Maskless Micro-nanopatterning and Bipolar Electrical-rectifying of MoS2 Flakes through Femtosecond Laser Direct Writing Processing

*Pei Zuo,**† Lan Jiang,\*,† Xin Li, † Mengyao Tian, † Peng Ran, † Bo Li, † Yongfeng Lu,§*

†Laser Micro/Nano Fabrication Laboratory, School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China, §Department of Electrical and Computer Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588-0511, USA

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**ABSTRACT**: MoS2 micro/nanostructures are desirable for tuning electronic properties, developing required functionality, and improve existing performance of multilayer MoS2 device. This work presents a useful method to flexibly microprocess multilayer MoS2 flakes through femtosecond laser pulse direct writing, which can directly fabricate regularly MoS2 nanoribbon arrays with ribbon widths of 179, 152, 116, 98, 77 nm, respectively, and arbitrarily pattern MoS2 flakes forming micro-nanostructures such as single nanoribbon, labyrinth array, and cross structure. This method has advantages of mask-free, simplicity, high flexibility, strong controllability, and high precision. Moreover, numerous oxygen molecules are chemically and physically bonded to laser-processed MoS2, attributed to roughness defect-sites and edges of micro-nanostructures that contain numerous unsaturated edge-sites and highly active centres. In addition, electrical test of prepared MoS2 nanoribbon arrays fabricated to be field effect transistor indicates new interesting features: output and transfer characteristics exhibit strong rectification (not goes through zero and exhibits bipolar conduction) of drain-source current, which is supposedly attributed to the coordinate structures and p-type chemical doping of oxygen molecules on MoS2 nanoribbon arrays. This work indicates the ability of femtosecond laser pulses to directly induce micro-nanostructures, property changes, and new device−properties of two-dimension materials, which may future enable new device applications.

**INTRODUCTION**

Transition metal dichalcogenides (TMDCs), representative layered materials like graphene, have been widely studied as a family of new-type semiconducting materials with extraordinary mechanical, electrical, and optical properties, and great promise for extensive applications.[1-6](#_ENREF_1) Molybdenum disulfide (MoS2), representative material belonging to the family of TMDs group, has lattice structure of a layer of molybdenum atoms sandwiched between two layers of sulfur atoms.[7-8](#_ENREF_7) Unlike graphene with zero-band-gap, MoS2 is a band-gap semiconductor with sizable energy band gap:[5](#_ENREF_5), [9](#_ENREF_9) MoS2 in bulk form with indirect energy gap of ~1.2 eV and MoS2 in monolayer form with direct band gap of ~1.8 eV.[3](#_ENREF_3) Hence, MoS2 can serve as a promising candidate of graphene, and has excellent potential in semiconductor-related applications of layered material such as thin-film transistors,[1](#_ENREF_1), [10](#_ENREF_10) integrated circuits,[11-12](#_ENREF_11) complementary inverter,[13](#_ENREF_13) photodetectors,[14](#_ENREF_14) light-emitting diodes,[15-16](#_ENREF_15) photovoltaics,[17-18](#_ENREF_17) superconductors,[19-20](#_ENREF_19) and chemical/biological sensors.[21-22](#_ENREF_21)

To develop desirable electronic properties and required functionality and improve existing performance of MoS2 devices, a microfabrication process is usually required to fabricate large arrays of orderly arranged MoS2 micro/nanostructures, commonly involving patterning and etching.[3](#_ENREF_3), [23](#_ENREF_23) Hence, it is important to carry on research on patterning of MoS2 with ordered micro/nanostructures, controlled structure-size, and device application with new features. Several approaches have been attempted to pattern MoS2 materials or fabricate micro/nanostructures of MoS2 deposited on substrates, including tape exfoliation,[24-25](#_ENREF_24) chemical vapour deposition (CVD),[26-27](#_ENREF_26) thermal decomposition of thiosalts,[28](#_ENREF_28) van der Waals epitaxial growth,[29-30](#_ENREF_29) patterned MoO3 sulfurization,[31-32](#_ENREF_31) CVD process in plasma-treated areas,[33-34](#_ENREF_33) block copolymer lithography,[35](#_ENREF_35) reactive ion etching (RIE) & deposition in plasma-treated areas,[3](#_ENREF_3) lithography & stamping,[23](#_ENREF_23) lithography & RIE,[36-37](#_ENREF_36) and continue wave (CW) laser direct processing.[38-39](#_ENREF_38) Among them, CVD process in plasma-treated areas, block copolymer lithography, lithography & deposition in plasma-treated areas, lithography & stamping, lithography & RIE, and CW laser direct processing can realize the control for the location, shape, and size of MoS2 micro/nanostructures. Whereas, in the methods involving lithography, plasma surface treatment and RIE, chemical organics (such as photoresist) and inorganic or organic masks were used, combined process was needed, and integral process was relatively complex. In the CW laser direct processing, this one-step operation process is simple, no special atmosphere system and mask are needed, cost is relatively low, and flexibility and controllability are high. Whereas, CW laser processing is a thermal process, and the strong thermal effect would cause thermal oxidization of materialsand lead to large recasting layer, hence processing precision is not enough high. Another kind of laser processing technology is femtosecond (ultrafast) laser pulse direct processing. Femtosecond laser pulses have ultrashort pulse width, ultrahigh power density, and nonlinear nonequilibrium processing feature, and multiphoton absorption and nonthermal effect can be realized, hence except including almost all the advantages of CW laser processing, femtosecond laser direct processing also has the advantage of high processing precision.[40](#_ENREF_40)

