Layer-by-Layer Thinning of MoS$_2$ by Plasma

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ABSTRACT The electronic structures of two-dimensional materials are strongly dependent on their thicknesses; for example, there is an indirect to direct band gap transition from multilayer to single-layer MoS$_2$. A simple, efficient, and nondestructive way to control the thickness of MoS$_2$ is highly desirable for the study of thickness-dependent properties as well as for applications. Here, we present layer-by-layer thinning of MoS$_2$ nanosheets down to monolayer by using Ar$^+$ plasma. Atomic force microscopy, high-resolution transmission electron microscopy, optical contrast, Raman, and photoluminescence spectra suggest that the top layer MoS$_2$ is totally removed by plasma while the bottom layer remains almost unaffected. The evolution of Raman and photoluminescence spectra of MoS$_2$ with thickness change is also investigated. Finally, we demonstrate that this method can be used to prepare two-dimensional heterostructures with periodical single-layer and bilayer MoS$_2$. The plasma thinning of MoS$_2$ is very reliable (with almost 100% success rate), can be easily scaled up, and is compatible with standard semiconductor process to generate heterostructures/patterns at nanometer scale, which may bring out interesting properties and new physics.

KEYWORDS: MoS$_2$ · plasma-induced thinning · Raman · photoluminescence · contrast

Two-dimensional layered materials have received great attention since the first experimental discovery of graphene in 2004.¹–⁴ Among them, single-layer and multilayer MoS$_2$ have exhibited interesting properties compared to its bulk form⁵ and other two-dimensional materials. MoS$_2$ devices exhibit a room-temperature current on/off ratio of $\sim 1 \times 10^8$ (due to the large intrinsic band gap) and carrier mobility up to $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶–⁸ An indirect to direct band gap transition from multilayer to single-layer MoS$_2$ was also reported, which results in great enhancement of photoluminescence (PL).⁹,¹⁰ More interesting phenomena were presented; for example, electronic structure enables valley polarization,¹¹–¹³ robust mechanical properties, and strain tunable band gap.¹⁴–¹⁶ The fabrication of large-scale MoS$_2$ film using chemical vapor deposition¹⁷–¹⁹ and a large quantity of MoS$_2$ nanosheets using solution-based chemical exfoliation²⁰,²¹ also represents important steps for its wafer-scale application in electronic devices and flexible and transparent optoelectronics.

The electronic properties of two-dimensional layered materials are strongly dependent on their thicknesses.⁴,²² Single-layer MoS$_2$ has a direct band gap of $\sim 1.9 \text{ eV}$, which makes it promising for application in optoelectronic devices, such as photodetectors,²³,²⁴ photovoltaics,¹⁶ and light emitters.²⁵ In addition, multilayer MoS$_2$ may also provide different and interesting properties, similar to what happened in multilayer graphene.²²,²⁶,²⁷ The thickness-modulated optical energy gap of MoS$_2$ is desirable for phototransistors.²⁶ Electronic devices based on multilayer MoS$_2$ were also reported.²⁷,²⁸,²⁹ Therefore, a simple and efficient approach to control the thickness of MoS$_2$ is highly desirable. It will also enable the study of thickness-dependent properties of MoS$_2$. Recently, Castellanos-Gomez et al. presented an exciting work using a...
laser to thin MoS2 sheets down to monolayer thickness. However, the origin of laser thinning is thermal ablation which makes it only possible to produce single-layer MoS2 and challenging for scale-up. It would also be difficult to use this method to make high-resolution patterns (e.g., down to nanometer size), due to the optical diffraction limit of the laser spot.

Here, we present layer-by-layer thinning of multi-layer MoS2 down to the monolayer by using Ar+ plasma. The thickness change is confirmed by atomic force microscopy (AFM), transmission electron microscopy (TEM), optical contrast, Raman, and PL spectra. The top layer MoS2 is totally removed by plasma, while the bottom layer remains almost unaffected. We also demonstrate that, combined with standard lithographic techniques, this method can be used to prepare two-dimensional MoS2 heterostructures with different thicknesses and sizes. A heterostructure composed of periodical single-layer and bilayer MoS2 is presented. This method enables large-scale thickness control of MoS2 and other two-dimensional materials.

