Controlled Plasma Thinning of Bulk MoS$_2$ Flakes for Photodetector Fabrication

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Supporting Information

ABSTRACT: The electronic properties of layered materials are directly determined based on their thicknesses. Remarkable progress has been carried out on synthesis of wafer-scale atomically molybdenum disulfide (MoS$_2$) layers as a two-dimensional material in the past few years in order to transform them into commercial products. Although chemical/mechanical exfoliation techniques are used to obtain a high-quality monolayer of MoS$_2$, the lack of suitable control in the thickness and the lateral size of the flakes restrict their benefits. As a result, a straightforward, effective, and reliable approach is widely demanded to achieve a large-area MoS$_2$ flake with control in its thickness for optoelectronic applications. In this study, thick MoS$_2$ flakes are obtained by a short-time bath sonication in dimethylformamide solvent, which are thinned with the aid of a sequential plasma etching process using H$_2$, O$_2$, and SF$_6$ plasma. A comprehensive study has been carried out on MoS$_2$ flakes based on scanning electron microscopy, atomic force microscopy, Raman, transmission electron microscopy, and X-ray photoelectron microscopy measurements, which ultimately leads to a two-cycle plasma thinning method. In this approach, H$_2$ is used in the passivation step in the first subcycle, and O$_2$/SF$_6$ plasma acts as an etching step for removing the MoS$_2$ layers in the second subcycle. Finally, we show that this technique can be enthusiastically used to fabricate MoS$_2$-based photodetectors with a considerable photoresponsivity of 1.39 A/W and a response time of 0.45 s under laser excitation of 532 nm.

1. INTRODUCTION

Today, two-dimensional (2D) materials have attracted increasing interest because of their outstanding physical and chemical properties. Until now, a variety of 2D structures such as graphene, transition-metal dichalcogenides (MoS$_2$ and WS$_2$), Franckeite, monoelemental materials (phosphor-ene, silicone, and germanene), hexagonal boron nitride, and layered metal oxide materials (In$_2$O$_3$) have been extensively investigated and widely used in many ongoing research studies. Among these large number of 2D materials, molybdenum disulfide (MoS$_2$) has attracted much attention for its excellent properties such as thickness-tunable band gap$^9$ and remarkable field effect mobility$^{10,11}$ in addition, a MoS$_2$ monolayer (a layer of molybdenum atoms coupled with layers of sulfur atoms in both sides via van der Waals interaction) undergoes an indirect to direct gap transition$^{12}$ making it a promising candidate for optoelectronic device applications such as phototransistors,$^{13}$ photodetectors,$^{14}$ light emitters,$^{15}$ solar cells,$^{16}$ and so on. To date, a variety of methods have been established to prepare layered MoS$_2$ nanosheets including mechanical exfoliation,$^{17}$ liquid-phase exfoliation,$^{18}$ physical/chemical vapor depositions (CVDs),$^{19,20}$ and hydrothermal synthesis.$^{21}$

Mechanical exfoliation is known as a low-throughput technique with difficulty in achieving desired large-scale monolayers.$^{22}$ Liquid-phase exfoliation is suitable for mass production. However, lack of control on sheet size and thickness as well as prolonged high-power sonications are responsible for nanometric dimension of mono and few layers of MoS$_2$, which dramatically limits their device applications.$^{23}$ In addition, residual solvents cannot be completely removed from the surface of sheets, which causes unwanted electrical properties.$^{24}$ Chemical/hydrothermal synthesis methods are associated with toxicity and high material consumption, and CVD techniques result in high cost and time-consuming growth of layers.$^{14,19,21}$ Therefore, efforts are underway to develop current methods or introduce new efficient techniques that promise a controlled preparation of MoS$_2$ few layers (in terms of size and thickness). Among all novel suggested techniques to yield mono and few layers of MoS$_2$, the layer-by-layer thinning process has attracted particular interest because of its significant control on reducing the thickness of flakes.

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while their lateral sizes are kept nearly unchanged. So far, various MoS2-based layer-by-layer thinning approaches have been reported in the literature such as physical plasma etching,25,26 laser thinning,27 thermal annealing thinning,28 electrochemical thinning,29 and dry chemical plasma etching.30,31 Physical plasma etching takes advantage of high-energy heavy ion bombardment (Ar+ or O−) to atomically remove the layers.32 An increase in surface roughness and severe physical damages to the thinned flakes are some drawbacks of this method.25,32 Laser thinning is able to yield only monolayers of MoS2, whose resolution is restricted by optical diffraction limitation.33 In other side, thermal annealing thinning (in O2, Ar, or steam vapor atmospheres) requires a high operating temperature (250−650 °C) and long processing time.28,34 In a different approach, electrochemical etching is used to eliminate the unwanted top layers in an aqueous electrolyte via a three-electrode electrochemical system.29 Based on it, an initial flake is thinned through electrochemical reactions between the flake surface and an ionic solution across a conductive working electrode. Introduction of impurities and the need for an extra transfer step (from working electrodes to electronic devices) are disadvantages of this technique.29 Unlike the mentioned methods, dry chemical plasma etching (SF6, XeF2, and CF4) has gained particular interest because of promising selective and soft layer thinning.30,35−37 Most of the previous works have focused on one reactive gas to etch MoS2 layers that result in a nonlinear etching rate with introducing unwanted surface compounds to the remained layers. To overcome the current problems, a sequential dry etching process with a combination of H2, O2, and SF6 gases is hereby proposed as a great solution to uniformly etch thick MoS2 flakes in a controlled and reliable method without increasing surface roughness or considerable change in the lateral dimensions. In addition, most of the previous reports have studied thinning of one flake but is here presented for a set of flakes with different thicknesses, which is much more practical and associated with the easier fabrication process.