In this work, we proposed a useful method of utilizing femtosecond laser pulse direct writing processing to modify multilayer MoS2 flakes, directly fabricate regularly MoS2 nanoribbon arrays with different ribbon widths, and arbitrarily pattern MoS2 flakes forming different MoS2 micro-nanostructures. Moreover, the laser-fabricated MoS2 structures were chemically and physically bonded with numerous oxygen molecules in the air, which can be attributed to the roughness defect sites and long edges on and of the nanoribbons that may contain numerous unsaturated edge sites and highly active centres. At last, electronic properties of the MoS2 nanoribbon arrays fabricated to be field effect transistor (FET) were tested, and its output and transfer characteristics exhibited strong rectification (not went through zero and exhibited bipolar conduction) of drain-source current, supposedly attributed to the coordinate structures and p-type chemical doping of oxygen molecules on MoS2 nanoribbon arrays, which may cause transition of n-type channel to p-type channel or properties similar to pn junction. The proposed method had advantages of simplicity, maskless, strong controllability, high flexibility, and high precision, and also indicated the ability of femtosecond laser pulses to directly induce two-dimension micro/nanostructures/patterns, property changes of two-dimension material, and new device features.

**RESULTS AND DISCUSSION**

In this work, multilayer MoS2 flakes were mechanically exfoliated from a natural crystal by using adhesive tape and deposited on 300nm-SiO2/Si substrates. The thickness of MoS2 flakes selected for experiments was about several to dozens of nanometers. The processing schematic of our method to fabricate MoS2 nanoribbons/patterns is shown in Figure 1a, which relies on the formation of regularly nanostructures/material remove by femtosecond laser pulse irradiation. When femtosecond laser pulse beam is focused and irradiated on material surface, surface plasmons (SPs) can be induced on material surface, the interference of which with incident laser field can lead to the formation of initial grating structures on material, then these initial grating can assiste the coupling of SPs and incident laser field, leading to the further formation of final grating structures with deeper gaps.[41](#_ENREF_41) The depth of gaps of laser induced grating structures is related to the number and energy of ultrafast laser pulses on unit area of material, and can be micrometer scale.[40](#_ENREF_40), [42-43](#_ENREF_42) The used MoS2 in our work was nano-scale thin flake, therefore controlling scan speed of laser beam enough slow (laser pulse number on unit area of MoS2 enough large) can control the gaps penetrating whole MoS2 thin flake, enabling surface nanogratings to become independent nanoribbons. Figure 1b shows the optical comparison of pristine MoS2 and femtosecond laser-processed (FLP-) MoS2, which showed obviously color change of optical image of the MoS2 flake after femtosecond laser irradiation, indicating the change of thickness or surface roughness. Figure 1c shows atomic force microscope (AFM) of MoS2 flake in Figure 1b, which shows the reduction of outline height of FLP-MoS2 flake, indicating the thinning effect on thickness of MoS2 by femtosecond laser irradiation. Figure 1d shows the high resolution AFM image of FLP-MoS2, which indicated the formation of MoS2 grating structures.



Figure 1. Principle and preliminary characterization of this method. a) Schematic diagram of femtosecond laser direct wiring processing to induce MoS2 nanoribbons array. b) Optical comparison of pristine MoS2 (upper part) and FLP-MoS2 (lower part). c) AFM and d) high resolution AFM of FLP-MoS2 flake.

To future investigate the FLP-MoS2 micro/nanostructures, scanning electron microscope (SEM) was carried out to characterize its physical morphology, as shown in Figure 2. Figure 2a-e show regularly MoS2 nanoribbon arrays with different ribbon widths of approximate 179, 152, 116, 98, and 77 nm, respectively. Figure 2f shows two independent MoS2 nanoribbons with small and big width of 56 and 420 nm, respectively. Figure 2g and h show two kind of MoS2 patterned structures through material remove by femtosecond laser direct writing, which were a labyrinth array and a cross structure, respectively, indicating the flexible processing capability of femtosecond laser even for arbitrary patterens.



Figure 2. FLP-MoS2 micro/nanostructures and patterns. a-e) SEM images of regularly MoS2 nanoribbon arrays with widths of 179, 152, 116, 98, and 77 nm, respectively. f) SEM images of two independent MoS2 nanoribbons with width of (up) 56 and (down) 420 nm. SEM images of g) MoS2 labyrinth array and h) MoS2 cross structure, respectively.

