2D Materials

LETTER

Strongly adhesive dry transfer technique for van der Waals heterostructure

2D Materials

LETTER

Strongly adhesive dry transfer technique for van der Waals heterostructure

RECEIVED
5 May 2020

REVISED
9 June 2020

ACCEPTED FOR PUBLICATION
6 August 2020

PUBLISHED
21 August 2020

Suhan Son[1,2,3,9], Young Jae Shin[4,5,9], Kaixuan Zhang[1,2,3], Jeacheol Shin[2], Sungmin Lee[2,3], Hiroshi Idzuchi[4], Matthew J Coak[2,3,6], Hwangsun Kim[3,7], Jangwon Kim[8], Jae Hoon Kim[8], Miyoung Kim[3,7], Dohun Kim[2], Philip Kim[4] and Je-Geun Park[1,2,3]

[1] Center for Quantum Materials, Seoul National University, Seoul 08826, Republic of Korea
[2] Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea
[3] Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Republic of Korea
[4] Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States of America
[5] Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States of America
[6] Department of Physics, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, United Kingdom
[7] Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Republic of Korea
[8] Department of Physics, Yonsei University, Seoul 03722, Republic of Korea
[9] Authors with equal contributions

E-mail: jgpark10@snu.ac.kr

Keywords: two-dimensional materials, van der Waals heterostructures, polycaprolactone, dry transfer technique, $NbSe_2$, transition metal thiophosphate

Supplementary material for this article is available online

Abstract

That one can stack van der Waals materials with atomically sharp interfaces has provided a new material platform of constructing heterostructures. The technical challenge of mechanical stacking is picking up the exfoliated atomically thin materials after mechanical exfoliation without chemical and mechanical degradation. Chemically inert hexagonal boron nitride (hBN) has been widely used for encapsulating and picking up vdW materials. However, due to the relatively weak adhesion of hBN, assembling vdW heterostructures based on hBN has been limited. We report a new dry transfer technique. We used two vdW semiconductors ($ZnPS_3$ and $CrPS_4$) to pick up and encapsulate layers for vdW heterostructures, which otherwise are known to be hard to fabricate. By combining with optimized polycaprolactone (PCL) providing strong adhesion, we demonstrated various vertical heterostructure devices, including quasi-2D superconducting $NbSe_2$ Josephson junctions with atomically clean interface. The versatility of the PCL-based vdW stacking method provides a new route for assembling complex 2D vdW materials without interfacial degradation.

1. Introduction

Mechanical exfoliation and van der Waals stacking of atomically thin materials have been one of the significant experimental methods to produce functional 2D materials heterostructures [1–11]. Experimentally, this technique requires reliable mechanical exfoliation of single crystals on a silicon/SiO_2 substrate, followed by picking up or dropping down the atomically thin crystals using various polymer layers such as polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), polycarbonyl (PC), and polypropylene carbonate (PPC) [12–15]. However, these polymer layers are known to leave chemical residues on the 2D materials interfaces [12]. Often chemically inert hexagonal boron nitride (hBN) or graphite/graphene layers are used to interface between these polymer layers and target 2D materials for picking up to form vdW heterostructures [9, 14–16]. This method has been widely adopted for graphene, hBN, and some other gapped semiconducting transition metal dichalcogenides such as TMX_2, where TM = W and Mo, and X = S, Se and Te. However, relatively weak adhesion of hBN and graphene makes it challenging to extend this method to other more complex 2D materials, in particular, metallic and superconducting TMX_2 such as TM = Ta and Nb, and X = S, Se and Te.

In this work, we report a novel pick-up method by using optimally formed polymer layers using

polycaprolactone (PCL). Furthermore, we developed the technique by combining with vdW large gap semiconductors, i.e. $ZnPS_3$ and $CrPS_4$. Employing improved chemical adhesion of both $ZnPS_3$ and $CrPS_4$ together with mechanical stability provided by PCL, we demonstrate complex vdW heterostructures consisting of superconductors and magnetic materials, where the functional interfaces are completely encapsulated thus free from chemical degradation.

