U²⁸⁺ ion beam irradiation,²⁶ and Mathew *et al.* studied ferromagnetism in MoS_2 bulk materials following 2 MeV proton beam irradiation.²⁷ However, a comprehensive study of high-energy particle beams on MoS_2 atomic film-based FET devices has not yet been investigated. Therefore, it would be important to understand and develop irradiationmediated engineering in MoS_2 FET devices.

Here, we studied the effect of proton irradiation on MoS_2 FET devices prepared with a few layers of MoS_2 flakes. The devices were irradiated with 10 MeV proton beams under fluence conditions of 10^{12} , 10^{13} , and 10^{14} cm⁻², corresponding to beam irradiation times of 20, 200, and 2000 s, respectively. We systematically measured and compared the electrical properties of the devices, including current level, conductance, and threshold voltage, before and after proton irradiation for each proton beam fluence condition. The changes in the electrical properties of the proton-irradiated devices can be attributed to irradiation-induced traps, such as positive oxide-charge traps in the SiO₂ layer and interface trap states.

RESULTS AND DISCUSSION

We fabricated MoS_2 FET devices using the following process. First, we transferred MoS_2 flakes from a bulk MoS_2 crystal (purchased from SPI Supplies, USA) onto Si wafer pieces using a mechanical exfoliation method. The Si substrate used in this study had a 270-nm-thick SiO_2 layer on highly doped Si and could be used as a gate electrode. Following the mechanical transfer of the MoS_2 flakes, suitable MoS_2 flakes were located with an optical microscope (Figure 1a). Although it was possible to transfer single-layer MoS_2 films, we more routinely transferred multilayer MoS_2 films comprising a few MoS_2 atomic layers. The thickness of the typically selected MoS_2 flakes was approximately 2–8 nm, as determined by atomic force microscopy (AFM) (Park Systems, NX10) (Figure 1c). Because the thickness of a single MoS_2 layer is 0.65 nm, this flake thickness corresponds to 3–12 layers. After the locations and coordinates of the MoS_2 flake were determined with an electron-beam lithography system, source and drain electrodes were made by depositing Au (100 nm)/Ti (10 nm) with an electron beam evaporator. More detailed information describing the device fabrication is provided in Figure S1 of the Supporting Information.

Following the fabrication of the MoS₂ FET devices, their electrical characteristics were measured. The devices were subsequently irradiated by a proton beam. The proton beam facility used for this research was the MC-50 cyclotron at the Korea Institute of Radiological and Medical Sciences. The proton beam exhibited an energy of 10 MeV, an average beam current of 10 nA, and a beam uniformity of approximately 90%. Beam irradiation times of 20, 200, and 2000 s were investigated, corresponding to total fluence (or dose) values, Φ , of $\sim 10^{12}$, 10^{13} , and 10^{14} cm⁻². The fabricated MoS₂ FET devices were divided into three groups according to the proton beam fluence conditions. The electrical characteristics of each device were measured before and after proton irradiation and systematically compared.

Figure 2 illustrates the electrical characteristics of the MoS_2 FET devices. The left and right plots in Figure 2a show the output characteristics (source–drain current *versus* source–drain voltage, $I_{DS}-V_{DS}$) measured for a MoS_2 FET at gate voltages (V_G) ranging from -30 to 30 V in increments of 10 V before and after, respectively, proton beam irradiation with a fluence of 10^{12} cm⁻² (corresponding to an irradiation time of 20 s). Figure 2b



Figure 1. (a) Optical images showing the fabrication of a MOS_2 FET device. (b) Schematic illustration of proton beam irradiation on a MOS_2 FET device. (c) AFM image of the MOS_2 FET device with a cross-sectional topographic profile indicated by the blue line (MOS_2 flake). Red dashed lines in (a) and (c) indicate MOS_2 flakes.