To prove the formation of MoS2 nanoribbons rather than surface structures on MoS2, energy Dispersive X-ray (EDX) analysis was performed. Figure 3a-c show the SEM images of the edge of a FLP-MoS2 flake, and its S and Si EDX mapping images. The grey part was MoS2, the black part was substrate, and the regularly stripe structures were induced by the irradiation of femtosecond laser pulses (Figure 3a). Figure 3b shows the clearly separated MoS2 nanoribbons, and Figure 3c shows the clearly gaps between these MoS2 nanoribbons. Figure 3d-f shows the SEM image of MoS2 nanoribbon arrays, and its S and Si EDX mapping images, which also indicated the separation of MoS2 nanoribbons, proving the formation of MoS2 nanoribbons rather than surface structures on MoS2.



Figure 3. Proving the formation of separated MoS2 nanoribbons. a) SEM images of the edge of a FLP-MoS2 flake, and its b) S and c) Si EDX mapping images. d) SEM image of MoS2 nanoribbon arrays, and its e) S and f) Si EDX mapping images.

To investigate the change of chemical property of FLP-MoS2 flaks, Raman and X-ray photoelectron spectroscopy (XPS) characterizations were conducted. Figure 4a shows the Raman spectra of pristine MoS2 (black line) and FLP-MoS2 (red line). There was no Raman peak at 820 cm-1 originating from MoO3, which indicted no formation of MoO3 thus no obviously thermal oxidation for FLP-MoS2,[44](#_ENREF_44) due to the non-thermal effect of femtosecond laser processing.[40](#_ENREF_40) No Raman peak of SiO2 at 520 cm-1 was detected on pristine MoS2 flake, however, there was an obviously Raman peak of SiO2 was detected on FLP-MoS2 flake, which indicated that substrate was also detected on FLP-MoS2 flake.[45-46](#_ENREF_45) This also proved the separation of MoS2 nanoribbons and penetrating gaps between them, which was consistent with the results in Figure 3. XPS Mo, O, and S spectra of pristine MoS2 and FLP-MoS2 were shown in Figure S1, Figure 4b and c, and Figure S2. Figure S1a shows the Mo 3d spectra for pristine MoS2, which shows three peaks at 227.2, 229.3, and 232.4 eV, respectively assigned to the S 2s orbital of divalent sulfur, and the Mo4+ 3d5/2 and 3d3/2 orbitals of tetravalent molybdenum. However, in Mo 3d spectra for FLP-MoS2 (Figure 4b), except the three peaks as shown in pristine MoS2, there is a new peak at ~235 eV, which is assigned to the Mo6+ 3d3/2 orbital of hexavalent molybdenum. The Mo6+ in FLP-MoS2 was attributed to the Mo-O bonds formed through oxygen bonding to the unsaturated Mo bonds, defect sites, or edge of nanoribbons,[47-48](#_ENREF_47) which generated from the damage and material removing of MoS2 induced by femtosecond laser pulses. Figure S1b shows the O 1s spectra for pristine MoS2, which shows two peak at 532.6 and 533.4 eV, attributed to the divalent oxygen of Si–O bonds and the nonvalent oxygen of oxygen molecules physically adsorbed on MoS2 surface (O2/MoS2), respectively.[49-51](#_ENREF_49) The divalent oxygen of Si–O bonds was derived from the 300-nm SiO2/Si substrate, and oxygen molecules on MoS2 surface should be attributed to the intrinsic defect and edge of the flake, which were active sites with physical adsorption capacity. However, in O 1s spectra for FLP-MoS2 (Figure 4c), except the strong and dominant peak assigned to divalent oxygen of Si–O bonds as shown in pristine MoS2, it revealed stronger peak of nonvalent oxygen of O2/MoS2, indicating more oxygen molecules physically adsorbed on MoS2 surface, it also revealed a new peak at approximately 530.5 eV, assigned to the divalent oxygen of Mo–O bonds,[52-53](#_ENREF_52) which was consistent with the result of XPS Mo 3d spectra. These results indicated that more oxygen atoms/molecules were chemical and physical bonded to FLP-MoS2. This can be attributed to the roughness defect sites on MoS2 nanoribbons and the long edges of the nanoribbons, which contained numerous unsaturated edge sits and were numerous highly active centers which can physically and chemically bond with adsorbates such as O2 molecules.[54-56](#_ENREF_54) The oxygen absorption on MoS2 not only led to the change of chemical valence of MoS2, but also, according to previous reports, can lead p-type doping effect on MoS2 with O2 as electron acceptor while MoS2 as electron donator.[54](#_ENREF_54)



Figure 4. Raman and XPS spectra of FLP-MoS2. a) Raman spectra of pristine MoS2 (black line) and FLP-MoS2 (red line). XPS peak-split results of b) Mo 3d and c) O 1s spectra of FLP-MoS2.

