Letters

Automated Mechanical Exfoliation of MoS_2 and $MoTe_2$ Layers for Two-Dimensional Materials Applications

Kyle DiCamillo, Sergiy Krylyuk, Wendy Shi, Albert Davydov, and Makarand Paranjape

Abstract—**An automated technique is presented for mechanically exfoliating single-layer and few-layer transition metal dichalcogenides using controlled shear and normal forces imposed by a parallel plate rheometer. A thin sample that is removed from bulk MoS_2 or $MoTe_2$ is initially attached to the movable upper fixture of the rheometer using blue dicing tape while the lower base plate also has the same tape to capture and exfoliate samples when the two plates are brought into contact then separated. A step-and-repeat exfoliation process is initiated using a preprogrammed contact force and liftoff speed. It was determined that atomically thin films of these materials could be obtained reproducibly using this technique, achieving single-layer and few-layer thicknesses for engineering novel two-dimensional transistor devices for future electronic technologies. We show that varying the parameters of the rheometer program can improve the mechanical exfoliation process.**

Index Terms—**Mechanical exfoliation, molybdenum disulfide, molybdenum ditelluride, two-dimensional materials, nanomaterials.**

I. INTRODUCTION

TWO-DIMENSIONAL materials are of great interest due to their unique electronic and optical properties. Graphene has received much attention for its excellent electron mobility and other unique properties [1]. Its use as a gas sensing material has also been tested due to its excellent surface to volume ratio [2]. Unfortunately, graphene lacks the semiconducting properties that gas sensing layers (such as indium tin oxide) traditionally possess [3]. Molybdenum disulfide (MoS_2) and molybdenum ditelluride ($MoTe_2$) are two dimensional materials that are analogous to graphene and are made of stacked layers of molybdenum sandwiched between layers of chalcogen atoms. Part of a group of materials known as transition metal dichalcogenides, MoS_2 and $MoTe_2$ are naturally semiconducting. MoS_2 is already of interest for its optoelectronic [4], catalysis [5], and battery applications [6]. MoS_2 shares the same hexagonal lattice structure as graphene and its layers are only held together by van der Waals forces. Bulk MoS_2 has an indirect band gap of 1.29 eV while monolayer MoS_2 has a direct band gap of 1.78 eV [7]. $MoTe_2$ has an indirect band gap of 1.0 eV in bulk and a direct band gap of 1.1 eV as a monolayer [8], reinforcing its similarity to MoS_2. These two materials have potential for use in gas sensing applications [2], [9] where a semiconducting film is more useful than a graphene with no band gap because of the larger changes in conduction semiconductors exhibit in response to changes in charge carrier concentration.

One of the challenges of using two dimensional films in devices such as gas sensors is the difficulty of mass-producing these materials at an acceptable quality and performance level. The methods of producing few layer films of MoS_2 or $MoTe_2$ currently include many mechanical exfoliation techniques [10], [14]–[22] or growth methods such as chemical vapor deposition (CVD) and chemical vapor transport (CVT) [11], [12]. However, mechanical exfoliation has little control over the number of layers in the flakes produced. A programmable mechanical tool would be useful for adding consistency to the technique of mechanical exfoliation. A rheometer is a tool that can apply stresses to, typically, soft solid materials and gather data about their mechanical properties. This makes the rheometer a nice candidate to reproduce the pressing and peeling of mechanical exfoliation done by hand. We show that automating the mechanical exfoliation using a rheometer adds greatly to the reproducibility of this fabrication technique. It also establishes machine parameters that can be varied to optimize and standardize a mechanical exfoliation recipe.

