Mechanical deformation of atomically thin layers during stamp transfer.

Tatiana V Ivanova, Dmitry Permyakov and Ekaterina Khestanova

Department of Physics and Engineering, ITMO University, St. Petersburg, 197101, Russia
Corresponding authors: ekaterina.khestanova@metalab.ifmo.ru

Abstract. The way transition metal dichalcogenide (TMD) strains during its transfer from one substrate to another is very interesting and holds a special place in the creation of heterostructures. In our work we observe the spectrum of photoluminescence in TMD during the transfer. For this we use a specially designed transfer system with inverted geometry. During transfer we observe a modification of exciton photoluminescence linewidth and resonance shift in atomically thin layers of TMD. We believe that our results lay grounds for the future work on the assessment of the atomically thin layer inhomogeneity introduced by the typical mechanical transfer.

1. Introduction

Nowadays, one of the most interesting directions in solid-state physics are two-dimensional materials such as graphene, transitional metal dichalcogenides (TMDs) and their heterostructures. Bulk TMD crystals are semiconductors with an indirect band gap, while monolayers are direct gap semiconductors. This is experimentally evidenced by the excitonic photoluminescence (PL) line shift and intensity increase with the decrease of sample thickness. Unlike in GaAs quantum wells, excitons in TMD monolayers have large binding energies and are sustained up to room temperature.

At the same time, such excitons and the corresponding photoluminescence lines are highly sensitive to external lattice perturbations via mechanical strains. The onset of stretching in a monolayer is a well-studied phenomenon. For example, monolayers were subjected to stretching in different configurations, strain was measured in single-, bi- and tri-layer in different TMDs, uniaxial strain dependence of A-exciton PL peak energy shift for monolayer TMDs was studied. Other studies in chemical vapor deposition grown crystals unveiled the effect of strain on the energy and intensity of the peaks in the photoluminescence spectra.

However, to date, TMD monolayers of the best quality are obtained by mechanical exfoliation. Their combination with other two-dimensional materials by mechanical stacking with a polymer stamp makes it possible to create van der Waals (vdW) heterostructures which, in turn, host a plethora of exciting phenomena such as long-lived indirect and highly localized Moiré excitons, making them promising for optoelectronics applications.

Nevertheless, there are no reported attempts to assess the strain arising in the process of stacking the layers. The aim of this work is to observe the photoluminescence of an exciton line in atomically thin layers of WS₂ during transfer onto a rigid substrate. For this purpose, we engineered an
inverted transfer setup which relates to the field of precision manipulation and can be used to observe the emerging strain in TMD during the transfer in-situ. We believe that our results lay the foundation for the next crucial technological step — the elimination of interfacial inhomogeneities caused by strains induced during typical mechanical transfer.

2. Experiment

Here we have studied the spatial distribution of a PL signal of WS$_2$ monolayers during transfer onto a glass slide from a bare polydimethylsiloxane (PDMS) stamp (Fig. 1(a)) and pick-up by a hexagonal boron nitride (hBN)/polycarbonate (PC)/PDMS stamp and subsequent transfer onto a hBN substrate (Fig. 1(b)). WS$_2$ monolayers were used due to their predicted high PL sensitivity to the strain.

2.1 Sample preparation and transfer setup.

To obtain atomically thin layers of WS$_2$, mechanical exfoliation technology was used. Blue NittoTM Scotch Tape was used to exfoliate the bulk crystal onto a commercially available (gel-film from Gelpak) viscoelastic PDMS stamp (for transfer onto glass) or a SiO$_2$/Si substrate (for pick-up and transfer with hBN stamp). After the thin layer was found in bright field reflection, its single layer thickness was confirmed by photoluminescence spectroscopy with the characteristic spectrum shown on Fig.3 (b). The PL characteristics can serve as both a measure of the layer thickness and a measure of its homogeneity.

Then we have used a specially designed inverted system to transfer the monolayer on the substrate. The essence of the transfer method in inverted geometry is that a transparent plate with a polymer stamp containing a layer of atomically thin material is installed in the movable stage of an inverted microscope, and the substrate on which the layer of atomically thin material is transferred is fixed on the manipulator holder. After that, the substrate is brought in contact with a certain area of the stamp.