www.acsnano.org



Figure 2. Representative electrical characteristics of MOS_2 FET devices. (a) Before and (b) after proton irradiation with a beam fluence of 10^{12} cm⁻². (c) Before and (d) after proton irradiation with a fluence of 10^{14} cm⁻². (a, c) Output characteristics ($I_{DS}-V_{DS}$) measured for different gate voltages. (b, d) Transfer characteristics ($I_{DS}-V_G$) measured at a fixed $V_{DS} = 0.5$ V. The inset figures of (b) and (d) are the transfer characteristics on a log scale.

shows the transfer characteristics (source-drain current versus gate voltage, $I_{DS} - V_G$) of the same device at a fixed source-drain voltage (V_{DS}) of 0.5 V before and after proton irradiation under the same proton beam conditions used in Figure 2a. The MoS₂ FET device exhibited n-channel behavior, with the current increasing as a more positive gate voltage was applied. The results in Figure 2a suggest that the electrical properties of the MoS₂ FET device did not change substantially following the proton irradiation with a small fluence condition of 10^{12} cm⁻² (*i.e.*, a short proton irradiation time of 20 s). However, the MoS₂ FET devices were influenced noticeably when irradiated with the proton beam for a longer period of time. Figure 2c shows the output characteristics measured for another MoS₂ FET device before and after proton beam irradiation with a fluence of 10¹⁴ cm⁻² (corresponding to an irradiation time of 2000 s). Figure 2d displays the corresponding transfer characteristics. Importantly, we observed that the current of the device decreased dramatically following proton beam irradiation. For example, the current of the device was measured as $\sim 20 \,\mu$ A at $V_{DS} = 5 \,V$ and $V_{\rm G} = 20$ V prior to proton irradiation, whereas after proton irradiation, the current was measured as $\sim 1 \,\mu A$ under the same measurement conditions (see inset of the plot on the right in Figure 2c). Hence, the current decreased by nearly 95% as a result of proton irradiation. This effect was clearly observed in the transfer curves (Figure 2d); that is, the current decreased significantly following proton beam irradiation. For the MoS₂ FET devices irradiated by a proton beam with a

fluence of 10¹³ cm⁻² (corresponding to an irradiation time of 200 s), the current level also decreased following proton irradiation, although the decrease was smaller than that observed under a fluence of 10^{14} cm⁻²; the current decreased from \sim 17.5 μ A (before proton irradiation) to \sim 5 μ A (after proton irradiation) when measured at $V_{DS} = 5$ V and $V_G = 20$ V, as shown in Figure S2 of the Supporting Information. The subthreshold slope of the device that was irradiated with a lowfluence proton beam $(10^{12} \text{ cm}^{-2})$ was almost the same before and after the proton irradiation, as shown in the inset of Figure 2b. On the contrary, the subthreshold slope of the device that was irradiated with a high-fluence proton beam (10¹⁴ cm⁻²) became worse after the proton irradiation, as shown in the inset of Figure 2d. Such degradation of the subthreshold slope after high-fluence proton beam irradiation is attributed to the proton beam-induced trap states at the interface.

Figure 3a-c show the statistical results for the MoS_2 FET devices that were irradiated by proton beams under the three different fluence conditions. Here, we measured three devices under each fluence condition. A total of nine MoS_2 FET devices were therefore investigated, divided into three groups, and exposed to proton beams under the three different beam fluence conditions of 10^{12} , 10^{13} , and 10^{14} cm⁻². We subsequently compared the measurements before and after each proton irradiation condition. The error bars in the figures represent the standard deviations from the individual measurements. In Figure 3a, the current levels of the proton-irradiated devices

VOL. 8 • NO. 3 • 2774-2781 • 2014



Figure 3. Statistical data for the (a) normalized conductance, (b) normalized current, and (c) change in the threshold voltage of the devices following proton irradiation with different beam fluences $(10^{12}, 10^{13}, and 10^{14} \text{ cm}^{-2})$. Raman spectra of MoS₂ flakes before and after proton beam irradiation with the fluences of (d) $\Phi = 10^{12} \text{ cm}^{-2}$ and (e) $\Phi = 10^{14} \text{ cm}^{-2}$. (f) Schematic illustrations of MoS₂ vibration modes.