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II. EXPERIMENTAL METHOD

Commercial MoS_2 flakes were used for the exfoliation experiments. $MoTe_2$ single-crystalline flakes were grown by
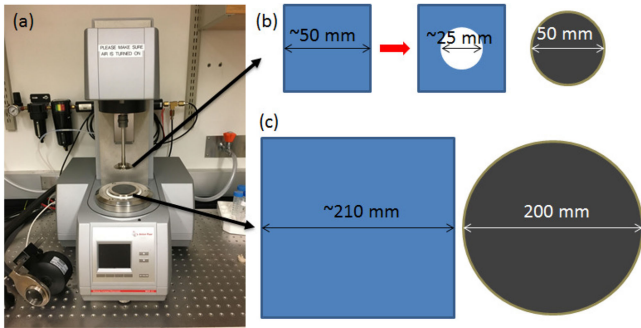
Fig. 1. (a) The rheometer used in this experiment with (b) a 50 mm diameter tool with a similarly sized square of blue tape with a circular cutout attached and (c) a 200 mm diameter stage with a similarly sized square of blue attached.

Fig. 2. The rheometer with wafer dicing tape attached as it exfoliates MoTe$_2$ crystals.(Top left) The rheometer plate descending towards the stage; (top right) the plate as it contacts the stage; (bottom left) the plate as it ascends from the stage; (bottom right) the plate after completing one cycle of exfoliation.
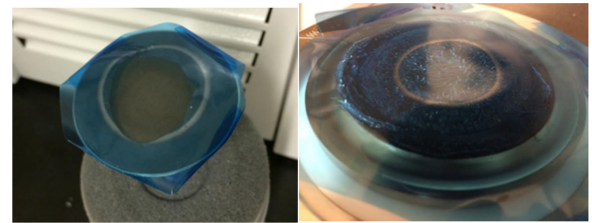

Fig. 3. (Left) The top plate of the rheometer with blue dicing tape covered in exfoliated MoTe$_2$ flakes. (Right) The bottom stage of the rheometer with blue dicing tape covered in exfoliated MoTe$_2$ flakes.

chemical vapor transport (CVT) method. First, polycrystalline MoTe$_2$ powder was synthesized by reacting stoichiometric amounts of molybdenum (99.999%) and tellurium (99.9%) at 750 °C in a vacuum-sealed quartz ampoule. Next, MoTe$_2$ crystals were grown at 800 °C using approximately 1 g of MoTe$_2$ charge and a small amount of TeCl$_4$ (99.9%, 5.7 mg/cm^3) sealed in evacuated quartz ampoules. The ampoules were ice-water quenched after 140 h of growth yielding 2H MoTe$_2$ flakes with the (0001) basal surface. To exfoliate MoS$_2$ and MoTe$_2$, a large square of Nitto blue tape was attached, adhesive side up, to the non-moving base of the rheometer using vacuum grease to hold the tape flat. Further pieces of tape were attached at the sides of the square to prevent lateral sliding. A second square of tape was affixed to the flat end of a 50-mm diameter movable rheometer tool using several pieces of tape wrapped around the rod of the tool. This square of tape had a circular hole cut from its center to reduce the surface area of adhesive tape (see Fig. 1), preventing problems with the two pieces of tape not fully releasing from one another as they were pulled apart. To this top piece of tape a small flake of bulk MoS$_2$ or MoTe$_2$ was attached, offset from the center. A recipe was programmed into the rheometer that allowed for the contact force to be varied and rotated the rheometer tool in between each successive adhesion and peel away process of the tapes, as seen in Fig. 2. Separately, the ascending and descending of the tool while running a recipe could be varied in its program's settings.

This recipe was run 60 times which gave us a dust-like covering of exfoliated flakes on both pieces of tape which can be seen in Fig. 3. Squares of thermal release tape were then applied to the original pieces of tape before being pressed onto silicon chips with 300 nm of SiO$_2$. Using thermal release tape as an intermediate step in the transfer to the SiO$_2$ substrate created a large improvement in the number of flakes successfully transferred. These were then placed on a hot plate at 180 °C for 2 min to complete the transfer of exfoliated flakes to our desired substrate.

After being transferred to Si/SiO$_2$ chips, the flakes were inspected under an optical microscope. By observing the color of flakes and the contrast between flakes and the background color of the silicon, it was possible to identify few layer (<6) flakes. For MoS$_2$ flakes, a dark violet color was indicative of

few layer flakes. Among those, the amount of contrast to the background was noticeably different between monolayer and multilayer samples. Similarly, MoTe$_2$ displayed a dark blue color that, while less purple than MoS$_2$, showed the same decrease in contrast to the background as layer count decreased. Flakes that were identified as few layer were photographed at multiple magnifications for reference.

