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Maskless Micro/Nanopatterning and Bipolar Electrical-Rectification Electrical Rectification of MoS₂ Flakes Through Femtosecond Laser Direct Writing

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Abstract

MoSMolybdenum disulfide (MoS₂) micro/nanostructures are desirable for tuning electronic properties, developing required functionality, and improving the existing performance of multilayer MoS₂ devices. This work presents a useful method to flexibly microprocess multilayer MoS₂ flakes through femtosecond laser pulse direct writing, which can directly fabricate regular MoS₂ nanoribbon arrays with ribbon widths of 179, 152, 116, 98, and 77 nm, and arbitrarily pattern MoS₂ flakes to form micro/nanostructures such as single nanoribbon, labyrinth array, and cross structure. This method is mask-free and simple,simple and has high flexibility, strong controllability, and high precision. Moreover, numerous oxygen molecules are chemically and physically adsorbed on laser-processed MoS₂, attributed to roughness defect sites defect sites and edges of micro/nanostructures that contain numerous unsaturated edge-sites edge sites and highly active centres centers. In addition, electrical tests of the field effect field-effect transistor fabricated from the prepared MoS₂ nanoribbon arrays reveal new interesting features: output and transfer characteristics exhibit a strong rectification (not going through zero and bipolar conduction) of drain-source current, which is supposedly attributed to the parallel structures with many edge-defects edge defects and p-type chemical doping of oxygen molecules on MoS₂ nanoribbon arrays. This work demonstrates the ability of femtosecond laser pulses to directly induce micro/nanostructures, property changes, and new device-properties device properties of two-dimensional materials, which may future enable new applications atin electronic devices based on MoS₂ such as logic circuits, complementary circuits, chemical sensors, and p-np-n diodes.

Keywords

MoS₂ flakes; femtosecond laser direct writing; micro/nanopatterning; oxygen bonding; electrical rectification

INTRODUCTIONIntroduction

ASSOCIATED CONTENTSupporting Information.AUTHOR INFORMATIONCorresponding AuthorAuthor ContributionsFunding SourcesNotesThe authors declare no competing financial interest.For Table of Contents OnlyTransition metal_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, optical properties, and great promise for extensive applications. 1–6 Molybdenum disulfide (MoS₂), representative material belonging to the TMDC group, has layered structures composed of a layer of molybdenum atoms sandwiched between two layers of sulfur atoms. 7,8 Unlike graphene with zero-band-gap, a zero band gap, MoS₂ is a band-gap-band gap semiconductor with a sizable energy band gap:5,9 bulk MoS₂ has an indirect energy gap of 1,2,1,2 eV and monolayer MoS₂ has a direct band gap of 1,8,1,8 eV.3 Hence, MoS₂ can serve as a promising candidate of graphene, graphene and has excellent potential in semiconductor-related applications of layered materials such as thin-film transistors, 1,10 integrated circuits, 11,1,1,1,1,1,2 complementary inverter, 13 photodetectors, 14 light-emitting diodes, 15,16 photovoltaics, 17,18 superconductors, 19,20 and chemical/biological sensors. 21,22

To achieve desirable the desired electronic properties and required functionality or improve the 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.^{3,23} Hence, it is crucial to conduct research on MoS₂ patterning with ordered micro/nanostructures, controlled structure-size, structure size, and new features for device application. Several approaches have been attempted to pattern MoS₂ materials or fabricate micro/nanostructures of MoS₂ deposited on substrates, including tape exfoliation,^{24,25} chemical vapor deposition (CVD),^{26,27} thermal decomposition of thiosalts,²⁸ van der Waals epitaxial growth,^{29,30} patterned MoO₃ sulfurization,^{31,32} CVD in plasma-treated areas,^{33,34} block eopelymercopolymer lithography,³⁵ reactive ion etching (RIE) combined with deposition in plasma-treated areas, lithography combined with stamping,²³ lithography combined with RIE,^{36,37} and continuecontinuous wave (CW) laser direct writing.^{38,39} Among them, CVD in plasma-treated areas, block copolymercopolymer lithography, lithography combined with deposition in plasma-treated areas, lithography combined with stamping, lithography combined with RIE, and CW laser direct writing can realize control for the location, shape, and size of MoS₂ micro/nanostructures. Whereas, However, in the methods involving [AQ1] lithography, plasma surface treatment, and RIE, chemical organics (such as photoresist) and inorganic or organic masks are used, combined process are required, and the integral