![Figure 1. Schematics of transfer of monolayer WS$_2$ onto glass substrate using bare PDMS(a) or hBN(b) stamp. Red arrow indicates stacking direction.](image)

2.2 Photoluminescence measurements.

A neodymium laser TORUS with a 532nm wavelength and a power of 15-30 µW is used to excite PL. In the experiment, the beam is focused on the sample to an approximately 1µm spot by the objective lens (water-immersion objective Olympus 60x, NA=1.2). The collected PL signal is analyzed by a slit spectrometer (Horiba LabRAM HR). The setup for PL spectroscopy mapping is shown in Fig.2.
Figure 2. Setup for photoluminescence spectroscopy mapping. The optical image shows a clear transfer front of PDMS/WS\textsubscript{2} onto glass substrate.

As the stamp with a monolayer is slowly moved down to contact with the substrate, it develops the stamp-substrate contact front, which is clearly visible in the camera (Fig. 3(a)). To measure the strain, induced during transfer, the PL signal is spatially mapped by the objective scanning with a piezo PI AIST-NT model P-517K079. The resulting PL map is presented in Fig. 3(b).

Fig. 3(b) shows the PL intensity map for a WS\textsubscript{2} transfer from PDMS to glass. Three regions with different photoluminescence intensities and uniformity are seen: region A, where the WS\textsubscript{2} monolayer is on the PDMS stamp and not yet in contact with the glass, region B, where the front of the PDMS/WS\textsubscript{2} contact with glass is seen and region C is the PDMS/WS\textsubscript{2} in full contact with glass. The corresponding spectra taken at points A, B and C are shown in Fig. 3(c). Also, Fig. 3(c) shows spectrum 0 (PDMS/WS\textsubscript{2}/air) corresponding to the reference before transfer, featuring the main PL peak around 2.021 eV for PDMS/WS\textsubscript{2} reference system, in agreement with the previous findings\textsuperscript{18}. This peak corresponds to the A-exciton, and the asymmetry of the left wing of the spectrum is associated with a closely spaced trion\textsuperscript{19}, with the intensity significantly suppressed at room temperature. To analyze the evolution of the observed peak across the transfer line, we have fitted it with a Voight function, given by the convoluted Lorenzian and Gaussian functions, which allowed us to evaluate both homogeneous (w\textsubscript{L}) and inhomogeneous (w\textsubscript{G}) broadening. The results of the fitting are presented in Table 1.

First, we note that the reference spectrum peak coincides with that from point A, indicating region A is intact despite its proximity to the transfer front. As front approaches the region B PL intensity increases by approximately 40% compared to the PDMS/WS\textsubscript{2}/air region and then abruptly drops for the PDMS/WS\textsubscript{2}/glass region C, also becoming spatially less homogeneous. Furthermore, the PL line spectral position redshifts across the front line: it is 2.020 eV for the A (WS\textsubscript{2} on PDMS) and B (front) regions and 2.015 eV in the C region (PDMS/WS\textsubscript{2}/glass).

The article\textsuperscript{18} reports significant changes in the band gap in TMD monolayers caused by uniaxial strain. The observed 5 meV redshift for the flake on PDMS in contact with glass can be associated with strain of 0.1-0.5%, depending on the PL shift/strain coefficient used\textsuperscript{7}. We also note that as the monolayer is put in contact with the glass substrate, its dielectric environment changes significantly (\(\varepsilon_{\text{PDMS}} = 2.5, \varepsilon_{\text{glass}} = 6.7\)), which also can influence the PL signal. Indeed, the observed effect of a sharp change in the photoluminescence signal from area A to area C can be associated with
a strong screening of the Coulomb interaction by glass as the intensity of photoluminescence $I_{PL}$ directly depends on the dielectric constant of the environment$^{21}$: $I_{PL} \propto \frac{|d_{cv}|^2}{\varepsilon} n_{ex}$, where $|d_{cv}|^2$ is the square of the module of the matrix element of the dipole transition for the excited electron to the ground state, $n_{ex}$ is the concentration of excitons. Moreover, the larger dielectric constant of the glass substrate would reduce the exciton binding energy and blueshift the observed PL emission, which is the opposite of what we observe in our experiment. We, therefore, conclude, that our estimate 0.1-0.5% of transfer-induced strain is an underestimate of the real strain value.