In this technique, MoS2 flakes are moderately exfoliated with a low-power sonication in dimethylformamide (DMF) solvent and drop-cast onto the prepatterned Cr electrodes (Figures S1−S3), followed by two cycles of plasma irradiation (subcycle 1: H2 200 sccm, 200 W, and 30 s; subcycle 2: O2 200 sccm, 200 W, and 30 s). Atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) analyses are employed to evaluate the controlled layer-by-layer etching. In addition, a thinned MoS2-based photodetector is fabricated via our proposed technique, and corresponding photoresponsivity is investigated under different wavelengths and optical power illuminations. In detail, a photoresponsivity of ∼1.39 A/W is achieved under 532 nm laser irradiation at 0.5 V bias voltage at room temperature in air, while very poor optical response is observed for the device prior to plasma etching process.

Figure 1. SEM characterizations. (a) (i) Pristine flake. (ii) After 5 min of exposure to H2 plasma (200 sccm, 200 W). (iii) After 10 min of exposure to H2 plasma (200 sccm, 200 W). (b) (i) Pristine flake. (ii) After 5 min of exposure to O2 plasma (200 sccm, 200 W). (iii) After 10 min of exposure to O2 plasma (200 sccm, 200 W). (c) (i) Pristine flake. (ii) 20-cycle plasma sequence (subcycle 1: H2 200 sccm, 200 W, and 30 s; subcycle 2: O2 200 sccm, 200 W, and 30 s). (iii) 40-cycle plasma sequence (subcycle 1: H2 200 sccm, 200 W, and 30 s; subcycle 2: O2 200 sccm, 200 W, and 30 s).
2. RESULTS AND DISCUSSION

2.1. Effect of H$_2$, O$_2$, and H$_2$/O$_2$ Plasma Etching Treatment. In order to obtain plenty of thick MoS$_2$ flakes, a few droplets of MoS$_2$ dispersion is drop-cast on Si substrates and air-dried at 70 °C for 24 h. A number of flakes are inspected using SEM imaging prior to any plasma treatment. To evaluate the impact of H$_2$, O$_2$, and H$_2$/O$_2$ plasma bombardment on the MoS$_2$ flakes, samples are placed in a reactive-ion etching (RIE) chamber. According to it, the samples are initially exposed to the given plasma at 200 W plasma power for 5 min at room temperature. The field emission SEM (FE-SEM) images of some selected as-prepared flakes are shown in part i of Figure 1a–c. After a 5 min exposure to H$_2$ plasma at a flow rate of 200 sccm (part ii of Figure 1a), the flakes do not bear any trace of exfoliation. To ensure, the H$_2$ plasma is exposed to the flakes for a further 5 min, which results in no etching. It seems that the H$_2$ plasma does not have the potential to thin the MoS$_2$ flakes. Figure 1b shows the FE-SEM image of a MoS$_2$ flake before and after O$_2$ plasma etching. The bombardment is performed at a plasma power of 200 W for two individual 5 min at a flow rate of 200 sccm. According to part ii of Figure 1b, after 5 min of O$_2$ plasma exposures, the flakes are partially exfoliated in some regions, but it is observed that plasma thinning is done slowly and nonuniformly. The O$_2$ plasma etching is done for another 5 min, which results in further etching of the flakes, however, in an anisotropic profile (part iii, Figure 1b). It is worth noting that a process with uniform thinning and a reasonable etching rate is desirable while oxygen and hydrogen plasma do not show this capability.

To further study the effect of O$_2$ and H$_2$ plasma on flakes, the ability of sequential H$_2$/O$_2$ plasma cycle in removing the MoS$_2$ layers is evaluated. Plasma etching process is done in a 20-cycle sequence where gases are fed into the chamber in two separate subcycles. At the first subcycle, a 200 sccm H$_2$ gas is introduced into the chamber and samples are exposed to H$_2$ plasma at 200 W power for 30 s. At the second subcycle, a 200 sccm O$_2$ gas is fed into the chamber and plasma at 200 W power is applied to the samples for 30 s. According to the FE-SEM images, flakes are not thinned at the end of the 20-cycle sequence process. To ensure that the flakes are not etched, the process continues for another 20 cycles. Part iii of Figure 1c presents the SEM image of the MoS$_2$ flake after a 40-step H$_2$/O$_2$ plasma treatment, through which any trace of thinning can be observed. This result shows that H$_2$ plasma tends to passivate the upper layer of the MoS$_2$ flakes, while O$_2$ plasma etching is physically dominated. In other words, hydrogen ions interact with sulfur vacancies or edge sites and prevent them from reacting with oxygen radicals. This fact helps us to develop an effective method to thin MoS$_2$ flakes. Moreover, to further clarify the impact of H$_2$/O$_2$ plasma on flakes, simultaneous plasma bombardment of both oxygen and hydrogen gases is investigated on the pristine flakes. The pristine flakes are exposed to H$_2$/O$_2$ plasma (200 sccm:200 sccm) at 200 W power for 5 min at room temperature. However, no evidence of layer etching is observed after this plasma irradiation (Figure S4). It seems that in the competition between the H$_2$ passivation and the physical O$_2$ etching, the first is the winner.