To evaluate the electronic properties of prepared MoS2 nanoribbon arrays, we fabricated back gate FET by using MoS2 nanoribbon arrays (NbA) on SiO2/p+ Si substrates as channel, with 5 nm Ti/ 75 nm Au as source and drain electrodes, through technologies of electron beam lithography (EBL), metal evaporation deposition, and a lift-off process. The electrical measurements of fabricated FET were performed by using a Keithley 4200 semiconductor characterization system in air and at room temperature. The schematic diagram of structure and measurement of fabricated MoS2 NbA-FET was shown in Figure 5a. Figure 5b shows the SEM image of MoS2 nanoribbon arrays used to fabricate FET with channel length of L ≈ 7.3 μm, integral channel width of W ≈ 3.6 μm, ribbon number of about 38, and gate dielectric thickness of d = 300 nm. As comparison, pristine MoS2 flake was also be fabricated to be a back-gated FET. Figure 5c shows the drain-source current (*IDS*) versus drain-source voltage (*VDS*) characteristics of this NbA-FET under different gate voltages (*VG*) ranging from -15 to 15 V. For this output characteristic curve, the drain-source current changed linearly with the drain-source voltage, indicating nearly ohmic contact for this FET device. In addition, the output curve did not go through zero and exhibited a strong rectification of the drain-source current, which was different from the output characteristic curve of the FET fabricated by using pristine/undamaged MoS2 flake as shown in Figure S3a. This may be attributed the p-type chemical doping of oxygen molecules on MoS2 nanoribbon arrays, which might cause transition of n-type channel to p-type channel or properties similar to pn junction.[3](#_ENREF_3)

Figure 5d shows the drain-source current (*IDS*) versus gate voltages (*VG*) characteristics of this NbA-FET under different drain-source voltage (*VDS*) ranging from 6 to 10 V. The trend of this transfer curve was non-monotone variation and exhibited a strong rectification of the drain-source current, which was different from the transfer characteristic curve of the FET fabricated by using pristine/undamaged MoS2 flake. As shown in Figure S3b, the transfer characteristic curve of pristine/undamaged MoS2 FET exhibited n-type conduction. However, the transfer characteristic curve of MoS2 NbA-FET exhibits bipolar conduction, similar to p-n type transfer conduction (Figure 5d), with current chopping by a small voltage range. To future evaluate the electronic properties of this device, the on/off ratio, carrier mobility (μ), and subthreshold swing (SS) were calculated. The on/off ratio of the device was calculated to be 1.2×102 (p-type segment) and 1.7×103 (n-type segment) at the drain-source voltage (*VDS*) of 10V. The carrier mobility (μ) was calculated according to the equation from previous reports,[23](#_ENREF_23) as shown in Equation 1,

 (1)

where *L* and *W* are the length and width of FET channel, respectively; *d*, *ε0*, and *εr* are the thickness, vacuum permittivity, and relative permittivity of grid dielectric layer, respectively; can be calculated from the *IDS*−*VG* curve. For this FET device, the length and width of channel were L ≈ 3.6 μm and W ≈ 7.3 μm; the grid dielectric layer was SiO2, its thickness was *d* ≈ 300 nm, and its vacuum permittivity and relative permittivity were *ε0* ≈ 8. 85 × 10-12 F/m and *εr* ≈ 3.9 F/m,[23](#_ENREF_23) respectively. Hence, the carrier mobility of this device was calculated to be approximate 2.5×10-3 cm2 V-1 s-1. The subthreshold swing (SS) was calculated according to the equation from previous reports,[57](#_ENREF_57) as shown in Equation 2,

 (2)

and the SS of this device was calculated to be ~21 V/dec according Equation 2. The obvious strong rectification behavior of *IDS*-*VDS* and *IDS*-*VG* of the MoS2 NbA-FET indicted property change of material and new device properties, which may enable new device applications. In addition, moderate modification of MoS2 flakes by femtosecond laser pulses would also tuning the n-type electronic properties of MoS2 FET, as shown in Figure S3, the on/off ratio of MoS2 FET was increased by two magnitude, and as shown in Figure S4, the drain-source current (*IDS*) increased quicker and reached saturation faster with the increase of gate voltages (*VG*).



Figure 5. Electrical test of MoS2 NbA-FET. a) Schematic diagram of structure and measurement of fabricated MoS2 NbA-FET. b) SEM image of MoS2 nanoribbon arrays used to fabricate FET. c) Output and d) transfer characteristic curve of fabricated MoS2 NbA-FET.