![Figure 3. In-situ photoluminescence spectroscopy and spatial mapping.](image)

(a) The optical microphotograph of the PL-mapped region of the WS$_2$.
(b) The spatial photoluminescence map of the WS$_2$ transfer from PDMS onto glass slide.
(c) Photoluminescence spectra taken at different locations, corresponding to points A (PDMS/WS$_2$/air), B (PDMS/WS$_2$/front), C (PDMS/WS$_2$/glass) of the heterostructure during transfer. Point 0 (PDMS/WS$_2$/air) corresponding to WS$_2$ reference before transfer was started.

Next, an hBN dielectric was used as both the stamp and the substrate layer in order to reduce the possible influence of the dielectric constant of glass (Fig.1 (b)). The hBN crystals are one of the strongest electrically insulating materials and its high interlayer integrity makes them good support as mechanical reinforcements$^{22}$ with dielectric constant value $\varepsilon = 3.5^{23}$.

Similar to the first experiment, the photoluminescence spectra were measured from the three distinct regions corresponding to areas A, B, C. Fig. 4 shows three regions with photoluminescence signal at 1.997 eV, in agreement with literature$^{24}$, our PL map is featuring different intensities and uniformity. First, we note that for PDMS/PC/hBN/WS$_2$ to hBN transfer the front region is much wider and does not exhibit PL intensity increase. However, similar to the first experiment, the overall PL intensity declines as PDMS/PC/hBN/WS$_2$ comes into contact with the bottom hBN, which is consistent with the increase of the effective dielectric constant as WS$_2$ becomes encapsulated by hBN on both sides. However, there is no spectral shift in PL within the sensitivity of our spectrometer (0.5 nm), due to the mechanical support of the WS$_2$ monolayer by the hBN layer and the suppression of mechanical strains.
Figure 4. In-situ photoluminescence spectroscopy and spatial mapping.
(a) The optical microphotograph of the PL-mapped region of the WS$_2$ between two hBN.
(b) The spatial photoluminescence map of the WS$_2$ transfer from PDMS/PC/hBN onto hBN.
(c) Photoluminescence spectra taken at different locations, corresponding to points A (PDMS/PC/hBN/WS$_2$/air), B (PDMS/PC/hBN/WS$_2$/front), C (PDMS/PC/hBN/WS$_2$/hBN) of the heterostructure during transfer.

Table 1. Results of experimental data fitting

| Material       | Peak (eV) | wL (meV) | wG (meV) | Intensity (arbitrary units) |
|----------------|-----------|----------|----------|-----------------------------|
| PDMS/WS$_2$/air(ref.) | 2.021     | 21.3     | 9.8      | 978                         |
| PDMS/WS$_2$/air    | 2.020     | 21.6     | 9.3      | 1024                        |
| PDMS/WS$_2$/front  | 2.021     | 21.8     | 8.3      | 1550                        |
| PDMS/WS$_2$/glass  | 2.015     | 24.5     | 5.7      | 882                         |
| hBN/WS$_2$/air     | 1.997     | 25.9     | 0.0002   | 747                         |
| hBN/WS$_2$/front   | 1.997     | 28.0     | 0.0027   | 423                         |
| hBN/WS$_2$/hBN     | 1.997     | 28.4     | 0.0002   | 95                          |

Conclusions

We have demonstrated a method to quantify transfer-induced strains and experimentally observe the photoluminescence spectral and intensity variation across the transfer front.

In the first series of experiments, PL quenching due to the increased Coulomb screening by a high-$\varepsilon$ substrate is observed, as well as strong PL enhancement in the narrow region close to the transfer front, which is not fully understood. A redshift of 5-6 meV is observed and is consistent with the lower
estimate of 0.1-0.5% strain during transfer. We emphasize that it is an underestimated value, as the increase dielectric constant of the substrate acts to blueshift PL during transfer.

In order to reduce the influence of high dielectric contrast between the substrate and the stamp in the second series of experiments, we used hBN both as a stamp and a substrate. There is no shift during encapsulation in hBN, but there is a contribution to the intensity decrease, which we relate to the increase of the effective dielectric constant during both-side hBN encapsulation.