2.2. Effect of SF$_6$, H$_2$/SF$_6$, and O$_2$/SF$_6$ Plasma Etching Treatment. According to the previous section, the hydrogen plasma has a passivation effect on MoS$_2$ flakes, whereas oxygen plasma performs physical etching. However, O$_2$ plasma shows poor uniformity and slow etching rate that limit its potential to thin the initially thick MoS$_2$ flakes. Therefore, in order to find an efficient method, the effect of SF$_6$ plasma gas on MoS$_2$ flakes is studied. Accordingly, an SF$_6$ plasma (200 sccm, 200 W, 2 min) is applied to the as-prepared MoS$_2$ flake in an RIE chamber at room temperature. During plasma irradiation, SF$_6$ molecules decompose into highly reactive F radicals that easily etch flakes. Figure 2a shows the MoS$_2$ flakes before (part i) and after (part ii) SF$_6$ plasma treatment. It can be clearly seen that most of the MoS$_2$ flakes are deeply and anisotropically etched after only 2 min of plasma exposure (part ii of Figure 2a). Therefore, in contrast to H$_2$ and O$_2$ plasma, SF$_6$ plasma can aggressively thin MoS$_2$ flakes. It is an important point that SF$_6$ plasma etching cannot be considered as a desirable method because controlled isotropic plasma thinning is preferred while the presence of active fluorine radicals results in rapid removal of the MoS$_2$ layers.

To slow down the etch rate of layers, the combination of SF$_6$, H$_2$, and O$_2$ plasma is investigated. As a result, two different processes are introduced based on the SF$_6$/O$_2$ and SF$_6$/H$_2$ plasma to evaluate their impact on MoS$_2$ flakes. Figure 2b shows the MoS$_2$ flake before (part i) and after SF$_6$/H$_2$ plasma treatment (part ii) with no noticeable thinning. Accordingly, SF$_6$ and H$_2$ gases are fed into the chamber at a flow rate of 50 and 200 sccm. The plasma power is set to 200 W and the whole process lasts for 2 min. During plasma treatment, fluorine radicals react with hydrogen ions to form hydrogen fluoride (HF) molecules and leave the chamber without any impact on the MoS$_2$ flakes. Therefore, it is
observed that the SF₆/H₂ plasma irradiation does not affect the flakes. In the next study, the effect of SF₆/O₂ plasma upon MoS₂ flakes is investigated. Consequently, SF₆ and O₂ gases with a flow rate of 50 and 200 sccm are entered into the chamber. The plasma power is adjusted to 200 W and the process is completed within 5 min. Figure 2c shows the FE-SEM images of the pristine and as-bombarded MoS₂ flakes. As can be seen, 5 min of plasma irradiation yields an incomplete and nonisotropic etching. During this process, the following reactions occur

\[ \text{SF}_6 + e \rightarrow \text{SF}_5 + F + e \]  
\[ \text{O}_2 + e \rightarrow 2\text{O} + e \]  
\[ \text{SF}_5 + \text{O} \rightarrow \text{SOF}_4 + \text{F} \]  
\[ \text{MoS}_2 + 6\text{F} \rightarrow \text{MoF}_6 + 2\text{SF}_6 \]

Therefore, the mixture of SF₆/O₂ plasma not only associates with the decrease in density of O/F free radicals but also results in highly volatile SOF₄ (a boiling point of −49.0 °C) and MoF₆ byproducts which leave the chamber without reaction. As a result, it is observed that oxygen and fluorine radicals play a major role in flake etching, and SF₆/O₂ mixture tends to be more efficient than individual SF₆ and O₂ gases in thinning of MoS₂ flakes.

2.3. Effect of H₂/O₂/ SF₆ and Sequential H₂/O₂/ SF₆ Plasma Etching Treatment. With regard to the results from the two previous sections, it would be understandable that SF₆ plasma has a high chemical etching potential, while O₂ plasma does physical etching, and passivation treatment is occurred by H₂ plasma. In the following, the effect of a mixture of SF₆, O₂, and H₂ plasma irradiations on the MoS₂ flakes is investigated. Accordingly, SF₆, O₂, and H₂ gases are fed into the chamber at flow rates of 50, 100, and 100 sccm. Figure 3a shows the Raman spectra of the pristine MoS₂ flakes before and after plasma irradiation. For bulk MoS₂, two characteristic peaks are observed around ~382 and ~407 cm⁻¹ corresponding to the E₂̂g and A₁̂g phonon modes. As can be seen, after H₂ plasma irradiation, no displacement occurred in the E₂̂g and A₁̂g peak positions, indicating no exfoliation or etching. For H₂/O₂ and H₂/SF₆ plasma irradiations, the E₂̂g peak has slightly suffered a red shift, while the A₁̂g peak shifted to the higher wave number. The origin of such shifts can be expressed as follows: the red shift of the E₂̂g peak is due to a strain induced by the ion interaction, while the blue shift of the A₁̂g peak is originated from the introduction of ions or removal of sulfur atoms in the flake surface. The peak shifts are more pronounced for H₂/O₂/ SF₆ plasma irradiation because more ions interact with the surface of the MoS₂ flakes. However, no evidence of flake exfoliation is observed in all samples.