measured at $V_{\rm G}$ = 30 V and $V_{\rm DS}$ = 0.5 V were compared with those of the devices before proton irradiation. The normalized current value in Figure 3a means the ratio of the current of the proton-irradiated device to that (value = 1.0, dashed line) of the same device before proton irradiation. In Figure 3b, the normalized conductance values were calculated and compared in a similar manner to that in Figure 3a. Here, the low-field conductance values were determined from the slope for a linear segment at the low bias region ($-0.3 < V_{DS} <$ 0.3 V). Figure 3c displays the changes in threshold voltages following proton irradiation. First, the current, conductance, and threshold voltage values for the devices irradiated by proton beams under a low fluence of 10¹² cm⁻² did not change significantly. In contrast, for the devices irradiated by a proton beam with a medium fluence of 10^{13} cm⁻², the current and conductance values decreased substantially, accompanied with a shift of the threshold voltage to the positive gate voltage direction. These changes in the current, conductance, and threshold voltage became more significant for the devices irradiated by proton beams with a high fluence of 10^{14} cm⁻², as indicated by the greater decreases in the current and conductance and the more positive shifts of the threshold voltage.

We measured Raman spectra of MoS₂ flakes before and after proton beam irradiation with fluences of $\Phi =$ 10^{12} cm⁻² (Figure 3d) and $\Phi = 10^{14}$ cm⁻² (Figure 3e). The two prominent E^{1}_{2g} (~380 cm⁻¹) and A_{1g} (~405 cm⁻¹) peaks are due to in-plane and out-ofplane vibrations of MoS₂ atoms,²⁸ as illustrated in Figure 3f. There was no significant change found in the E^{1}_{2g} and A_{1g} modes of MoS₂ in the Raman spectra

KIM ET AL.

before and after the proton irradiation. Note that we did Raman or electrical measurements on the protonirradiated samples at least 1 day after the proton irradiation because we were not allowed to pick up the proton-exposed samples right after the proton irradiation due to radioactivity safety regulations. Importantly, we observed significant changes in the electrical properties of MoS₂ FETs (Figures 2 and 3a–c), while we did not observe noticeable changes in the Raman spectra of MoS₂ flakes (Figures 3d,e). These results suggest that the change of the electrical characteristics of MoS₂ FET devices after the proton irradiation is not due to MoS₂ itself; instead it is due to the proton-irradiation-induced oxide traps in the SiO₂ layer or the interface trap states at the SiO₂/MoS₂ interface.

We investigated the time-dependence of the electrical characteristics of the proton-irradiated devices by measuring the devices before proton irradiation and 1 day, 3 days, and 5 days after proton irradiation. Figure 4a-c show the transfer curves of three MoS₂ FET devices that were irradiated by proton beams with fluence conditions of either 10^{12} , 10^{13} , or 10^{14} cm⁻². For the 10^{12} cm⁻² fluence condition, the current of the proton-irradiated device remained nearly constant with time (Figure 4a), consistent with the results of Figures 2 and 3. For the cases of the 10^{13} and 10^{14} cm⁻² fluences, the currents of the proton-irradiated devices decreased following proton irradiation (for example, see the day 1 data). However, the current typically recovered; for the middle fluence condition $(10^{13} \text{ cm}^{-2})$, the current recovered to nearly its original level after 5 days (Figure 4b), whereas for the highfluence condition $(10^{14} \text{ cm}^{-2})$, the current recovered