RESULTS AND DISCUSSION

Figure 1a,b shows the optical images of MoS2 sheets with a thickness of 1–4 layers. The optical contrast of MoS2 increases with the increase of its thickness. In our previous work, we proposed to use the contrast between R/G/B values of the sample and substrate in an optical image to precisely determine the thickness of two-dimensional materials. Here, the R channel contrast is used to determine the thickness of MoS2 with the following equation:

\[ C = \frac{R_{\text{sub}} - R_{\text{sam}}}{R_{\text{sub}}} \]

where C is the contrast of the MoS2 sheet, \( R_{\text{sub}} \) and \( R_{\text{sam}} \) are the R channel values of the SiO2/Si substrate and MoS2 sheets obtained from the optical image. The contrast values for 1–4 layers of MoS2 are 0.125, 0.25, 0.31, and 0.36 (red stars in Figure 1c), which agree quite well with the results obtained by Li et al. (R value differences between sample and substrate are 28, 56, and 72 for 1, 2, and 3 layers of MoS2, respectively). In our work, the use of contrast to determine the layer thickness is more quantitative as it does not depend on the intensity of incident light and parameters of the microscope. However, care should be taken when using contrast to determine the thickness of two-dimensional materials. The contrast value could be affected by the thickness of an oxide capping layer; for example, the contrast values of single-layer MoS2 on 300 and 285 nm SiO2/Si substrates are ~0.125 and ~0.11, respectively. The thickness of MoS2 is further confirmed by Raman spectra. Raman spectroscopy has been widely used to study two-dimensional materials and to identify their thicknesses. The Raman spectra of 1–4 layer MoS2 are shown in Figure 1d. Two main Raman features are clearly presented, which correspond to \( E_{2g} \) (385 cm\(^{-1}\), in-plane vibration of two S atoms with respect to the Mo atom) and \( A_{1g} \) (405 cm\(^{-1}\), out-of-plane vibration of S atoms).
The intensities of these two peaks increase with the increase of thickness. In addition, the frequency of the $E_{2g}$ peak decreases and that of the $A_{1g}$ peak increases with the increase of thickness, due to the change of force constant and also variation in the dielectric screening environment. The frequency difference of these two peaks can then be used to identify the thickness of MoS$_2$ sheets. The red stars in Figure 1e show the frequency differences of $E_{2g}$ and $A_{1g}$ peaks, and the values are 18, 21, 23, and 24 cm$^{-1}$ for 1–4 layer MoS$_2$, respectively. These results agree quite well with previous reports.

Figure 1f shows the PL spectra of 1–4 layer MoS$_2$. The PL spectra contain two peaks located at $\sim$670 and $\sim$630 nm, corresponding to the direct excitonic transitions between the minimum of the conduction band and the maxima of split valence bands (A1 and B1 excitons) in MoS$_2$. The single-layer MoS$_2$ has a direct band gap structure; therefore, it has the strongest PL intensity. The PL intensity decreases with the increase of thickness. The intensity difference between single-layer and multilayer MoS$_2$ is not as distinct as that reported by Mak et al. but is similar to the result of Splendiani et al. The PL intensity of single-layer MoS$_2$ can be greatly enhanced (by more than 10 times) after annealing in 300 °C in vacuum, while that of multilayer MoS$_2$ does not show noticeable changes. This might be the reason why different relative PL intensities of single-layer and multilayer MoS$_2$ were observed by different groups. The contrast values, Raman frequency differences, as well as PL intensities were used to monitor the thickness change of MoS$_2$ sheets after Ar$^+$ plasma irradiation.

Figure 2a,b shows Raman and PL spectra of single-layer MoS$_2$ after Ar$^+$ plasma irradiation (0–115 s). The Raman peaks become weak and broadened after plasma irradiation (10–85 s), which suggests that MoS$_2$ becomes disordered. After 115 s irradiation, the Raman peaks disappear, indicating that the single-layer MoS$_2$ is totally removed by plasma. The PL intensities of MoS$_2$ become much weaker with the increase of irradiation time (10–85 s), and it almost disappears after 115 s irradiation. The changes of Raman and PL spectra suggest that single-layer MoS$_2$ becomes disordered and can finally be removed by Ar$^+$ plasma. For bilayer MoS$_2$, the results are quite different. As can be seen in Figure 2c, the $E_{2g}$ peak of bilayer MoS$_2$ splits after 10 s irradiation, as denoted by the black arrows. The emerging peak at $\sim$380 cm$^{-1}$ becomes broader and weaker (10–85 s) and finally
disappears (115 s) with the increase of irradiation time, similar to the $E_{2g}^1$ peak of plasma-irradiated single-layer MoS$_2$ (Figure 2a). This suggests that the emerging peak belongs to the top layer MoS$_2$. Another interesting phenomenon is that, with the increase of irradiation time, the $E_{2g}^1$ peak (the sharp peak belongs to the bottom layer) of bilayer MoS$_2$ shifts to higher frequency, toward the $E_{2g}^1$ frequency of pristine single-layer MoS$_2$ ($\sim$385 cm$^{-1}$). It has been theoretically explained that the decrease of $E_{2g}^1$ frequency with the increase of MoS$_2$ thickness is due to the stronger dielectric screening of the long-range Coulomb interaction in multilayer and bulk MoS$_2$. The $\text{Ar}^+$ plasma irradiation introduces defects in the top layer MoS$_2$ and makes it disordered. As a result, the interlayer interaction between the top and bottom MoS$_2$ layers as well as the dielectric screening effect become much weaker, which results in the blue shift of $E_{2g}^1$ peak after plasma irradiation. After 115 s irradiation, the $E_{2g}^1$ and $A_{1g}$ peaks of “bilayer” MoS$_2$ are very sharp and the frequency difference of these two peaks decreases from 21.5 cm$^{-1}$ of bilayer MoS$_2$ to 18.5 cm$^{-1}$, which is the value of single-layer MoS$_2$ (purple squares in Figure 1e). In addition to Raman spectra, PL spectra of MoS$_2$ should give much clearer evidence of the thickness change, as the PL intensities of MoS$_2$ increase with the decrease of thickness. As can be seen in Figure 2d, the PL intensities of bilayer MoS$_2$ decrease with the increase of irradiation time (10–85 s), as the top layer MoS$_2$ becomes disordered after plasma irradiation. After 115 s irradiation, the PL intensity has an abrupt increase, which is in agreement with the thickness change from bilayer to single-layer (indirect to direct band gap transition).