In order to uniformly remove the layers, a method is established based on the two-subcycle plasma process including SF₆/O₂ etching and H₂ passivation subcycles. According to this method, in the first subcycle, oxygen and fluorine radicals etch the MoS₂ layers, and in the second subcycle, hydrogen ions passivate the sulfur vacancies. The role of the second subcycle is critical because it promises an isotropic etching profile. Figure 4a–c shows three different conditions of the applied plasma to the MoS₂ flakes. In all the three exposures, plasma power is set to 200 W and SF₆, O₂, and H₂ gases are fed into the chamber at flow rates of 50, 200, and 200 sccm, respectively. The only difference between them lies in the operating time of the etching subcycle. Figure 4a indicates the SEM images of the pristine (part i) and plasma-exposed MoS₂ flakes under the plasma condition of 20 sequential cycles with 30 s etching and 30 s passivation subcycles (part ii). As shown in part ii, the flake is not properly thinned and etching is partially done on the MoS₂ surface. This nonuniformity may be originated from the long-time etching process compared to the corresponding passivation subcycle. To challenge it, the plasma exposing time is adjusted to 60 and 5 s for the etching step to see its impact on the final etching profile. By fixing the etching time to 60 s, the flake is dramatically etched in an anisotropic profile (part ii of Figure 4b), maybe due to the dominant chemical etching step. Moreover, by shortening the etching time to 5 s, evidence of etching is negligible (part iii of Figure 4c). These results highlight the key role of the etching subcycle and especially its time processing in the final etching profile of the MoS₂ flakes.
Considering the importance of the etching subcycle, the best etching time is observed to be 15 s, which provides the possibility of thinning the MoS$_2$ flakes to mono and few layers in a large lateral size. Figure 4 presents the results of 30 s passivation and 15 s etching steps for a pristine MoS$_2$ flake. As can be seen, after 20 sequential plasma irradiations, mono and few MoS$_2$ layers are obtained. The initial thickness of the pristine flake is about 157 nm (Figure 5a), which decreases to few nanometers after exposing to plasma. It is observed that each sequential plasma process (including two subcycles) can remove approximately 9–10 layers of the bulk MoS$_2$ flakes because the MoS$_2$ monolayer possesses a thickness of ~0.7 to 0.8 nm. Based on Figure 5b, a large fraction of the flake area is thinned into the monolayer, along with bi-, tri-, and few layers that can be due to the variation of the initial thickness of the pristine flake and also their orientation to plasma irradiation. Figure 5c shows the thickness measured by AFM, which is depicted on the SEM image in part (b), where different thicknesses are distinguished by colors. The height profile of the dashed arrow is also shown in Figure 5d. Figure 5e presents the differential reflectance spectra of the mono-, bi-, and more than 20 layers of the MoS$_2$ flakes.

Figure 4. SEM characterizations. SEM image of (a) (i) pristine MoS$_2$ flake (ii) after exposure to 20 sequential cycles. First subcycle of H$_2$ plasma at 200 W power for 30 s at a flow rate of 200 sccm. Second subcycle: O$_2$/SF$_6$ plasma (200 W) for 30 s at a flow rate of 200:50 sccm. (b) (i) Pristine MoS$_2$ flake (ii) after exposure to 20 sequential cycles. First subcycle of H$_2$ plasma at 200 W power for 30 s at a flow rate of 200 sccm. Second subcycle of O$_2$/SF$_6$ plasma (200 W) for 60 s at a flow rate of 200:50 sccm. (c) (i) Pristine MoS$_2$ flake (ii) after exposure to 20 sequential cycles. First subcycle of H$_2$ plasma at 200 W power for 30 s at a flow rate of 200 sccm. Second subcycle of O$_2$/SF$_6$ plasma (200 W) for 5 s at a flow rate of 200:50 sccm.

Figure 5. SEM, AFM, and differential reflectance characterizations: (a) SEM image of pristine MoS$_2$ flake with its corresponding height profile. (b) SEM image of the 20 sequential cycle plasma-exposed flake. First subcycle of H$_2$ plasma at 200 W power for 30 s at a flow rate of 200 sccm. Second subcycle of O$_2$/SF$_6$ plasma (200 W) for 15 s at a flow rate of 200:50 sccm. (c) Thickness measurement by AFM system corresponding to the SEM image in part (b) and distinguishing different thicknesses by colors. (d) Height profile of the dashed arrow in part (c). (d) Differential reflectance spectra of the mono-, bi-, and more than 20 layers of the MoS$_2$ flakes.