Then Raman spectroscopy was used to give us a better idea of layer count. MoS$_2$ has the E$^1_{2g}$ peak at 383 cm^{-1} and the A$_{1g}$ peak at 408 cm^{-1} that shift towards each other in samples of less than 6 layers [13]. This allowed for confident differentiation between one, two, and three layer samples. Raman spectroscopy was less conclusive for MoTe$_2$, as the distance between peaks changes much less noticeably as layer count decreases. Unlike MoS$_2$, MoTe$_2$ does not show a large shift in the wave numbers of the peaks associated with the A$_{1g}$ and E$^1_{2g}$ as the material goes from bulk to few layer samples. The associated peak of the B$^1_{2g}$ mode grows with intensity once the material is no longer bulk and reaches its highest intensity in bilayer MoTe$_2$, but disappears entirely in monolayer samples due to the loss of the interlayer interaction [12]. Therefore, the presence of the B$^1_{2g}$ peak as well as the ratio between it and the E$^1_{2g}$ peak give the most information about the number of layers present in a sample
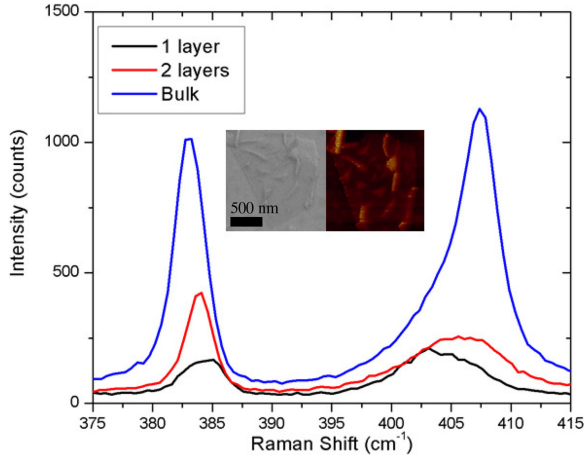
Fig. 4. Raman spectra of bulk (red), bilayer (blue), and monolayer (green) MoS_2. Inset: An SEM (left) and AFM (right) image of a monolayer MoS_2 flake.
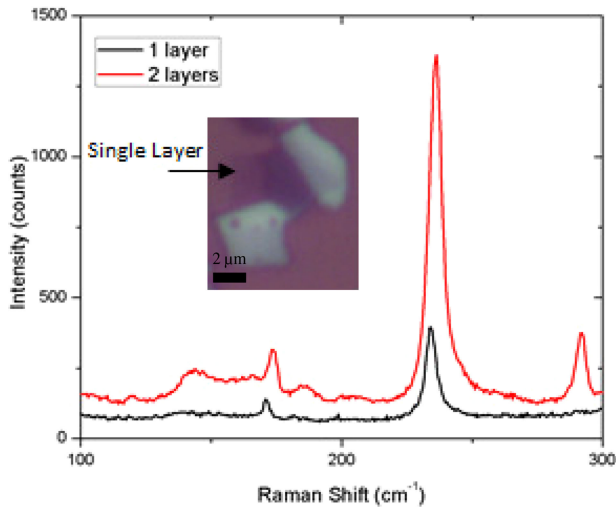

Fig. 5. Raman spectra of bilayer (red) and monolayer (black) $MoTe_2$. Inset: An optical image of $MoTe_2$ flakes, including a monolayer flake.