VOL. 8 • NO. 3 • 2774-2781 • 2014



Figure 4. Time-dependence of the $I_{DS}-V_G$ curves of the MoS₂ FET devices before proton irradiation and 1, 3, and 5 days after proton irradiation with fluences of (a) 10^{12} cm⁻², (b) 10^{13} cm⁻², and (c) 10^{14} cm⁻². The (d) normalized current, (e) normalized conductance, and (f) change in the threshold voltages of the devices are plotted as a function of time (*i.e.*, before proton irradiation) for the three different fluence conditions of 10^{12} , 10^{13} , and 10^{14} cm⁻².

but remained diminished even after 5 days (Figure 4c). Figure 4d–f summarize the normalized current, normalized conductance, and changes in the threshold voltage before and after proton irradiation with fluence conditions of 10^{12} , 10^{13} , and 10^{14} cm⁻². These plots show that the electrical parameters were not significantly influenced by the weak fluence proton irradiation $(10^{12} \text{ cm}^{-2})$ and that these values typically recovered with time but that the recovery was not complete for the high-fluence proton irradiation $(10^{14} \text{ cm}^{-2})$.

We now discuss the results of our proton irradiation experiments on MoS₂ FET devices. When high-energy particles are irradiated on silicon-based materials and devices, they lose the majority of their energy near the stopping position.^{29,30} We calculated the energy-loss depth profiles of irradiated protons using Stopping and Range of lons in Matter (SRIM 2008) software, which is a computer program that calculates the interactions of energetic particles with matter. The SRIM simulation results are provided in Figure S5 of the Supporting Information.^{30,31} From these simulation results, we found that protons could penetrate and stop \sim 700 μ m from the top surface. Because the structure of our MoS₂ FET devices comprised stacks of MoS2/SiO2/Si (2-8 nm/ 270 nm/500 μ m), the majority of protons could simply penetrate through the entire structure, generating electron-hole pairs along the path of the proton beam. It is known that when high-energy particles such as electrons and protons are irradiated on silicon-based FET devices, they can ionize atoms and generate electron-hole pairs in the oxide (SiO₂) layer, which is the layer that is most sensitive to ionizing irradiation.^{32,33} The generated electrons are quickly swept out of the bulk SiO₂ layer in a few picoseconds due to their high

mobility.³⁴ The remaining holes wander through the SiO₂ layer and may be trapped at localized trap sites in the bulk SiO₂ layer, leading to positive oxide-trapped charges. In addition, the irradiation-induced holes and protons in the SiO₂ can transport to the SiO₂/MoS₂ interface, leading to the formation of interface trap states, which are negatively charged electron trap centers for n-channel transistors. The positive oxide traps in the SiO₂ layer enhance the gate electric field, leading to an increased carrier concentration. In contrast, the negative interface trap states act as electron trap centers, leading to a reduction in the carrier concentration. Furthermore, the irradiationinduced interface trap states occur on a time scale that is much slower than that of the positive oxide-charge traps in the SiO₂ layer. Therefore, the effects of proton irradiation on the MoS₂ FET devices can be attributed to the combined effects of positive oxide-charge traps in the SiO₂ layer and interface trap states.^{35–37}

For low-fluence (short irradiation time) proton irradiation, neither positive oxide-charge traps nor interface trap states will be generated in sufficient quantities to significantly affect the electrical characteristics of the devices. As a result, no significant changes in the electrical parameters of the proton-irradiated devices were observed for proton irradiation under a 10^{12} cm⁻² fluence (see Figures 2a,b, 3a-c, 4a and d-f). However, at high fluence (long irradiation time), the interface trap states will play a major role in influencing the electrical performances of the proton-irradiated devices. These effects were observed in the MoS₂ FET devices irradiated by proton beams with 10^{13} or 10^{14} cm⁻² fluences (Figures 2c,d, 3a-c, and 4b-f). Note that for the 10¹² cm⁻² fluence condition, the currents of a portion of the proton-irradiated devices increased slightly