Figure 6. AFM characterization of the (a) pristine MoS$_2$ flake with its corresponding height profile (shown at the bottom). (b) After 20 sequential plasma exposure to 30 s H$_2$ and 15 s O$_2$/SF$_6$ with a power of 200 W. Corresponding height profile is shown at the bottom. (c) Raman spectroscopy of the pristine and plasma-thinned MoS$_2$ samples.
vibrational modes at a thickness of 1, 2, and more than 20 layers. According to it, a bulk MoS2 sample indicates laser beam to a plasma exposing. To measure the spectrum, it was tried to focus the laser beam to a plasma, and as a result, 20 sequential plasma irradiations are performed before and after the plasma thinning process. Our method has an etch rate of approximately 0.187 eV (A exciton) and ~2.04 eV (B exciton) relating to the direct transitions at the K point. The spectrum also reveals a wide peak about ~2.82 eV originating from singularities around the Γ point of the valence band. The A and C peaks demonstrate a strong thickness dependence, while the B exciton does not have any dependency. Accordingly, by the increase of MoS2 thickness, a red shift is observed in the spectra, which can be utilized to estimate the number of layers.

To further evaluate our technique, AFM and Raman analyses are conducted for the whole sample surface containing more flakes before and after plasma exposing. Based on the AFM measurement, the initial thickness of the selected flake is about 200 nm corresponding to ~250 layers of MoS2. Our method has an etch rate of ~10 layers per two cyclic plasma, and as a result, 20 sequential plasma irradiations are required to decrease the thickness to ~4 nm corresponding to approximately five layers of MoS2. The corresponding height profile of the flakes is presented at the bottom of Figure 6a. The thickness of the other flakes is also decreased dramatically. Moreover, Raman spectroscopy of the MoS2 sample is performed before and after the plasma thinning process. To measure the spectrum, it was tried to focus the laser beam to a fixed position in the samples before and after plasma exposing. According to it, a bulk MoS2 sample indicates two characteristic peaks known as in-plane (E2g) and out-plane (A1g) vibrational modes at ~382 and ~407 cm−1, respectively. After plasma irradiations, the corresponding Raman peaks are shifted to ~385 and ~405 cm−1 referring to successful thinning of the pristine bulk sample to few layer MoS2.

To better analyze our introduced method, TEM and XPS measurements are carried out for pristine and plasma-assisted thinned MoS2 flakes. The TEM image of the thinned MoS2 flake is presented in Figure 7a with a higher magnified image shown in Figure 7b. The TEM images exhibit electron transparent layers implying the high-level exfoliation of bulk flakes. Moreover, no evidence of porosity or damage to the MoS2 sheets is inspected in the TEM images as a result of plasma exposure process, indicating the clean/well thinning of flakes. In addition, the selected area electron diffraction (SAED) pattern reveals the hexagonal symmetry of the thinned flakes, which supports the high degree of crystallinity for the thinned 2H MoS2 sheets. The XPS spectra of the pristine and thinned MoS2 flakes are also shown in Figure 7d–g. For both MoS2 structures, the characteristic peaks of S 2p3/2, 2p1/2, S 2s, Mo4+ 3d3/2, Mo4+ 3d5/2, and O 1s are observed at 162.7, 164.0, 225.3, 229.0, 232.1, and 529.6 eV, respectively. Furthermore, additional peaks are found in the thinned MoS2 flakes as follows: 165.2, 235.0, 529.1, and 685.3 eV peaks that are associated with oxidation of sulfur, damage to the Mo−S bonding, S−O bonding, and fluorine incorporation in the remaining MoS2 surface, respectively. The atomic percentage of S, Mo, and O atoms is measured to be 53.4, 31.0, and 15.6% in the pristine MoS2 while it changes to 51.4, 30.2, and 14.7% for thinned flakes, respectively. Although the atomic percentage of oxygen is expected to experience an increase because of the presence of S−O bonding, the partially fluorinated surface of MoS2 slightly decreases the possibility of formation of oxygen bonding in the plasma-treated MoS2 flakes. As a result, an atomic percentage of 3.7% is calculated for F atoms originating from SF6 plasma irradiation and fluorine bonding with Mo atoms.

Table 1 provides a summary of all the plasma processes applied to the pristine MoS2 flakes, as well as the results of plasma exposure and their mechanism. According to the obtained data, it is observed that the H2 plasma passivates the sulfur vacancies on MoS2 surface. Moreover, hydrogen ions can react with fluorine radicals to form HF molecules and leave fluorine bonding with Mo atoms. As a result, an atomic percentage of 3.7% is calculated for F atoms originating from SF6 plasma irradiation and fluorine bonding with Mo atoms.
Table 1. Summary of the All-Plasma Treatments on the Pristine MoS₂ Flakes

| plasma | action | mechanism |
|--------|--------|-----------|
| H₂     | no etching | H₂ passivates sulfur vacancies |
| O₂     | slow etching rate | O₂ physically etches MoS₂ through sulfur vacancies |
| H₂/O₂  | no etching | H₂ passivates sulfur vacancies and prevents O₂ etching |
| SF₆    | high etching rate | F free radical reacts highly with MoS₂ and etch it |
| O₂/SF₆ | moderate etching rate | products: SO₂F₂ gas, F, and O radicals. Produce volatile gas and lower density of F and O radicals |
| H₂/SF₆ | no etching | F free radicals reacts with H ions and form an HF molecule that leaves the chamber |
| O₂/SF₆/H₂ | no etching | products are SO₂F₂ (~43.8 °C), SO₃F₂ (~55.4 °C), and F free radical which react with H and produce an HF molecule that leaves the chamber. Moreover, H₂ can passivate MoS₂ |
| subcycle 1: O₂/SF₆ | optimum etching | subcycle 1 produces F and O free radicals |
| subcycle 2: H₂ | etching | subcycle 2 passivates sulfur vacancies |
|        |         | moderate and isotropic etch |
|        |         | each sequence etches about 10 layers of MoS₂ |