**CONCLUSIONS**

Femtosecond laser pulse direct writing processing was used to nonthermally modify multilayer MoS2 flakes, induce separated MoS2 nanoribbon arrays, and arbitrarily pattern MoS2 flakes forming different MoS2 micro-nanostructures. Optical microscope, AFM, and SEM was performed to characterize the physical micromorphology of laser processed-MoS2 flakes. EDX mapping indicated the separation of MoS2 nanoribbons, proving the formation of MoS2 nanoribbons rather than surface structures on MoS2. Raman spectra indicated the non-thermal effect of femtosecond laser processing, also proved the separation of MoS2 nanoribbons and the penetrating gaps between them. XPS spectra indicated that more oxygen molecules were chemical and physical bonded to FLP-MoS2, attributed to the roughness defect sites on MoS2 nanoribbons and the long edges of the nanoribbons that contained numerous unsaturated edge sites and were numerous highly active centres. To evaluate the electronic properties of prepared MoS2 nanoribbon arrays, MoS2 NbA-FET was fabricated and electrical test was conducted. Results indicated that the output and transfer characteristic curves exhibited strong rectification (not went through zero and exhibited bipolar conduction) of drain-source current, which were different from that of FET fabricated by using pristine/undamaged MoS2 flake. This may be attributed the coordinate structures and p-type chemical doping of oxygen molecules on MoS2 nanoribbon arrays, which might cause transition of n-type channel to p-type channel or properties similar to pn junction. At last, on/off ratio, carrier mobility, and subthreshold swing were also calculated. The proposed method indicated the ability of femtosecond laser pulses to directly induce two-dimension nanostructures, property change of material, and new device properties, which may future enable new device applications.

**METHODS**

**Femtosecond laser pulse processing**: The light path setup of our femtosecond laser pulse processing system was reported in our previous study.[8](#_ENREF_8)

**Characterization of MoS2 nanostructures**: The optical images were obtained using an Olympus microscope. The AFM characterization was performed using a SPM-960 AFM. The SEM images and EDX maping spectra were obtained using a Hitachi scanning electron microscope. Raman spectra were obtained using a Renishaw InVia Reflex spectrometer with a 532 nm light source. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI Quantera X-ray photoelectron spectrometer.

**Device fabrication and electrical characterization**: Multilayer MoS2 flakes were on p+Si/SiO2 (300 nm) substrates and were processed by femtosecond laser pulse. Then the substrates were spin-coated with poly methyl methacrylate (PMMA) solution. The source and drain electrodes were fabricated through three main steps: standard electron-beam lithography (EBL) was performed by Zeiss Supra55 SEM and Raith pattern generator to pattern the PMMA masks; 5 nm Ti/75 nm Au were deposited by electronic beam evaporation technique; a lift-off process was performed in acetone. The electrical measurements of the fabricated MoS2 FET were performed by using a Keithley 4200 semiconductor characterization system in air and at room temperature.

**ASSOCIATED CONTENT**

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website.

Supplementary XPS Mo, O, and S spectra of pristine MoS2, XPS S spectra of FLP-MoS2, and supplementary electrical test results of MoS2 FETs with moderate surface modification by femtosecond laser pulses (PDF).

**AUTHOR INFORMATION**

**Corresponding Author**

\*E-mail (Lan Jiang): [jianglan@bit.edu.cn](mailto:jianglan@bit.edu.cn)

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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The authors declare no competing financial interest.

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**REFERENCES**

1. Chhowalla, M.; Jena, D.; Zhang, H. Two-dimensional semiconductors for transistors. *Nature Reviews Materials* **2016,** *1*, 16052.

2. Bertolazzi, S.; Bonacchi, S.; Nan, G.; Pershin, A.; Beljonne, D.; Samorì, P. Engineering Chemically Active Defects in Monolayer MoS2 Transistors via Ion-Beam Irradiation and Their Healing via Vapor Deposition of Alkanethiols. *Advanced Materials* **2017,** *29*, 1606760.

3. Nam, H.; Wi, S.; Rokni, H.; Chen, M.; Priessnitz, G.; Lu, W.; Liang, X. MoS2 Transistors Fabricated via Plasma-Assisted Nanoprinting of Few-Layer MoS2 Flakes into Large-Area Arrays. *ACS Nano* **2013,** *7*, 5870-5881.

4. Eda, G.; Maier, S. A. Two-dimensional crystals: managing light for optoelectronics. *ACS Nano* **2013,** *7*, 5660-5665.

5. Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer MoS2. *Nat. Mater.* **2013,** *12*, 207-211.

6. Yu, Y.; Ji, Z.; Zu, S.; Du, B.; Kang, Y.; Li, Z.; Zhou, Z.; Shi, K.; Fang, Z. Ultrafast Plasmonic Hot Electron Transfer in Au Nanoantenna/MoS2 Heterostructures. *Adv. Funct. Mater.* **2016,** *26*, 6394-6401.

7. Behura, S.; Berry, V. interfacial nondegenerate doping of MoS2 and other two-dimensional semiconductors. *ACS Nano* **2015,** *9*, 2227-2230.

8. Zuo, P.; Jiang, L.; Li, X.; Li, B.; Ran, P.; Li, X.; Qu, L.; Lu, Y. Metal (Ag, Pt)–MoS2 Hybrids Greenly Prepared Through Photochemical Reduction of Femtosecond Laser Pulses for SERS and HER. *ACS Sustainable Chemistry & Engineering* **2018,** *6*, 7704-7714.

9. Lu, J.; Liu, H.; Tok, E. S.; Sow, C.-H. Interactions between lasers and two-dimensional transition metal dichalcogenides. *Chem. Soc. Rev.* **2016,** *45*, 2494-2515.