process is relatively complex. CW laser direct writing is a simple_one-step process and is simple, process, needs_no special atmosphere system and mask are needed, cost is mask, has a relatively low, low cost, and has high flexibility and controllability are high. Whereas, controllability. However, the CW laser processing is a thermal process, and the strong thermal effect would cause thermal oxidization of materials and large recasting layer, hence processing precision is insufficient. Femtosecond (ultrafast) laser pulse processing is another kind of laser processing technology. 40,41 Femtosecond laser pulses have an ultrashort pulse width, an ultrahigh power density, and nonlinear-nonequilibrium a nonlinear-nonequilibrium processing feature, and multiphoton absorption and nonthermal effecteffects can be realized, hence except realized; hence, almost all the advantages of CW laser processing, processing and femtosecond laser processing also possesses are expected as well as a high processing precision. 42-44

In this work, we proposed a useful method of utilizing femtosecond laser direct writing to modify the multilayer MoS₂ flakes, directly fabricate regular MoS₂ nanoribbon arrays with different ribbon widths, and arbitrarily pattern MoS₂ flakes to form different MoS₂ micro/nanostructures. Moreover, the laser-fabricated MoS₂ structures were chemically and physically bonded with numerous oxygen molecules in the air, attributed to the roughness defect-sites defect sites and long edges of the nanoribbons that may contain numerous unsaturated edge-sites edge sites and highly active centres centers. At last, electronic properties of MoS₂ nanoribbon arrays fabricated to be field-effect transistor (FET) were tested, and the output and transfer characteristics exhibited a strong rectification (not went through zero and exhibited bipolar conduction) of drain-source current. This rectification was supposedly attributed to the parallel structures with many edge-defects edge defects 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-the p-n junction. The proposed method had advantages of simplicity, maskless, masklessness, strong controllability, high flexibility, and high precision, precision and indicated the ability of femtosecond laser pulses to directly induce two-dimensiontwo-dimensional micro/nanostructures/patterns, property changes of two-dimensional material, and new device features.

RESULTS AND DISCUSSIONResults and Discussion

In this work, multilayer MoS₂ flakes were mechanically exfoliated from a natural crystal and deposited on 300 nm-SiO₂/Si substrates. The thickness of MoS₂ flakes selected for experiments was several to dozens of nanometers. Schematic of our method of fabricating MoS₂ nanoribbons/patterns is shown in Figure 1a, which is based on the formation of regular nanostructures and the material removal by femtosecond laser pulse irradiation. When focused femtosecond laser beam is irradiated on material surface, surface plasmons (SPs) of material can be induced, interference of which with incident laser field can lead to the formation of initial grating structures on material, then these initial grating structures can assist the coupling of SPs and incident laser field, leading to the further formation of final grating structures with deeper gaps. 45 The depth of gaps of laser-induced grating structures is influenced by the number and energy of ultrafast laser pulses on the unit area of material, and can be on a micrometer scale. 42,46,47 The MoS₂ used in our experiment was nano-scale a nanoscale thin flake, therefore controlling flake; therefore, keeping the scan speed of laser beam enough (laser pulse number on unit area of MoS₂ enough large)large enough) can control the gaps penetrating the whole MoS₂ thin flake, enabling surface nanogratings to become independent nanoribbons. Figure 1b shows the optical comparison of pristine MoS2 with femtosecond laserprocessed (FLP-) MoS2, which showed obviously an obvious optical color change of the MoS2 flake after femtosecond laser irradiation, indicating the change in the thickness or surface roughness. Figure 1c shows the atomic force microscope (AFM) results of the MoS₂ flake in Figure 1b, which indicates the reduction of the outline height of the FLP-MoS₂ flake, suggesting a thinning effect fem to second laser processing on MoS₂. Figure 1d shows the high resolution high-resolution AFM image of FLP-MoS₂, which indicated the formation of MoS₂ grating structures.