Hence, the deposited solution covers almost the entire surface of the electrodes (as shown in Figure 8b). After 20 etching cycles (30 s H₂ and 15 s O₂/SF₆ plasma irradiation at a power of 200 W), the SEM image demonstrates thinned flakes with thickness about few nanometers according to the AFM measurement (inset of Figure 8c). By applying the plasma etching process, flakes considerably become thin while their lateral sizes experienced a slight change. Because the initial thickness of the flakes varies, during the plasma etching process, a portion of them is removed, leaving only a fraction of the sheets with a few nanometers in thickness. As shown in the inset of Figure 8c, the SEM image of the plasma-etched device displays highly transparent layers with a remarkable large lateral size. The AFM image of the device’s channel reveals a profile height of ∼5 nm referring to six or seven layers of MoS₂ (inset of Figure 8c). In addition, Raman spectroscopy (Figure 8d) shows two characteristic peaks at ∼384 and ∼404 cm⁻¹, which proves the presence of few MoS₂ layers within the device’s channel.³²

To fabricate a desired TMF photodetector, electrical and optical properties of the devices are evaluated after every five sequential plasma cycles. Prior to plasma exposure, the thickness distribution of the deposited flakes is counted by AFM analysis, and the electrical property of the devices is measured at a bias voltage of 0.5 V at room temperature (Figure 9a). It is observed that most of the devices possess electrical currents around 100–1000 μA with very poor optical response to laser excitation of 532 nm. After applying the plasma, at each step, a fraction of the device current is reduced mainly because of reduction in the flake’s thickness that results in an increase of the device electrical resistance. At the end of 15 plasma cycles, the devices exhibit poor optical response to laser excitation, where one further step of plasma etching process results in significant enhancement of the optical response of the devices. It can be deduced that after 20 steps of plasma exposure, the thickness of the flakes is thinned to a few nanometers, which is very well suited for investigation of the optoelectronic properties. As shown in Figure 9c, the thickness of the flakes is mostly decreased to the few nanometers. Any further attempts to improve the optical response of the devices are limited by the decrease of electrical current, as well as photoreponsivity of the devices. Finally, after 30 steps of plasma exposure, most devices turn into an open-circuit state and can no longer be used (Figure 9b).

Figure 8. (a) Plasma-assisted fabrication process of the MoS₂ photodetector. (b) SEM image of the device covered with pristine-thick MoS₂ flakes. (c) SEM image of the thinned MoS₂ flakes after exposing to 20 sequential plasma etching cycles. Inset shows higher magnified SEM image and AFM measurement of the plasma-thinned flakes. (d) Raman spectrum of the device channel corresponding to part c.
According to the obtained results, 20 plasma cycles are used in the oncoming fabrication of the MoS2-based photodetectors. Figure 10 gives results for the photoresponse performance of the TMF photodetector. Electrical characterization of the device is performed in dark and under laser illumination in air and at room temperature. A schematic illustration of the TMF photodetector and the corresponding measurement circuit are displayed in Figure 10a. According to energy band diagram of the bulk MoS2 and Cr contacts (Figure 10b), the electron affinity of MoS2 is ∼4.0 eV, and the Cr work function is equal to ∼4.5 eV, which results in a low Schottky barrier under equilibrium condition. Under laser illumination and biasing voltage, electron/hole pairs are generated in the thinned MoS2 and extracted from the channel (Figure 10c). Current-voltage characteristics (I−V) of the device are investigated in dark and under 532 nm laser illumination with 2.20 μW incident power before and after plasma etching process. Based on it, a relatively high current (up to 400 μA) is carried by the bulk MoS2 flake (b-MF) at a bias voltage of 0.5 V (Figure S5). According to the resistor network model, each MoS2 flake has a number of stacking layers with a finite interlayer resistance.