VOL. 8 • NO. 3 • 2774-2781 • 2014

JAI

www.acsnano.org



Figure 5. Energy band diagrams of a MoS₂ FET device (a) prior to proton irradiation (no irradiation) and (b) after proton irradiation with high beam fluence (10¹³ and 10¹⁴ cm⁻²). E_{F} : Fermi level energy, E_{C} : conduction band minimum, E_{V} : valence band maximum, $\Phi_{\rm B}$: Schottky barrier height. The green arrow indicates the proton beam irradiation, the blue circles with plus signs represent the oxide-trapped charges, and the red circles with minus signs represent the interface-trapped charges.

compared with those measured prior to proton irradiation (see Figure 3a), which could be due to the effect of positive oxide-trap charges in the SiO₂ layer. However, this effect was too small to be confirmed, and a modified experimental design would be necessary to distinguish the effect of the positive oxide-trap charges in the SiO₂ layer from that of the interface trap states. The recovery phenomena (Figure 4) can also be attributed to the traps generated by the proton irradiation.^{37,38} The recovery of the current indicates that the protonirradiation-induced traps are not permanent and do not act as charge traps for an extended period unless the fluence of the proton irradiation is beyond a certain threshold. We observed that the current was fully recovered for a middle fluence of 10^{13} cm⁻² approximately 5 days after proton irradiation (Figure 4b), but was not fully recovered at this time point for the high fluence condition of 10^{14} cm⁻² (Figure 4c).

The observations in this study can be explained using energy band diagrams, as shown in Figure 5. Figure 5a shows the energy band diagrams for V_{DS} = 0 V and $V_{\rm G}$ = 0 V. The MoS₂ flakes have a band gap of \sim 1.2 eV, which is similar to the band gap of bulk MoS₂.⁸ In addition, the work function (Φ_{MoS2}) and electron affinity (χ_{MoS2}) of the flakes are 4.6–4.9 eV and \sim 4.0 eV, respectively.³⁹⁻⁴² We used Au/Ti as the source and drain electrodes in contact with the MoS₂ and a work function for Au (Φ_{Au}) of 5.4 eV and that for Ti (Φ_{Ti}) of 4.3 eV.⁴¹ Therefore, the contact between Ti and MoS₂ will have a very small Schottky barrier ($\Phi_{\rm B}$), as indicated

in the energy band diagram (Figure 5a, right).⁴¹ When protons are irradiated on the devices, the proton beam induces positive oxide-trap charges in the SiO₂ layer and interface trap states at the SiO₂/MoS₂ interface. When the proton beam fluence is sufficient, the interface trap states influence the current flow in the MoS₂ channel, which hinders charge flows by trapping conduction electrons in the n-channel MoS₂. This will decrease the conduction electron concentration, raising the conduction band. In other words, an increasing interface trap density in the channel region by proton irradiation increases trapped electrons in the channel and reduces the current conductance, as shown in the right panel in Figure 5b.

CONCLUSION

In summary, we studied the effect of proton beam irradiation on multilayer MoS₂ FET devices. The n-channel MoS₂ FET devices irradiated by proton beams with sufficiently high fluence conditions exhibited decreases in the current and conductance and a shift of the threshold voltage toward the positive gate voltage direction. The recovery of these changes was observed over a time scale of days. These phenomena can be attributed to the interface trap states at the SiO_2/MOS_2 interfaces. This study improves our understanding of the influence of high-energy proton beams on MoS₂-based nanoelectronic devices and may provide a method to control the electrical properties of MoS₂ FET devices through changing interface states using proton beams.

METHODS

The multilayer MoS₂ was exfoliated using the micromechanical exfoliation method from a bulk MoS₂ crystal purchased from SPI Supplier. The multilayer MoS₂ flakes were transferred by 3M Scotch tape to SiO_2 on a heavily doped p++ Si wafer (resistivity \sim 5 \times 10⁻³ Ω cm) that can be used as a back gate.