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

To further 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 shows regular MoS₂ nanoribbon arrays with different ribbon widths of approximate approximately 179, 152, 116, 98, and 77 nm, respectively. Figure 2f shows two independent MoS₂ nanoribbons with small and big widthwidths of 56 and 420 nm, respectively. Figure 2g,h showshows two kindkinds of MoS₂ patterned structures obtained through material removal by femtosecond laser direct writing, which were a labyrinth array and a cross structure, indicating the flexible processing capability of femtosecond laser for arbitrary patterns. The formation way of MoS₂ micro/nanostructures and the dependence of widths of nanoribbons on laser processing parameters (pulse energy and scan speed) are analyzed in the Supporting Information.

2—.FLP-MoS₂ micro/nanostructures and patterns. (a-e)(a-e) SEM images of regular MoS₂ nanoribbon arrays with widths of 179, 152, 116, 98, and 77 nm, respectively. (f) SEM images of two independent MoS₂ nanoribbons with widthwidths of (above) 56 and (below) 420 nm. SEM images of (g) MoS₂ labyrinth array and (h) MoS₂ cross structure. The laser processing parameters for MoS₂ micro/nanostructures are shown in Table S1.

To investigate the formation of MoS_2 nanoribbons rather than surface structures on MoS_2 , energy dispersive energy-dispersive X-ray (EDX) analysis was performed. Figure 3a-c show a-c shows the SEM images of the edge of a FLP- MoS_2 flake, and its S and Si EDX mapping images. The greygray part denotes MoS_2 , black part denotes the substrate, and regular stripestriped structures were obtained through femtosecond laser processing (Figure 3a). Figure 3b shows clearly separated MoS_2 nanoribbons, and Figure 3c shows the clear gaps between these MoS_2 nanoribbons. Figure 3d-fd-f shows the SEM image of MoS_2 nanoribbon array, and its S and Si EDX mapping images, which also indicated the separation of MoS_2 nanoribbons, thus evidencing the formation of MoS_2 nanoribbons.

3.-. The formation of separated MoS₂ nanoribbons. (a) SEM image of the edge of a FLP-MoS₂ flake, flake and its (b) S and (c) Si EDX mapping images. (d) SEM image of MoS₂ nanoribbon arrays, arrays and its (e) S and (f) Si EDX mapping images. The laser processing parameters were pulse energy of 0.015 µJ, JJ, scan interval of 0.5 µm, um, and scan speed of 5 µm/s. um/s.