TABLE I
THICKNESS COMPARISON DURING EXFOLIATION

Round	Avg Thickness (nm)
10	61.5 +/- 13.5
15	75.3 +/- 14.5
20	57.0 +/- 12.3
25	58.5 +/- 9.7
30	52.6 +/- 10.5
35	67.2 +/- 11.2
40	47.7 +/- 8.3
45	42.8 +/- 8.5
50	39.2 +/- 8.1
55	27.3 +/- 8.0
60	25.1 +/- 8.4

TABLE II
FORCE VS NUMBER OF FEW LAYER FLAKES

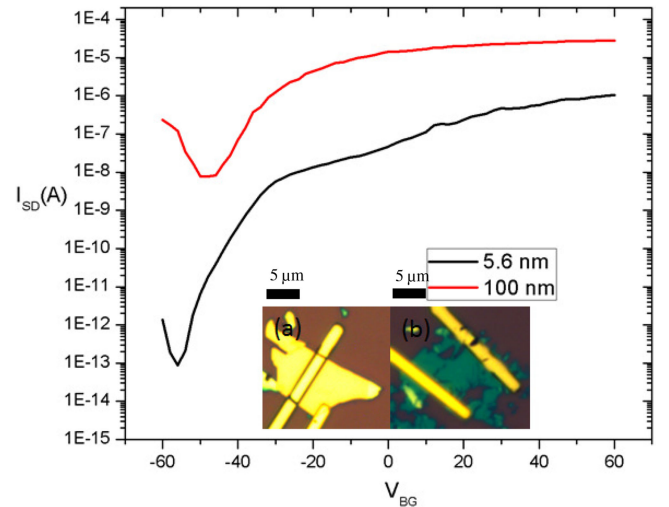| Force	Yield (per Si chip)
<35 N	No few layer flakes
40 N	1 to 2 few layer flakes
45 N	3 to 5 few layer flakes
50 N	5 to 7 few layer flakes

Fig. 6. The transfer characteristics of a 5.6 nm MoS_2 flake and a 100 nm MoS_2 flake with one Ti/Au and one Nb/Pd electrodes. Source/drain bias was 2 V. Inset: Optical images of (a) 100 nm flake and (b) 5.6 nm flake.

of $MoTe_2$. Figs. 4 and 5 show the expected shift in Raman spectra that we observed for both MoS_2 and $MoTe_2$ flakes.

To solve this problem for $MoTe_2$ and to provide confirmation of our MoS_2 layer count, atomic force microscopy (AFM) was used to image flakes believed to be few layer and measure their height profiles. A random sampling of flakes taken at different points during the exfoliation process are shown in Table I, showing that the greatest amount of thinning for flakes occurred after the tapes had been peeled apart at least 40 times. Thickness seems to vary randomly until that point and then again vary random until about 55 or 60 rounds. This implies that our technique may not produce a linear thinning of the flakes but that large flakes into many smaller ones at discrete points in the process. The randomness is possibly due to the combination of normal and shear forces caused by the tape as well as fragmentation of flakes occurring irregularly during the exfoliation process [23]. The contact force of the rheometer could be varied, thereby allowing a comparison on the amount of few layer flakes found, which is shown in Table II.

Afterwards, electron beam lithography was used to deposit electrodes using 2 nm of Nb as an adhesion for 60 nm of Pd on our characterized MoS_2 flakes. The Si substrate was also used as a back gate to make the flakes into FETs. The transfer and output characteristics of the flakes were measured, showing a slight ambipolar behavior, as seen in Fig. 6. Several thicknesses
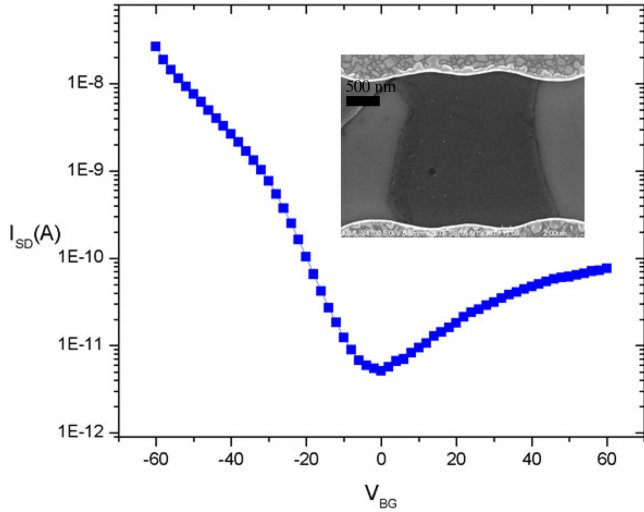
Fig. 7. The transfer characteristics of a 4.5 nm MoTe2 flake with Ti/Au electrodes. Source/drain bias was 2 V. Inset: SEM image of the 4.5 nm flake.