Figure 3a,b shows the $R$ channel optical image of a bilayer MoS$_2$ before and after plasma thinning. The $R$ channel optical images of the same sample before (c) and after (d) plasma thinning.

Figure 3a,b shows the $R$ channel optical image of a bilayer MoS$_2$ before and after plasma thinning. The contrast values derived from these two images are 0.26 and 0.13 (purple squares in Figure 1c), respectively, close to the values of pristine bilayer and single-layer MoS$_2$. The AFM images are also presented in Figure 3c, d to study the morphologies of MoS$_2$ before and after plasma thinning. The thickness of pristine bilayer MoS$_2$ is $\sim$1.77 nm, which is a bit larger than the theoretical value. This is a common observation for AFM images of layered materials, as there might be water or molecules trapped between the sample and substrate, and the trapping responses of the sample and substrate are also different. The thickness of MoS$_2$ after plasma thinning is $\sim$1.08 nm, with a thickness difference of $\sim$0.69 nm compared to the pristine sample. This is quite close to the 0.62 nm interlayer spacing of bulk MoS$_2$. It is worth noting that the surface of single-layer MoS$_2$ obtained by plasma thinning is still very smooth, with a roughness of 0.19 nm (0.18 and 0.13 nm for pristine single-layer and bilayer MoS$_2$), indicating that there are very few unremoved MoS$_2$ traces on the surface.

High-resolution TEM is used to study the atomic structures of a bilayer MoS$_2$ before (Figure 4a–c) and
after (Figure 4d–f) plasma thinning. The electron diffraction patterns (Figure 4a,d) and high-resolution TEM images (Figure 4b,e) reveal the hexagonal lattice structure of MoS2 with a lattice spacing of ∼2.7 Å (100 plane) and ∼1.6 Å (110 plane). No noticeable difference in the lattice parameters of MoS2 is found before and after plasma thinning within the resolution of the system. The folded edges of two-dimensional materials are frequently adopted to identify the number of layers in TEM. Bilayer MoS2 presents two dark fringes with a space of ∼6.0 Å, in good agreement with the interlayer distance of MoS2. On the other hand, plasma-thinned single-layer MoS2 has only one dark fringe. The most important observation of high-resolution TEM is that the structure of plasma-thinned single-layer MoS2 remains extremely high quality (Figure 4e), indicating that the top layer MoS2 is totally removed while the bottom layer remains almost unaffected by plasma. This may relate to the strong bonding strength of the S–Mo–S structure and the weak interlayer interaction. Plasma irradiation was also used to thin down graphene sheets. However, reactive sources such as H2O2 and hydrogen were used, which induced excessive defects in graphene. High-temperature (900 °C) post-annealing in O2 was also used to etch the disordered top layer. The S–Mo–S bonding of MoS2 is not as strong as that of C–C bonding of graphene, which makes MoS2 more easily removed by Ar+ plasma. We would emphasize that the plasma thinning of MoS2 is highly reproducible and has

Figure 4. Diffraction patterns, high-resolution TEM images and folded edges of a pristine bilayer MoS2 (a–c) and a plasma-thinned single-layer MoS2 (d–f).

Figure 5. Raman (a) and PL (b) spectra of a the quadrilayer MoS2 sheet after Ar+ plasma irradiation with different time.
almost 100% success rate for more than 10 processed samples. An important sign of thickness change is the abrupt increase of PL intensity after irradiation.