To investigate the change in chemical property of FLP-MoS₂ flaks, flakes. Raman and X-ray photoelectron spectroscopy (XPS) characterizations were conducted. Figure 4a-d showa-d shows the Raman spectra of pristine (P-) MoS2 and FLP-MoS2. There was no Raman $\frac{\text{peak}_{\text{peaks}}}{\text{peaks}}$ at 820 cm $^{-\frac{41}{2}}$ originating from MoO₃, which $\frac{\text{indicted}_{\text{indicated}}}{\text{indicated}}$ no formation of MoO₃, thus no $\frac{\text{obviously}_{\text{obvious}}}{\text{obviously}}$ thermal oxidation for FLP-MoS $_2$, 48 due to the $\frac{\text{non-thermal}}{\text{nonthermal}}$ effect of femtosecond laser processing. 42 No Raman peak of SiO $_2$ at 520 cm⁻¹ was detected on the P-MoS₂ flake, flake; however, an obviously obvious Raman peak of SiO₂ was detected on the FLP-MoS₂ flake, which indicated that the substrate was also detected on the FLP-MoS₂ flake. 49,50 This result also proved the separation of MoS₂ nanoribbons and penetrating gaps between them, consistent with the results in Figure 3. XPS Mo and O spectra of P-MoS₂ and FLP-MoS₂ are also shown in Figure 4, and their S 2p spectra are shown in Figure S8. The Mo 3d spectra of P-MoS2 is are shown in Figure 4b, which reveals three peaks (227.2, 229.3, and 232.4 eV) respectivelyeV), respectively, assigned to the S 2s orbital of the divalent sulfur, and the Mo⁴⁺ 3d_{5/2} and 3d_{3/2} orbitals of the tetravalent molybdenum. However, in Mo 3d spectra of FLP-MoS₂ (Figure 4e), except the three peaks as shown in pristine MoS₂, there is a new peak at ~ 235 ~ 235 eV, which is assigned to the Mo⁶⁺ 3d_{3/2} orbital of the hexavalent molybdenum (calculated content of Mo⁶⁺ in all Mo is shown in Table S2). The Mo⁶⁺ in FLP-MoS₂ was attributed to Mo-O-the Mo-O bonds formed through the combination of oxygen combined with unsaturated Mo bonds, defect-sites, defect sites, or edge of nanoribbons that are generated from the damage and material removal of MoS₂ induced by femtosecond laser pulses. 51,52 Figure 4c shows the O 1s spectra for P-MoS₂, which reveals two peaks (532.6 and 533.4 eV) respectively assigned to divalent oxygen from Si-OSi-O bonds and oxygen (zero valent) molecules that physically adsorbed on MoS₂ surface (O₂/MoS₂).^{53–55} The divalent oxygen from Si-OSi-O bonds came from the 300 nm SiO₂/Si substrate, and oxygen (zero valent) molecules adsorbed on the MoS₂ surface should be attributed to the intrinsic defect and edge of the flake, flakes, which were active sites with physical adsorption capacity. However, in the O 1s spectra for FLP-MoS₂ (Figure 4f), except the strong and dominant peak assigned to divalent oxygen from Si-OSi-O bonds as shown in P-MoS2, it revealed a stronger peak of a zero-valent oxygen of O₂/MoS₂, indicating the physical adsorption of more oxygen molecules on the MoS₂ surface; it also revealed a new peak at \sim 530.5 eV that \sim 530.5 eV, which is assigned to the divalent oxygen from Mo-OMo-O bonds, 56,57 in accordance with the result of XPS Mo 3d spectra (calculated content of O₂ and O-MoO-Mo in all O is shown in Table S2). These results indicated that more oxygen atoms/molecules were chemically and physically combined with FLP-MoS₂. This can be attributed to the roughness surface defectsites defect sites on MoS2 nanoribbons and long edges of nanoribbons (the defects generated by femtosecond laser ablation are elaborated in the Supporting Information), for they contained numerous unsaturated edge sites, were had numerous highly active centres, centers, and hence can physically and chemically bonded with adsorbates such as O2 molecules (the chemical and physical reaction $\frac{\text{mechanism}}{\text{mechanisms}}$ of $\frac{\text{the}}{\text{laser-processed}}$ MoS₂ with oxygen molecules are speculated in $\frac{\text{the}}{\text{supporting}}$ Information). The oxygen absorption on MoS₂ not only led to the change in chemical valence of MoS₂, but also, according to previous reports, can lead to ptype doping effect on MoS2 with O2 as an electron acceptor and MoS2 as an electron donor (the schematic of the charge-transfer process is shown in Figure S9).⁵⁸

4--_Raman and XPS spectra of P-MoS₂ and FLP-MoS₂. (a) Raman spectra of P-MoS₂. XPS peak-split results of (b) Mo 3d and (c) O 1s spectra of P-MoS₂. (d) Raman spectra of FLP-MoS₂, indicating no thermal oxidation for MoS₂ processed by femtosecond laser. XPS peak-split results of (e) Mo 3d and (f) O 1s spectra of FLP-MoS₂. The laser processing parameters were pulse energy of 0.015 μJ,μJ, scan interval of 0.5 μm,μm, and scan speed of 5 μm/s.μm/s.