of MoTe$_2$ flakes were used to make FET using photolithography. The electrodes were deposited with 40 nm of Ti as an adhesion layer for 350 nm of Au. Again, the silicon substrate was used for a back gate for the FETs. The output and transfer characteristics for these devices is seen in Fig. 7.

III. RESULTS

Five different types of tape were tested in our attempt to find a good yield of mechanically exfoliated flakes without a large amount of residue upon transfer from the tape to a SiO$_2$/Si substrate. Regular Scotch tape was quickly ruled out as an option due to the amount of residue left behind on the substrate, making characterization infeasible. To resolve the residue issue, samples of several different types of protective or processing tape were obtained since they were all for use in cleanroom applications. The results from several types of tape with varying stiffness and adhesiveness are tabulated here. Out of these, silicon wafer dicing tape had the highest number of few layer flakes while being the least adhesive and most flexible of the obtained tapes. However, with all the tapes tested, there was a low yield of MoS$_2$ flakes successfully transferred to the substrate. By using a brand of heat release tape, we improved our yield by using this new tape as an intermediate transfer tape to get flakes from the wafer dicing tape to our silicon substrates. This resulted in a massive increase in the number of exfoliated flakes successfully transferred to silicon while only introducing a mild increase in residue left behind by our tape transfer method. The success of each type of tape is compared in Table III. Then, the contact force of the rheometer could be varied, thereby allowing a comparison on the amount of few layer flakes found, which is shown in Table II.

Exfoliated flakes on the substrate were characterized optically as well as with AFM and Raman spectroscopy to determine layer count. It was found that few layer (less than five layers) flakes could be consistently found on Si chips with 300 nm SiO$_2$.

TABLE III
COMPARISON OF ADHESIVE TAPES

Tape	Yield	Residue
Pressure Sensitive	1 to 2 few layer flakes	Heavy
Plastic Protective	No few layer flakes	Low
Lens Protective	No few layer flakes	Low
Wafer Processing	1 to 2 few layers flakes	Low
Wafer Dicing	3 to 5 few layer flakes	Low
Wafer Dicing w/ Thermal Release	5 to 7 few layer flakes	Moderate

However, the exact layer count varied in what appears to be a random fashion. The contact force of the rheometer could be varied, thereby allowing a comparison on the amount of few layer flakes found, which is shown in Table II. It was also found that slowing the liftoff speed of the rheometer by half of its default setting (4000 μm/s to 2000 μm/s) led to an improvement in few layer samples obtained.

IV. CONCLUSION

We tested a new automated method for mechanically exfoliating MoS$_2$ and MoTe$_2$ crystals. This method has increased reproducibility of obtaining high quality thin film flakes of these materials. In addition, it has increased the number of these high quality thin film flakes. We have characterized these flakes with Raman spectroscopy and with AFM to confirm that we have thin flakes. We have also characterized the transport behavior of these MoS$_2$ and MoTe$_2$ flakes.

REFERENCES

[1] A. K. Geim and K. S Novoselov, "The rise of graphene," *Nature Mater.* vol. 6, pp. 183–191, 2007.
[2] F. Schedin *et al.*, "Detection of individual gas molecules adsorbed on graphene," *Nature Mater.*, vol. 6, pp. 652–655, 2007.
[3] B. Cho *et al.*, "Chemical Sensing of 2D Graphene/MoS$_2$ Heterostructure Device," *ACS Appl. Mater. Interfaces*, vol. 7, pp. 16775–1678, 2015.
[4] S. Mouri, Y. Miyauchi, and K. Matsuda, "Tunable photoluminescence of monolayer MoS$_2$ via chemical doping," *Nano Lett.*, vol. 13, p. 5944, 2013.