We can also do layer-by-layer thinning of MoS$_2$, as shown in Figure 5. A quadrilayer MoS$_2$ is irradiated by Ar$^+$ plasma with similar conditions (0–345 s). The E$_{2g}^1$ peak first splits (as indicated by the black arrows in Figure 5a), and then the emerging peak disappears after 115 s irradiation. At the same time, the PL intensity has an abrupt increase (Figure 5b), indicating the removal of the topmost layer of MoS$_2$. Similar changes of Raman and PL spectra repeat for the removal of additional layers. The E$_{2g}^1$ peak blue shifts, while the A$_{1g}$ peak red shifts with the decrease of MoS$_2$ thickness. The frequency difference of E$_{2g}^1$ and A$_{1g}$ at 23.4 cm$^{-1}$ (quadrilayer) to 21.5 cm$^{-1}$ (bilayer) and, finally, to 18.2 cm$^{-1}$ (single-layer) (as shown by the blue circles in Figure 1e). The R contrast value of MoS$_2$ decreases from 0.36 (quadrilayers) to 0.32 (trilayers) to 0.26 (bilayer) and, finally, to 0.125 (single-layer) (as shown by the blue circles in Figure 1c). These results suggest that the plasma thinning of MoS$_2$ is very reliable and can be used for devices which require structures with different thicknesses, such as phototransistors with thickness-modulated optical energy gaps. It can also be used to study the thickness-dependent properties of MoS$_2$ sheets.

As a demonstration, we fabricate a periodical 1/2/1/2/1...MoS$_2$ heterostructure. A pristine bilayer MoS$_2$ (Figure 6a) is spin-coated by a thin layer of polymethyl methacrylate (PMMA), followed by electron beam lithography to create a mask of periodical lines with a width of ~2 μm (Figure 6b). Ar$^+$ plasma is then used to thin down the uncovered area to form periodical heterostructures. The optical image of the obtained structure in Figure 6c shows MoS$_2$ patterns with different thicknesses/contrast. The Raman image created by the intensity of the E$_{2g}^1$ peak is shown in Figure 6d. The red color represents higher Raman intensity (bilayer), and green color represents lower intensity (single-layer). Figure 6 demonstrates that, by using plasma irradiation and standard lithography, we can achieve arbitrary MoS$_2$ heterostructures with different thickness. The width of the structure can be at nanometer scale with careful control of experimental conditions. The periodical heterostructures containing materials with different electronic properties (e.g., direct and indirect band gap structures for single-layer and bilayer MoS$_2$) may bring out interesting properties and new physics.

CONCLUSION

In summary, we have demonstrated that the thickness of MoS$_2$ sheets can be controlled layer-by-layer under Ar$^+$ plasma irradiation. AFM, high-resolution TEM, Raman, and PL spectra suggest that the top layer MoS$_2$ is totally removed, while the bottom layer MoS$_2$ remains almost unaffected, which makes this method
promising for fabricating electronic devices with different structures and thicknesses. We have also prepared a two-dimensional heterostructure containing periodical single-layer and bilayer MoS$_2$. The plasma thinning provides an easy and efficient way to control the properties of MoS$_2$ and other two-dimensional materials.

EXPERIMENTAL METHODS

Single-layer and multilayer MoS$_2$ are fabricated by mechanical exfoliation from single-crystal MoS$_2$ and deposited onto a 300 nm SiO$_2$/Si substrate. Optical microscopy, Raman, and AFM are used to identify the thickness. Ar$^+$ plasma (commercial 13.56 MHz RF source) with power of 50 W and pressure of 40 Pa is used to thin down the MoS$_2$ sheets with different irradiation time at room temperature. The Raman and PL spectra are recorded using a LabRAM HR8000 Raman system with 514.5 nm excitation. The laser power at the sample is lower than 0.5 mW to avoid laser-induced heating. To obtain the Raman images, an x–y stage is used to move the sample with a step size of 200 nm, and a Raman spectrum is recorded at every point. AFM is carried out with a Nanoscope 815 system. High-resolution TEM is carried out using an electron aberration-corrected TEM system (FEI Titan 80-300). An acceleration voltage of 80 kV is chosen to achieve enough resolution while maintaining the structure of MoS$_2$. The MoS$_2$ flakes are transferred to a TEM grid using a PMMA-based transfer technique.$^{44}$ A thin layer of PMMA is spin-coated on the SiO$_2$/Si substrate which contains a target. The SiO$_2$ is etched away by KOH solution. The MoS$_2$ flake will attach on PMMA and will then be transferred to the TEM grid. An optical microscope is used to locate the flake and make aligned transfer. Finally, PMMA is dissolved in acetone, and the sample is washed by isopropyl alcohol and water several times.

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

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REFERENCES AND NOTES