To evaluate the electronic properties of the prepared AQ2 AQ2

5-._Electrical test of MoS₂ NrA-FET. (a) Schematic of the structure and measurement of fabricated MoS₂ NrA-FET. (b) SEM image of MoS₂ nanoribbon arrays used for fabricating FET. (c) Output and (d) transfer characteristic curve of the fabricated MoS₂ NrA-FET. The laser processing parameters for NrA are pulse energy of 0.015 μJ,μJ, scan interval of 0.5 μm,μm, and scan speed of 10 μm/s.μm/s.

Figure 5d shows drain—source the drain—source current (I_{PSDS}) versus gate voltages (V_{PSDS}) characteristics of this NrA-FET under drain—source voltage (V_{PSDS}) ranging from 6 to 10 V. The trend of this transfer curve was non-monotone variation and exhibited a strong rectification of drain—source the drain—source current, which was different from the transfer characteristic curve of FET fabricated by using pristine/undamaged MoS₂ flake. As shown in Figure S10b, transfer characteristic curve of pristine/undamaged MoS₂ FET exhibited an entrype conduction. However, the transfer characteristic curve of MoS₂ NrA-FET exhibits a bipolar conduction, similar to pen the pen type transfer conduction (Figure 5d), with current chopping by a small voltage range. To further evaluate the electronic properties of this device, 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 drain—source the drain—source voltage (V_{PSDS}) of 10 V. The carrier mobility (μ), was calculated according to equation from reported reports, V_{PSDS} as shown in eq. 1

$$\mu = \frac{L}{W} \frac{d}{\varepsilon_0 \varepsilon_r} \frac{1}{V_{DS}} \frac{\partial I_{DS}}{\partial V_G}$$

where L and W are length and width of the FET channel, respectively; d, $\epsilon_{\underline{\ell}0}$, and $\epsilon_{\underline{\ell}\underline{\ell}}$ are thickness, vacuum permittivity, and relative $\ell_{\underline{\ell}0}$

permittivity of the grid dielectric layer, respectively; $\overline{\delta V_G}$ can be calculated from the $I_{DSDS} - V_{GS}$ curve. For this FET device, the length and width of the channel were $L \approx 3.4 \, \mu\text{m}_{\mu\text{m}}$ and $W \approx 6.6 \, \mu\text{m}$; μm , respectively; the grid dielectric layer was SiO₂, its thickness, vacuum permittivity, and relative permittivity were $d \approx 300 \, \text{nm}$, $\epsilon_{E0} \approx 8.85 \, \text{m} \cdot 10^{-1212} \, \text{F/m}$, and $\epsilon_{E\eta} \approx 3.9 \, \text{F/m}$, respectively. Hence, carrier mobility of this device was calculated to be approximately $2.6 \, \text{m} \cdot 10^{-33} \, \text{cm}^2 \, \text{V/V/s}$. The SS was calculated according to equation from previous reports, $\epsilon_{E0} \approx 1.0 \, \text{m} \cdot 10^{-1212} \, \text{m}$.

$$SS = \frac{\Delta V_{G}}{\Delta log I_{DS}}$$

and SS of this device was calculated to be -21-21 V/dec according to eq 2. The obvious strong rectification behavior of $l_{DSDS}-V_{DSDS}$ and $l_{DSDS}-V_{DSS}$ of the MoS₂ NrA-FET indicated the property change of material and new device properties, which may enable new applications at electronic devices based on MoS₂ such as logic circuits, complementary circuits, chemical sensors, and p-np-n diodes. In addition, moderate surface modification of MoS₂ flakes by femtosecond laser pulses would also tune the n-type electronic properties of MoS₂ FET: as shown in Figure S10, the on/off ratio of MoS₂ FET was increased by two magnitude; as shown in Figure S11, the drain—source current (l_{DSDS}) increased quicker and reached saturation faster with the increase of gate voltages (V_{CS}).