10. Cho, K.; Pak, J.; Kim, J.-K.; Kang, K.; Kim, T.-Y.; Shin, J.; Choi, B. Y.; Chung, S.; Lee, T. Contact-Engineered Electrical Properties of MoS2 Field-Effect Transistors via Selectively Deposited Thiol-Molecules. *Advanced Materials* **2018,** *30*, 1705540.

11. Cheng, R.; Jiang, S.; Chen, Y.; Liu, Y.; Weiss, N.; Cheng, H.-C.; Wu, H.; Huang, Y.; Duan, X. Few-layer molybdenum disulfide transistors and circuits for high-speed flexible electronics. *Nature Communications* **2014,** *5*, 5143.

12. Gao, G.; Wan, B.; Liu, X.; Sun, Q.; Yang, X.; Wang, L.; Pan, C.; Wang, Z. L. Tunable Tribotronic Dual-Gate Logic Devices Based on 2D MoS2 and Black Phosphorus. *Advanced Materials* **2018,** *30*, 1705088.

13. Yoo, H.; Hong, S.; On, S.; Ahn, H.; Lee, H.-K.; Hong, Y. K.; Kim, S.; Kim, J.-J. Chemical Doping Effects in Multilayer MoS2 and Its Application in Complementary Inverter. *ACS Applied Materials & Interfaces* **2018,** *10*, 23270-23276.

14. Pak, Y.; Park, W.; Mitra, S.; Sasikala Devi, A. A.; Loganathan, K.; Kumaresan, Y.; Kim, Y.; Cho, B.; Jung, G.-Y.; Hussain, M. M.; Roqan, I. S. Enhanced Performance of MoS2 Photodetectors by Inserting an ALD-Processed TiO2 Interlayer. *Small* **2018,** *14*, 1703176.

15. Woo, Y.; Hong, W.; Yang, S. Y.; Kim, H. J.; Cha, J.-H.; Lee, J. E.; Lee, K. J.; Kang, T.; Choi, S.-Y. Large-Area CVD-Grown MoS2 Driver Circuit Array for Flexible Organic Light-Emitting Diode Display. *Advanced Electronic Materials* **2018,** *0*, 1800251.

16. Choi, M.; Park, Y. J.; Sharma, B. K.; Bae, S.-R.; Kim, S. Y.; Ahn, J.-H. Flexible active-matrix organic light-emitting diode display enabled by MoS<sub>2</sub> thin-film transistor. *Science Advances* **2018,** *4*.

17. Zhang, J.; Lang, X. Y.; Zhu, Y. F.; Jiang, Q. Strain tuned InSe/MoS2 bilayer van der Waals heterostructures for photovoltaics or photocatalysis. *Physical Chemistry Chemical Physics* **2018,** *20*, 17574-17582.

18. Xu, M.; Chen, Y.; Xiong, F.; Wang, J.; Liu, Y.; Lv, J.; Li, Y.; Wang, Y.; Chen, Z.; Ma, Y. A hidden symmetry-broken phase of MoS2 revealed as a superior photovoltaic material. *Journal of Materials Chemistry A* **2018,** *6*, 16087-16093.

19. Chen, Q.; Lu, J.; Liang, L.; Zheliuk, O.; Ali El Yumin, A.; Ye, J. Continuous Low-Bias Switching of Superconductivity in a MoS2 Transistor. *Advanced Materials* **2018,** *30*, 1800399.

20. Saito, Y.; Nakamura, Y.; Bahramy, M. S.; Kohama, Y.; Ye, J.; Kasahara, Y.; Nakagawa, Y.; Onga, M.; Tokunaga, M.; Nojima, T.; Yanase, Y.; Iwasa, Y. Superconductivity protected by spin–valley locking in ion-gated MoS2. *Nature Physics* **2015,** *12*, 144.

21. Kumar, R.; Goel, N.; Kumar, M. UV-Activated MoS2 Based Fast and Reversible NO2 Sensor at Room Temperature. *ACS Sensors* **2017,** *2*, 1744-1752.

22. Ryu, B.; Nam, H.; Oh, B.-R.; Song, Y.; Chen, P.; Park, Y.; Wan, W.; Kurabayashi, K.; Liang, X. Cyclewise Operation of Printed MoS2 Transistor Biosensors for Rapid Biomolecule Quantification at Femtomolar Levels. *ACS Sensors* **2017,** *2*, 274-281.

23. Zhao, J.; Yu, H.; Chen, W.; Yang, R.; Zhu, J.; Liao, M.; Shi, D.; Zhang, G. Patterned Peeling 2D MoS2 off the Substrate. *ACS Applied Materials & Interfaces* **2016,** *8*, 16546-16550.

24. Huang, M.; Li, S.; Zhang, Z.; Xiong, X.; Li, X.; Wu, Y. Multifunctional high-performance van der Waals heterostructures. *Nature Nanotechnology* **2017,** *12*, 1148.

25. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS2 transistors. *Nature Nanotechnology* **2011,** *6*, 147.