[5] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin MoS_2: A new direct-gap semiconductor," *Phys. Rev. Lett.*, vol. 105, 2010, Art. no. 136805.

[6] T. Wang, R. Zhu, J. Zhuo, Z. Zhu, Y. Shao, and M. Li, "Direct detection of DNA below ppb level based on thionin-functionalized layered MoS_2 electrochemical sensors," *Anal. Chem.*, vol. 86, 2014, Art. no. 12064.

[7] A Splendiani *et al.*, "Emerging photoluminescence in monolayer MoS_2," *Nano Lett.*, vol. 10, 2010, Art. no. 1271e5.

[8] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, and W. Tang, "First principles study of structural, vibrational and electronic properties of graphene-like MX_2 (M = Mo, Nb, W, Ta; X=S, Se, Te) monolayers," *Phys. B.* vol. 406, p. 2254, 2011.

[9] D. J. Late *et al.*, "Sensing Behavior of Atomically Thin-Layered MoS_2 Transistors," *ACS Nano*, vol. 7, no. 6, pp. 4879–4891, 2013.

[10] H. Li, J. Wu, Z. Yin, and H. Zhang, "Preparation and applications of mechanically exfoliated single-layer and multilayer MoS_2 and WSe2Nanosheets," *Acc. Chem. Res.*, vol. 47, pp. 1067–1075, 2014.

[11] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, and J. Lou, "Large-area vapor-phase growth and characterization of MoS_2 atomic layers on a SiO_2 substrate," *Small*, vol. 8, 2012, Art. no. 966e71.

[12] Y.-F. Lin *et al.*, "Ambipolar $MoTe_2$ transistors and their applications in logic circuits," *Adv. Mater.*, vol. 26, 2014, Art. no. 3263.

[13] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, "Anomalous lattice vibrations of single and few-layer MoS_2," *ACS Nano*, vol. 4, 2010, Art. no. 2695e700.

[14] B. Jayasena and S. Subbiah, "A novel mechanical cleavage method for synthesizing few-layer graphenes," *Nanoscale Res. Lett.*, vol. 6, 2011, Art. no. 95.

[15] J. Chen, M. Duan, and G. Chen "Continuous mechanical exfoliation of graphene sheets via three-roll mill,", *J. Mater. Chem.*, vol. 22, 2012, Art. no. 19625.

[16] Y. Hernandez *et al.*, "High-yield production of graphene by liquid-phase exfoliation of graphite," *Nat. Nanotechnol.*, vol. 3, pp. 563–568, 2008.

[17] C. Knieke, A. Berger, M. Voigt, R. N. K. Taylor, J. Rohrl, and W. Peukert, "Scalable production of graphene sheets by mechanical delamination," *Carbon*, vol. 48, pp. 3196–3204, 2010.

[18] W. Zhao, M. Fang, F. Wu, H. Wu, L. Wang, and G. Chen, Preparation of graphene by exfoliation of graphite using wet ball milling," *J. Mater. Chem.*, vol. 20, 2010, Art. no. 5817.

[19] I. Y. Jeon *et al.*, "Edge-carboxylated graphene nanosheets via ball milling," *Proc. Natl. Acad. Sci., USA*, 2012, vol. 109, pp. 5588–5593.

[20] Z. Shen, J. Li, M. Yi, X. Zhang, and S. Ma, "Preparation of graphene by jet cavitation," *Nanotechnology*, 2011, vol. 22, Art. no. 365306.

[21] K. R. Paton *et al.*, Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids," *Nat. Mater.*, vol. 13, pp. 624–630, 2014.

[22] L. Liu, Z. Shen, M. Yi, X. Zhang, and S. Ma, "A green, rapid and size-controlled production of high-quality graphene sheets by hydrodynamic forces," *RSC Adv.*, vol. 4, 2014, Art. no. 36464.

[23] M. Yi and Z. Shen, "A review on mechanical exfoliation for the scalable production of graphene," *J. Mater. Chem. A.*, vol. 3, no. 22, pp. 11700–11715, 2015.