CONCLUSIONS Conclusions

Femtosecond laser direct writing was used to nonthermally modify the multilayer MoS2 flakes, induce separated MoS2 nanoribbon arrays, and arbitrarily pattern MoS₂ flakes to form different MoS₂ micro/nanostructures. Optical microscope, microscopy. AFM, and SEM were performed to characterize the physical micromorphology of laser processed-MoSlaser-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 nonthermal effect of the femtosecond laser processing, also proved the separation of MoS₂ nanoribbons and penetrating gaps between them. XPS spectra indicated that more oxygen molecules were chemically and physically physically bonded to FLP-MoS2, which was attributed to the roughness defect sites on MoS2 nanoribbons and the long edges of nanoribbons that contained numerous unsaturated edge sites and highly active centres, centers. A MoS₂ NrA-FET was fabricated and electrical tests were conducted to evaluate the electronic properties of the prepared MoS₂ nanoribbon arrays. Results indicated that output and transfer characteristic curves exhibited a strong rectification (not going through zero and bipolar conduction) of drain-sourcedrain-source current, which were different from that of FET fabricated by using pristine/undamaged MoS₂ flake. This may be attributed the parallel structures with many edge-defects edge defects 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 pnp_n junction. At last, the on/off ratio, carrier mobility, and SS were also calculated. The proposed method indicated the ability of femtosecond laser pulses to directly induce two-dimension nanostructures, propertytwo-dimensional nanostructures and change in material, the properties of the material and new device properties, device, which may future enable new applications atas electronic devices based on MoS₂ such as logic circuits, complementary circuits, chemical sensors, and p-np-n diodes.

METHODS Methods

Femtosecond laser processing System: Laser Processing System

The light path setup of our femtosecond laser processing system was reported in our previous study.⁸ The microscope objective $\frac{(50 \times, 100)}{(50 \times, 100)}$ was used to focus laser beam.

Characterization of MoS₂ nanostructures: Nanostructures

The optical images were obtained utilizing an Olympus microscope. The AFM characterization was carried out utilizing a SPM-960 AFM. The SEM images and EDX mapping spectra were obtained utilizing a Hitachi scanning electron microscope. Raman spectra were obtained utilizing a Renishaw InVia Reflex spectrometer (532 nm light source). XPS spectra was performed utilizing a PHI Quantera X-ray photoelectron spectrometer.

Device fabrication and electrical characterization: Electrical Characterization

Multilayer MoS_2 flakes were placed on p + Si/SiO_2 (300 nm) substrates and processed by femtosecond laser pulse. Then the substrates were spin-coated with poly methyl polymethyl methacrylate (PMMA) solution. The source and drain electrodes were fabricated through three main steps: standard electron-beam lithography (EBL) was performed by a Zeiss Supra55 SEM and Raith pattern generator to pattern the PMMA masks; 5 nm Ti/75 nm Au were deposited through electronic beam evaporation; a lift-off process was performed in acetone. The electrical measurements of the fabricated MoS_2 FET were performed by using a Keithley 4200 semiconductor characterization system in air and at room temperature.

Supporting information

The Supporting Information is available free of charge on the ACS Publications website. Supplementary table of laser Laser processing parameters for parameters: [AQ3] MoS₂ micro/nanostructures; supplementary analysis for the formation way of MoS₂ micro/nanostructures; dependence of widths of nanoribbons on laser processing parameters; defects generated by femtosecond laser ablation, and ablation; chemical/physical reaction mechanism of laser-processed MoS₂ with oxygen molecules; table of quantitative XPS results; supplementary electrical test results of MoS₂ FETs with moderate surface modification by femtosecond laser pulses (PDF)

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