26. Cong, R.; Qiao, S.; Liu, J.; Mi, J.; Yu, W.; Liang, B.; Fu, G.; Pan, C.; Wang, S. Ultrahigh, Ultrafast, and Self-Powered Visible-Near-Infrared Optical Position-Sensitive Detector Based on a CVD-Prepared Vertically Standing Few-Layer MoS2/Si Heterojunction. *Advanced Science* **2018,** *5*, 1700502.

27. Liu, H.; Zhu, Y.; Meng, Q.; Lu, X.; Kong, S.; Huang, Z.; Jiang, P.; Bao, X. Role of the carrier gas flow rate in monolayer MoS2 growth by modified chemical vapor deposition. *Nano Research* **2017,** *10*, 643-651.

28. 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.; Lai, C.-S.; Li, L.-J. Growth of Large-Area and Highly Crystalline MoS2 Thin Layers on Insulating Substrates. *Nano Letters* **2012,** *12*, 1538-1544.

29. Pak, S.; Lee, J.; Lee, Y.-W.; Jang, A. R.; Ahn, S.; Ma, K. Y.; Cho, Y.; Hong, J.; Lee, S.; Jeong, H. Y.; Im, H.; Shin, H. S.; Morris, S. M.; Cha, S.; Sohn, J. I.; Kim, J. M. Strain-Mediated Interlayer Coupling Effects on the Excitonic Behaviors in an Epitaxially Grown MoS2/WS2 van der Waals Heterobilayer. *Nano Letters* **2017,** *17*, 5634-5640.

30. Shi, Y.; Zhou, W.; Lu, A.-Y.; Fang, W.; Lee, Y.-H.; Hsu, A. L.; Kim, S. M.; Kim, K. K.; Yang, H. Y.; Li, L.-J.; Idrobo, J.-C.; Kong, J. van der Waals Epitaxy of MoS2 Layers Using Graphene As Growth Templates. *Nano Letters* **2012,** *12*, 2784-2791.

31. Xue, Y.; Zhang, Y.; Liu, Y.; Liu, H.; Song, J.; Sophia, J.; Liu, J.; Xu, Z.; Xu, Q.; Wang, Z.; Zheng, J.; Liu, Y.; Li, S.; Bao, Q. Scalable Production of a Few-Layer MoS2/WS2 Vertical Heterojunction Array and Its Application for Photodetectors. *ACS Nano* **2016,** *10*, 573-580.

32. Choudhary, N.; Park, J.; Hwang, J. Y.; Chung, H.-S.; Dumas, K. H.; Khondaker, S. I.; Choi, W.; Jung, Y. Centimeter Scale Patterned Growth of Vertically Stacked Few Layer Only 2D MoS2/WS2 van der Waals Heterostructure. *Scientific Reports* **2016,** *6*, 25456.

33. Chen, X.; Park, Y. J.; Das, T.; Jang, H.; Lee, J.-B.; Ahn, J.-H. Lithography-free plasma-induced patterned growth of MoS2 and its heterojunction with graphene. *Nanoscale* **2016,** *8*, 15181-15188.

34. Kim, H.-J.; Kim, H.; Yang, S.; Kwon, J.-Y. Grains in Selectively Grown MoS2 Thin Films. *Small* **2017,** *13*, 1702256.

35. Han, G. G. D.; Tu, K.-H.; Niroui, F.; Xu, W.; Zhou, S.; Wang, X.; Bulović, V.; Ross, C. A.; Warner, J. H.; Grossman, J. C. Photoluminescent Arrays of Nanopatterned Monolayer MoS2. *Advanced Functional Materials* **2017,** *27*, 1703688.

36. Jung, Y.; Shen, J.; Liu, Y.; Woods, J. M.; Sun, Y.; Cha, J. J. Metal Seed Layer Thickness-Induced Transition From Vertical to Horizontal Growth of MoS2 and WS2. *Nano Letters* **2014,** *14*, 6842-6849.

37. Mahjouri-Samani, M.; Lin, M.-W.; Wang, K.; Lupini, A. R.; Lee, J.; Basile, L.; Boulesbaa, A.; Rouleau, C. M.; Puretzky, A. A.; Ivanov, I. N.; Xiao, K.; Yoon, M.; Geohegan, D. B. Patterned arrays of lateral heterojunctions within monolayer two-dimensional semiconductors. *Nature Communications* **2015,** *6*, 7749.

38. Cao, L.; Yang, S.; Gao, W.; Liu, Z.; Gong, Y.; Ma, L.; Shi, G.; Lei, S.; Zhang, Y.; Zhang, S.; Vajtai, R.; Ajayan, P. M. Direct Laser-Patterned Micro-Supercapacitors from Paintable MoS2 Films. *Small* **2013,** *9*, 2905-2910.

39. Lu, J.; Lu, J. H.; Liu, H.; Liu, B.; Chan, K. X.; Lin, J.; Chen, W.; Loh, K. P.; Sow, C. H. Improved Photoelectrical Properties of MoS2 Films after Laser Micromachining. *ACS Nano* **2014,** *8*, 6334-6343.