We also strive to quantify the observed deformation and implement a method to reduce it to create homogeneous samples with a homogeneously narrow exciton line.

Acknowledgments

The study was funded by Russian Science Foundation according to project #20-72-00157.

References

1. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS2: A new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 2–5 (2010).
2. Hanbicki, A. T., Currie, M., Kioseoglou, G., Friedman, A. L. & Jonker, B. T. Measurement of high exciton binding energy in the monolayer transition-metal dichalcogenides WS 2 and WSe 2. *Solid State Commun.* **203**, 16–20 (2015).
3. Benimetskiy, F. A. et al. Measurement of local optomechanical properties of a direct bandgap 2D semiconductor Measurement of local optomechanical properties of a direct bandgap 2D semiconductor. *101126*, (2019).
4. Carrascoso, F., Li, H., Frisenda, R. & Castellanos-Gomez, A. Strain engineering in single-, bi- and tri-layer MoS2, MoSe2, WS2 and WSe2. *12*, (2020).
5. Lee, J. H., Chung, B., Park, S. H., Moon, H. C. & Lee, D. H. Fabrication of Grid-Type Transparent Conducting Electrodes Based on Controlled Mechanical Fracture. *Macromol. Res.* **26**, 157–163 (2018).
6. Conley, H. J. et al. Bandgap engineering of strained monolayer and bilayer MoS2. *Nano Lett.* **13**, 3626–3630 (2013).
7. Aas, S. & Bulutay, C. Strain dependence of photoluminescence and circular dichroism in transition metal dichalcogenides: A k · p analysis. *arXiv 26*, 28672–28681 (2018).
8. Zhang, Q. et al. Strain Relaxation of Monolayer WS2 on Plastic Substrate. *Adv. Funct. Mater.* **26**, 8707–8714 (2016).
9. Lloyd, D. et al. Band Gap Engineering with Ultralarge Biaxial Strains in Suspended Monolayer MoS2. *Nano Lett.* **16**, 5836–5841 (2016).
10. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. G. and A. A. F. Electric Field Effect in Atomically Thin Carbon Films. *306*, 666–669 (2016).
11. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature 499*, 419–425 (2013).
12. Calman, E. V. et al. Indirect excitons in van der Waals heterostructures at room temperature. *Nat. Commun.* **9**, 1–5 (2018).
13. Förg, M. et al. Moiré excitons in MoSe2-WSe2 heterobilayers and heterotrilayers. *arXiv 1–7* (2020) doi:10.1038/s41467-021-21822-z.
14. Novoselov, K. S. et al. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci. U. S. A.* **102**, 10451–10453 (2005).
15. Mueller, T. & Malic, E. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *2D Mater. Appl.* **2**, 1–12 (2018).
16. Ivanova T., Kulachenkov N., Permyakov D., Sinev I., Khestanova E., Patent of the Russian
17. Castellanos-Gomez, A. et al. Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping. 2D Mater. 1, (2014).
18. Eizagirre Barker, S. et al. Preserving the Emission Lifetime and Efficiency of a Monolayer Semiconductor upon Transfer. Adv. Opt. Mater. 7, (2019).
19. Wei, Ke, Yu Liu, Hang Yang, Xiangai Cheng, T. J. Large range modification of exciton species in monolayer WS2. Appl. Opt. 55, (2016).
20. Wang, Y. et al. Strain-induced direct–indirect bandgap transition and phonon modulation in monolayer WS2. Nano Res. 8, 2562–2572 (2015).
21. Chatterjee, S. et al. Excitonic Photoluminescence in Semiconductor Quantum Wells: Plasma versus Excitons. Phys. Rev. Lett. 92, 1–4 (2004).
22. Falin, A. et al. Mechanical properties of atomically thin boron nitride and the role of interlayer interactions. Nat. Commun. 8, 1–9 (2017).
23. Laturia, A., Van de Put, M. L. & Vandenberghe, W. G. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. 2D Mater. Appl. 2, (2018).
24. Nagler, P. et al. Zeeman Splitting and Inverted Polarization of Biexciton Emission in Monolayer WS2. Phys. Rev. Lett. 121, 57402 (2018).
25. Lin, Y. et al. Dielectric screening of excitons and trions in single-layer MoS2. Nano Lett. 14, 5569–5576 (2014).