The location of a MoS₂ flake was found using an optical microscope; then the MoS₂ flake's height was measured with an NX 10 AFM system (Park Systems). In order to make patterns of electrodes, we spin-coated MMA (8.5), MAA (9% concentration in ethyl lactate), and PMMA 950K (5% concentration in anisole) at 4000 rpm. After the two-step spin-coating, the sample was baked at 180 °C for 90 s on a hot plate. The electrodes were patterned using an electron beam lithography system (JSM-6510, JEOL) with a 30 kV exposure. For the development of pattern, MIBK/IPA (1:3) solution was used with a development time of 50 s. All the electrical measurements were conducted with a probe station (JANIS, ST-500) using a semi-in a vacuum ($\sim 10^{-4}$ Torr).

The Raman spectroscopic measurements were done with a Raman spectrometer (T64000 Horiba Jobin Yvon, at National Center for Inter-University Research Facilities) that uses an Ar ion laser (wavelength of 514.5 nm) as a source.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: MoS_2 FET device fabrication procedures, output and transfer characteristics of a device that was irradiated by a proton beam with a fluence of 10^{13} cm⁻², Raman spectroscopy data for the MoS₂ flakes before and after proton irradiation with fluence conditions of 10^{12} and 10^{14} cm⁻², and SRIM simulation data. This material is available free of charge *via* the Internet at http://pubs.acs.org.

Acknowledgment. The authors appreciate the financial support of the National Creative Research Laboratory program (Grant No. 2012026372) and the National Core Research Center program (Grant No. 2008-0062606) through the National Research Foundation of Korea (NRF) funded by the Korean Ministry of Science, ICT & Future Planning. We are especially thankful for the beam time grants from the proton beam facilities of the Korea Institute of Radiological and Medical Sciences, and the Korea Atomic Energy Research Institute (KAERI). S.H. acknowledges the support from the NRF grant (H-GUARD 2013M3A6B2078961).

REFERENCES AND NOTES

- Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* 2012, *7*, 699–712.
- 3. Fang, H.; Chuang, S.; Chang, T. C.; Takei, K.; Takahashi, T.; Javey, A. High-Performance Single Layered WSe₂ p-FETs with Chemically Doped Contacts. *Nano Lett.* **2012**, *12*, 3788–3792.
- 4. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- Schwierz, F. Graphene Transistors. Nat. Nanotechnol. 2010, 5, 487–496.
- 6. Jiang, H. Electronic Band Structures of Molybdenum and Tungsten Dichalcogenides by the GW Approach. J. Phys. Chem. C 2012, 116, 7664–7671.
- Coehoorn, R.; Haas, C.; Dijkstra, J.; Flipse, C.; De Groot, R.; Wold, A. Electronic Structure of MoSe₂, MoS₂, and WSe₂. I. Band-Structure Calculations and Photoelectron Spectroscopy. *Phys. Rev. B* **1987**, *35*, 6195.
- Kam, K.; Parkinson, B. Detailed Photocurrent Spectroscopy of the Semiconducting Group VI Transition Metal Dichalcogenides. J. Phys. Chem. **1982**, 86, 463–467.
- Yoon, J.; Park, W.; Bae, G. Y.; Kim, Y.; Jang, H. S.; Hyun, Y.; Lim, S. K.; Kahng, Y. H.; Hong, W. K.; Lee, B. H. Highly Flexible and Transparent Multilayer MoS₂ Transistors with Graphene Electrodes. *Small* **2013**, *9*, 3295–3300.