40. Jiang, L.; Wang, A.-D.; Li, B.; Cui, T.-H.; Lu, Y.-F. Electrons dynamics control by shaping femtosecond laser pulses in micro/nanofabrication: modeling, method, measurement and application. *Light: Sci. Appl.* **2018,** *7*, 17134.

41. Huang, M.; Zhao, F.; Cheng, Y.; Xu, N.; Xu, Z. Origin of Laser-Induced Near-Subwavelength Ripples: Interference between Surface Plasmons and Incident Laser. *ACS Nano* **2009,** *3*, 4062-4070.

42. Shuangshuang, H.; Yanyan, H.; Pingxin, X.; Yi, Z.; Shian, Z.; Tianqing, J.; Zhenrong, S.; Jianrong, Q.; Zhizhan, X. Formation of long- and short-periodic nanoripples on stainless steel irradiated by femtosecond laser pulses. *Journal of Physics D: Applied Physics* **2011,** *44*, 505401.

43. Xia, B.; Jiang, L.; Li, X.; Yan, X.; Zhao, W.; Lu, Y. High aspect ratio, high-quality microholes in PMMA: a comparison between femtosecond laser drilling in air and in vacuum. *Applied Physics A* **2015,** *119*, 61-68.

44. Paradisanos, I.; Kymakis, E.; Fotakis, C.; Kioseoglou, G.; Stratakis, E. Intense femtosecond photoexcitation of bulk and monolayer MoS2. *Applied Physics Letters* **2014,** *105*, 041108.

45. Serincan, U.; Kartopu, G.; Guennes, A.; Finstad, T. G.; Turan, R.; Ekinci, Y.; Bayliss, S. C. Characterization of Ge nanocrystals embedded in SiO 2 by Raman spectroscopy. *Semiconductor Science and Technology* **2004,** *19*, 247.

46. Nesheva, D.; Raptis, C.; Perakis, A. Raman scattering and photoluminescence from Si nanoparticles in annealed SiOx thin films. *Journal of Applied Physics* **2002,** *92*, 4678-4683.

47. Wei, X.; Yu, Z.; Hu, F.; Cheng, Y.; Yu, L.; Wang, X.; Xiao, M.; Wang, J.; Wang, X.; Shi, Y. Mo-O bond doping and related-defect assisted enhancement of photoluminescence in monolayer MoS2. *AIP Adv.* **2014,** *4*, 123004.

48. da Silveira Firmiano, E. G.; Rabelo, A. C.; Dalmaschio, C. J.; Pinheiro, A. N.; Pereira, E. C.; Schreiner, W. H.; Leite, E. R. Supercapacitor electrodes obtained by directly bonding 2D MoS2 on reduced graphene oxide. *Adv. Energy Mater.* **2014,** *4*.

49. Hollinger, G. Structures chimique et electronique de l'interface SiO2-Si. *Applications Surf. Sci.* **1981,** *8*, 318-336.

50. Shuxian, Z.; Hall, W. K.; Ertl, G.; Knözinger, H. X-ray photoemission study of oxygen and nitric oxide adsorption on MoS2. *J. of Catal.* **1986,** *100*, 167-175.

51. Finster, J.; Klinkenberg, E.-D.; Heeg, J.; Braun, W. ESCA and SEXAFS investigations of insulating materials for ULSI microelectronics. *Vacuum* **1990,** *41*, 1586-1589.

52. Colton, R. J.; Guzman, A. M.; Rabalais, J. W. Electrochromism in some thin‐film transition‐metal oxides characterized by x‐ray electron spectroscopy. *J. Appl. Phys.* **1978,** *49*, 409-416.

53. Chowdari, B.; Tan, K.; Chia, W.; Gopalakrishnan, R. X-ray photoelectron spectroscopic studies of molybdenum phosphate glassy system. *J. Non-cryst. Solids* **1990,** *119*, 95-102.

54. Nan, H.; Wang, Z.; Wang, W.; Liang, Z.; Lu, Y.; Chen, Q.; He, D.; Tan, P.; Miao, F.; Wang, X. Strong photoluminescence enhancement of MoS2 through defect engineering and oxygen bonding. *ACS Nano* **2014,** *8*, 5738-5745.

55. Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J.-C. Intrinsic structural defects in monolayer molybdenum disulfide. *Nano Lett* **2013,** *13*, 2615-2622.

56. Yan, Y.; Xia, B.; Ge, X.; Liu, Z.; Wang, J.-Y.; Wang, X. Ultrathin MoS2 nanoplates with rich active sites as highly efficient catalyst for hydrogen evolution. *ACS Appl. Mater. Interfaces* **2013,** *5*, 12794-12798.

57. Wang, X.; Zhang, T.-B.; Yang, W.; Zhu, H.; Chen, L.; Sun, Q.-Q.; Zhang, D. W. Improved integration of ultra-thin high-k dielectrics in few-layer MoS2 FET by remote forming gas plasma pretreatment. *Applied Physics Letters* **2017,** *110*, 053110.

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