For flakes that are thick enough, it is observed that the bulk MoS2 sample shows a very poor optical response to the 532 nm laser irritation (Figure S5a), but we believe that the thinned MoS2 sheets are more sensitive than the bulk MoS2 flakes to the laser irradiation for two reasons. First, in the thinned MoS2 flakes, the charge carrier density is increased through the generation of the direct electron−hole pairs and unlike the bulk flakes do not require phonons. Second, an increase in the surface area of the thinned MoS2 sheets makes the separation of the electron−hole pairs much easier under an electric field. In contrast to the bulk photodetector, after the plasma etching process, the flakes are thinned to few nanometers and optical response will be considerably pronounced. In this case, at an operating voltage of 0.5 V, the current increased from ∼1.50 to ∼2.00 μA under 532 nm laser excitation (part b of Figure S5). The decrease of the dark current (about 260%) from b-MF to TMF is attributed to loss of flake's thickness because of plasma etching process. In the as-etched MoS2 flakes, defects (including sulfur vacancies, impurities, and surface damages) are highly dominant because of ion bombardments. Hence, the as-thinned flakes show poor electrical and optical characteristics (Figure S5b). To overcome this issue, the devices are moderately annealed at 120 °C in a vacuum chamber (at 12 mTorr) for 30 min. After annealing treatment, electrical and optical properties of the devices are significantly improved and a remarkable photocurrent response (∼1.50 μA) is observed in the TMF photodetector (Figure 10d). Figure 10e indicates the photoswitching characteristics of the device at different laser excitations and same drain voltage and optical power intensity. (f) Photoswitching characteristics of the device at different incident optical powers and same drain voltage and laser excitation.
various laser power illuminations (electrons/holes, causing the decrease of the corresponding increase and traps are able to capture a great deal of generation of excitons. Thus, the recombination rate would be by the fact that higher incident powers result in more increase of incident power. This behavior could be explained 11a gives data of the device photoresponsivity as a function of literature

As clearly observed, the photocurrent is considerably enhanced with the optical power. In detail, the generated photocurrents are measured to be about 1.52, 1.21, 1.03, and 0.75 μA for 375, 405, 455, and 532 nm, respectively. Moreover, the photo-switching properties of the device are measured at various optical powers at a same bias voltage. As shown in Figure 10f, the photocurrent is increased from 0.2 to 2.0 μA by the increase of laser intensity from 0.14 to 36.60 μW.

The photoresponsivity of the TMF photodetector is evaluated under different powers and wavelength laser illuminations. The photoresponsivity of the device was calculated based on the following equation

\[ R = \frac{I_{ph}}{PA_D/A_L} \]  

where \( I_{ph} \) is the photocurrent, \( P \) is the incident power, \( A_D \) is the device channel area, and \( A_L \) is the laser spot area. In the TMF photodetector, \( A_D \) is measured to be about 4500 μm² through SEM imaging, and laser illumination is focused at a spot diameter of 400 μm covering almost the entire device. Figure 11a gives data of the device photoresponsivity as a function of various laser power illuminations (\( \lambda = 532 \) nm) at a 0.5 V bias voltage. It is found that photoresponsivity decreases with the increase of incident power. This behavior could be explained by the fact that higher incident powers result in more generation of excitons. Thus, the recombination rate would be increased and traps are able to capture a great deal of electrons/holes, causing the decrease of the corresponding photoresponsivity. The photoresponsivity dependency on the power illumination is modeled by the power law, \( R \propto P^\beta \), where \( \beta \), the fitting parameter, is equal to −0.54. More precisely, the photoresponsivity was measured to be 1.39 A/W at a power intensity of 0.14 μW under 532 nm laser illumination and a bias voltage of 0.5 V, and the lowest value \( (R = 0.05 \text{ A/W}) \) was obtained at an incident power of 36.60 μW.

In addition, photoresponsivity versus excitation wavelengths is plotted in Figure 11b at a fixed power intensity of 2.20 μW and a bias voltage of 0.5 V. Based on it, photoresponsivities of 0.65, 0.52, 0.43, and 0.32 A/W are measured for the laser wavelength of 375, 405, 455, and 532 nm, respectively. It can be seen that with the increase of the wavelength, the photoresponsivity is clearly decreased because higher energy photons (or lower wavelength photons) transfer more energy to the electrons in MoS₂, which gives them more chance to overcome the traps or overpass possible barriers. Time-trace measurement of the fabricated TMF photodetector is demonstrated in Figure 11c. The rise and fall times of the photodetector are measured to be 0.45 and 1.88 s, respectively, under 532 nm laser illumination, at an incident power of 2.20 μW and a bias voltage of 0.5 V.

Table 2 shows various MoS₂-based photodetectors in which their performances are compared based on the laser excitation, bias voltage, photoresponsivity, and rise/fall times. In detail, the photoresponsivity of MoS₂-based photodetectors ranged from 0.40 mA/W to 1.10 A/W under 532 nm laser illumination. Compared to other previous reports, our TMF photodetector shows a high photoresponsivity (1.39 A/W) at a low operating voltage of 0.5 V with an acceptable response time \( (\tau_{rise} = 0.45 \text{ s} \text{ and } \tau_{fall} = 1.88 \text{ s}) \), which suggests an excellent photodetection device.