- Sundaram, R. S.; Engel, M.; Lombardo, A.; Krupke, R.; Ferrari, A. C.; Avouris, P.; Steiner, M. Electroluminescence in Single Layer MoS₂. *Nano Lett.* **2013**, *13*, 1416–1421.
- Radisavljevic, B.; Kis, A. Mobility Engineering and a Metal-Insulator Transition in Monolayer MoS₂. *Nat. Mater.* 2013, *12*, 815–820.
- Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors based on Monolayer MoS₂. Nat. Nanotechnol. **2013**, *8*, 497–501.
- Lee, H. S.; Min, S.-W.; Chang, Y.-G.; Park, M. K.; Nam, T.; Kim, H.; Kim, J. H.; Ryu, S.; Im, S. MoS₂ Nanosheet Phototransistors with Thickness-Modulated Optical Energy Gap. *Nano Lett.* 2012, *12*, 3695–3700.
- Kim, S.; Konar, A.; Hwang, W.-S.; Lee, J. H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.-B.; Choi, J.-Y. High-Mobility and Low-Power Thin-Film Transistors based on Multilayer MoS₂ Crystals. *Nat. Commun.* **2012**, *3*, 1011.
- Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS₂ Transistors. *Nat. Nanotechnol.* 2011, 6, 147–150.
- Vijayaraghavan, A.; Kanzaki, K.; Suzuki, S.; Kobayashi, Y.; Inokawa, H.; Ono, Y.; Kar, S.; Ajayan, P. M. Metal-Semiconductor Transition in Single-Walled Carbon Nanotubes Induced by Low-Energy Electron Irradiation. *Nano Lett.* 2005, *5*, 1575–1579.
- Gomez-Navarro, C.; De Pablo, P.; Gómez-Herrero, J.; Biel, B.; Garcia-Vidal, F.; Rubio, A.; Flores, F. Tuning the Conductance of Single-Walled Carbon Nanotubes by Ion Irradiation in the Anderson Localization Regime. *Nat. Mater.* 2005, 4, 534–539.
- Gunho, J.; Hong, W.-K.; Choe, M.; Park, W.; Yung, H. K.; Lee, T. Proton Irradiation-Induced Electrostatic Modulation in ZnO Nanowire Field-Effect Transistors with Bilayer Gate Dielectric. *IEEE Trans. Nanotechnol.* **2012**, *11*, 918–923.
- Hong, W.-K.; Jo, G.; Sohn, J. I.; Park, W.; Choe, M.; Wang, G.; Kahng, Y. H.; Welland, M. E.; Lee, T. Tuning of the Electronic Characteristics of ZnO Nanowire Field Effect Transistors by Proton Irradiation. ACS Nano 2010, 4, 811–818.
- Liao, L.; Lu, H.; Li, J.; Liu, C.; Fu, D.; Liu, Y. The Sensitivity of Gas Sensor Based on Single ZnO Nanowire Modulated by Helium Ion Radiation. *Appl. Phys. Lett.* 2007, *91*, 173110.
- Childres, I.; Jauregui, L. A.; Foxe, M.; Tian, J.; Jalilian, R.; Jovanovic, I.; Chen, Y. P. Effect of Electron-Beam Irradiation on Graphene Field Effect Devices. *Appl. Phys. Lett.* **2010**, *97*, 173109.
- Hu, X.; Karmarkar, A. P.; Jun, B.; Fleetwood, D. M.; Schrimpf, R. D.; Geil, R. D.; Weller, R. A.; White, B. D.; Bataiev, M.; Brillson, L. J. Proton-Irradiation Effects on AlGaN/AIN/GaN High Electron Mobility Transistors. *IEEE Trans. Nucl. Sci.* 2003, *50*, 1791–1796.
- Krasheninnikov, A.; Nordlund, K.; Sirviö, M.; Salonen, E.; Keinonen, J. Formation of Ion-Irradiation-Induced Atomic-Scale Defects on Walls of Carbon Nanotubes. *Phys. Rev. B* 2001, 63, 245405.
- Srour, J. R.; McGarrity, J. M. Radiation Effects on Microelectronics in Space. *Proc. IEEE* **1988**, *76*, 1443–1469.
- Komsa, H.-P.; Kotakoski, J.; Kurasch, S.; Lehtinen, O.; Kaiser, U.; Krasheninnikov, A. V. Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping. *Phys. Rev. Lett.* **2012**, *109*, 035503.
- Ochedowski, O.; Marinov, K.; Wilbs, G.; Keller, G.; Scheuschner, N.; Severin, D.; Bender, M.; Maultzsch, J.; Tegude, F. J.; Schleberger, M. Radiation Hardness of Graphene and MoS₂ Field Effect Devices against Swift Heavy Ion Irradiation. *J. Appl. Phys.* 2013, *113*, 214306.
- Mathew, S.; Gopinadhan, K.; Chan, T.; Yu, X.; Zhan, D.; Cao, L.; Rusydi, A.; Breese, M.; Dhar, S.; Shen, Z. Magnetism in MoS₂ Induced by Proton Irradiation. *Appl. Phys. Lett.* **2012**, *101*, 102103.
- Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single-and Few-Layer MoS₂. ACS Nano 2010, 4, 2695–2700.
- Messenger, S.; Burke, E.; Summers, G.; Xapsos, M.; Walters, R.; Jackson, E.; Weaver, B. Nonionizing Energy Loss (NIEL) for Heavy Ions. *IEEE Trans. Nucl. Sci.* **1999**, *46*, 1595–1602.





- 30. Ziegler, J. F.; Biersack, J. P. *The Stopping and Range of Ions in Matter*; Springer: Berlin, 1985.
- Ziegler, J. F.; Ziegler, M. D.; Biersack, J. P. SRIM-The Stopping and Range of Ions in Matter. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268*, 1818–1823.
- 32. Schroder, D. K. Semiconductor Material and Device Characterization; John Wiley & Sons: New York, 2006; Chapter 6.
- Oldham, T. R. Ionizing Radiation Exects in MOS Oxides; World Scientific: Singpore, 1999; Vol. 3.
- Hughes, R. Chrage-Carrier Transport Phenomena in Amorphous SiO₂: Direct Measurement of the Drift Mobility and Lifetime. *Phys. Rev. Lett.* **1973**, *30*, 1333.
- Sze, S. M.; Ng, K. K. Physics of Semiconductor Devices, 3rd ed.; Wiley-Interscience: New York, 2007; Chapter 4.
- Schwank, J. R.; Shaneyfelt, M. R.; Fleetwood, D. M.; Felix, J. A.; Dodd, P. E.; Paillet, P.; Ferlet-Cavrois, V. Radiation Effects in MOS Oxides. *IEEE Trans. Nucl. Sci.* 2008, 55, 1833– 1853.
- Oldham, T. R.; McLean, F. Total lonizing Dose Effects in MOS Oxides and Devices. *IEEE Trans. Nucl. Sci.* 2003, *50*, 483–499.
- McLean, F.; Boesch, H.; McGarrity, J. Hole Transport and Recovery Characteristics of SiO₂ Gate Insulators. *IEEE Trans. Nucl. Sci.* 1976, 23, 1506–1512.
- Liu, K.-K.; Zhang, W.; Lee, Y.-H.; Lin, Y.-C.; Chang, M.-T.; Su, C.-Y.; Chang, C.-S.; Li, H.; Shi, Y.; Zhang, H. Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates. *Nano Lett.* **2012**, *12*, 1538–1544.
- Giridharagopal, R.; Kelly, K. F. Substrate-Dependent Properties of Polydiacetylene Nanowires on Graphite and MoS₂. ACS Nano 2008, 2, 1571–1580.
- Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multilayer MoS₂ Transistors with Scandium Contacts. *Nano Lett.* **2013**, *13*, 100–105.
- Han, S.; Kwon, H.; Kim, S. K.; Ryu, S.; Yun, W. S.; Kim, D.; Hwang, J.; Kang, J.-S.; Baik, J.; Shin, H. Band-Gap Transition Induced by Interlayer Van Der Waals Interaction in MoS₂. *Phys. Rev. B* **2011**, *84*, 045409.



www.acsnano.org