4. CONCLUSIONS

In summary, we have shown that the thick MoS₂ flakes can be thinned layer by layer by a sequential plasma irradiation. Based on it, at the first subcycle, H₂ passivates the sulfur vacancies, and at the second subcycle, O₂/SF₆ etches the MoS₂ layers. We found that under 30 s passivation and 15 s etching, approximately 10 layers of MoS₂ are removed. The plasma etching process is carefully investigated using SEM, AFM, TEM, XPS, and Raman analyses. Moreover, our introduced plasma etching method is developed to fabricate a MoS₂-based photodetector which demonstrates an excellent photoresponsivity under different laser excitations and incident optical powers. According to it, a photoresponsivity of 1.39 A/W and a rise time of 0.45 s are measured at a bias voltage of 0.5 V under laser irradiation of 532 nm, which shows the outstanding

![Image](https://example.com/image.png)

Figure 11. (a) Photoresponsivity vs optical power characteristic of the device under 532 nm laser excitation and a drain voltage of 0.5 V. (b) Photoresponsivity vs laser wavelength illumination characteristic of the device at an optical power of 2.20 μW and a drain voltage of 0.5 V. (c) Time-trace measurement of the device at an optical power of 2.20 μW and a drain voltage of 0.5 under laser excitation of 532 nm.

Table 2. Comparison of the Device Performance of Our TMF Photodetector with the MoS₂-Based Photodetectors in the Literature

| device          | excitation laser (nm) | bias voltage (V) | photoresponsivity | response time | refs |
|-----------------|-----------------------|------------------|-------------------|---------------|------|
| photodetector   | 532                   | 0.5              | 1.39 A/W          | \( \tau_{rise} = 0.45 \text{ s}, \tau_{fall} = 1.88 \text{ s} \) | here |
| phototransistor | 532                   | 8                | 5 mA/W            | \( \tau_{rise} = 0.5 \text{ s}, \tau_{fall} = 0.7 \text{ s} \) | 39   |
| photodetector   | 532                   | 5                | 1.04 A/W          | \( \tau_{rise} = 40 \mu s, \tau_{fall} = 50 \mu s \) | 49   |
| optical switch  | 532                   | 10               | 0.57 A/W          | \( \tau_{rise} = 70 \mu s, \tau_{fall} = 110 \mu s \) | 50   |
| photodetector   | 532                   | 3                | 0.55 A/W          | \( \tau_{rise} = 0.2 \mu s, \tau_{fall} = 1.7 \mu s \) | 51   |
| phototransistor | 532                   | 1                | 7.5 mA/W          | \( \tau_{rise} = 50 \mu s, \tau_{fall} = 50 \mu s \) | 48   |

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ability of our plasma thinning method in the fabrication of MoS2-based photodetectors.

5. EXPERIMENTAL SECTION

5.1. Materials. Bulk MoS2 powders (lateral size of 3–40 μm, 99% purity) were supplied from Sigma-Aldrich. Figure S1 shows the SEM image of the bulk powder. DMF solvent was purchased from Merck Company without any purification.

5.2. Preparation of MoS2 Dispersion. Bulk MoS2 powder (0.1 g) was mixed with 20 mL of DMF solvent followed by gentle bath sonication for 15 min. The sonication process was carried out in order to slightly exfoliate large thick flakes. Then, the dispersion was kept for 1 min at room temperature to allow adequate sedimentation of unexfoliated flakes. Finally, the top supernatant was carefully collected to obtain the MoS2 dispersion. The obtained dispersion was shaken with hand before drop-cast on any substrates. Figure S2 shows the SEM image of the prepared MoS2 flakes and the corresponding MoS2 dispersion (inset).

5.3. Device Fabrication. Initially, 285 nm of oxide was grown on a bare clean Si substrate by dry thermal oxidation. Then, 50 nm of Cr was deposited using an electron beam evaporation method on the SiO2/Si substrates followed by patterning into interdigital electrodes (line width of 8.5 μm, line length of 100 μm, and spacing of 5.0 μm) through standard photolithography process. At the next step, a few droplets of MoS2 dispersion were drop-cast on the prepatterned electrodes and air-dried at 70 °C for 24 h. A schematic illustration of the device fabrication steps is presented in Figure S3.

5.4. Plasma Etching Process. To attain a desired plasma etching process for thinning MoS2 flakes, three different plasma gases, hydrogen (H2), oxygen (O2), and sulfur hexafluoride (SF6), are used. All plasma processes are carried out at room temperature. The optimum plasma etching procedure is obtained through two subcycle sequences including O2/SF6 etching and H2 passivation steps. During the first etching step, O2/SF6 gases (200–50 sccm, 200 W) are fed into the chamber resulting in etching of the top layers of MoS2 flakes. After a 15 s etching step, the O2/SF6 and byproduct gases are vented, and H2 gas is introduced into the chamber (200 sccm, 200 W, 30 s) to passivate sulfur vacancies. The two sequences are repeated several cycles to gradually etch flakes and achieve the desired thinned MoS2 layers.

5.5. Characterizations. AFM imaging was performed in a noncontact mode (a resonance frequency of 200–300 kHz) with a NT-MDT system. TEM images were recorded by a Philips, CM30 transmission electron microscope operated at 150 kV. SEM images were taken with an FE-SEM, Hitachi, S-4160 at an accelerating voltage of 30 kV. Raman spectroscopy analysis (Senterra Raman, Bruker) was done with a laser at 532 nm. XPS was employed to evaluate the surface composition of the as-thinned MoS2 layers through Bestec XPS system with an Al Kα source (1486.6 eV) at a pressure of >10−7 Pa. The etching process is performed in a plasma etching system operating at 13.56 MHz at room temperature. The electrical measurements were carried out with a Keithley K361 source measure unit at room temperature in ambient air.
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