2. Method

2.1. Preparation of PCL stamp

The PCL stamp was prepared in the following way. First, polycaprolactone (Sigma Aldrich, average Mn: 80 000) was dissolved in tetrahydrofuran (THF) solvent. PCL concentration in the finally obtained solution was 15% in THF (mass percent). Afterward, the mixture was stirred using magnetic stirrer until completely dissolved (>48 h). The solution formed the viscous and transparent liquid. PDMS was prepared by mixing SYLGARD 184 base and curing agent (10:1 ratio, respectively), followed by curing for 2 h at 75 °C. As illustrated in figure 1(a), PDMS block was put on top of a glass slide and fixed by the transparent tape (Scotch® Crystal Tape). The PCL solution was then dropped on the tape and spin-coated with the rate of 2000 rpm for 1 min. and annealed at 75 °C for 10 min. to flatten the polymer.

2.2. Pick-up and drop-down of vdW flakes

We used a micro-manipulator to align the PCL stamp for the pick-up and drop-down vdW flakes. It was easy to distinguish the area of the PCL stamp attached to the substrate by its color and fringe around it as in ref [16]. As described in figure 1(b), the PCL stamp was first put on the substrate at 55 °C and then heated to 65 °C so that PCL was fully and uniformly melted. Finally, to pick up the flake, the micro-manipulator was retracted very slowly after being cooled to 30 °C. For the sequential pick-up (figure 1(d)), the same procedure was repeated. For the drop-down of vdW flakes at the final step, the temperature was again increased to 75 °C after touching the substrate. By heating above the melting point of PCL, 60 °C, we made PCL fully melted and thereby to lose most of the adhesion to the sample, which makes it easy to avoid the unintended pick-up during the drop-down process. Then, the micro-manipulator was slowly retracted, and the PCL stamp was finally isolated to the substrate, leaving all the flakes on the substrate because PCL was still in a liquid state. Every fabrication step was undertaken inside a glove box under an argon atmosphere. To remove the polymer on the flakes, the processed substrate was kept immersed in a THF solvent over-night.

2.3. Fabrication of $NbSe_2/SiO_2/NbSe_2$ heterostructure

The $NbSe_2$ flake was exfoliated on 285 nm SiO_2 substrate. First, $NbSe_2$ was directly picked up via a PCL stamp, after which SiO_2 was deposited on another prepared $NbSe_2$. As the final step, the already picked-up $NbSe_2$ was dropped on $SiO_2/NbSe_2$. After resolving PCL by THF, the electrode was deposited via a conventional e-beam lithography technique and e-beam evaporation. The metal electrode of 5 nm Ti and 60 nm Au were deposited on top of samples by the electron-beam evaporator.

2.4. Fabrication of $CrPS_4/NbSe_2/CrPS_4$ heterostructure

At first, all samples were exfoliated on 285 nm SiO_2 substrate. Then, the PCL stamp was used to pick up the top-most $CrPS_4$, which was followed by picking up $NbSe_2$ and $CrPS_4$ sequentially. Moreover, the combined structure of $PCL/CrPS_4/NbSe_2/CrPS_4$ was dropped on the pre-patterned electrodes that were prepared in the same way as that of the $NbSe_2/SiO_2/NbSe_2$ heterostructure. Metal contacts of 2 nm Ti and 8 nm Pt were deposited on top of samples by the electron-beam evaporator.

2.5. Cs-TEM measurement

Samples were prepared with a focused ion beam (FIB) milling with a FIB instrument (Helios 650, FEI) and ion milling with a nanomill (Model 1040, Fischione). Atomic resolution high angle annular dark-field scanning transmission electron microscopy (TEM) image and energy dispersive spectroscopy results were obtained with 80 kV spherical aberration-corrected TEM (JEM-ARM200F, JEOL).

3. Results and discussion

Layered transition metal thiophosphate ($TMPS_x$) is a class of 2D vdW semiconductors that exhibit various magnetic properties [17, 18]. For example, $ZnPS_3$ is a paramagnetic semiconductor, while $CrPS_4$ is an antiferromagnetic insulator with a Neel temperature of 36 K [19]. With the robust adhesive strength of PCL, we improved the chance of picking up van der Waals flakes. We also showed that with a PCL stamp, an insulating vdW $ZnPS_3$ could be used to pick up other vdW materials, which were previously known to be very challenging while maintaining a clean interface (figures 1(e)–(h) and 2(b)).

To fabricate novel vdW heterostructures, we have developed the PCL-based stamp to handle vdW flakes, which has been technically challenging using the conventional polymer/hBN based method. The schematics of the PCL stamp are illustrated in figures 1(a) and (b). By adhesive strength measurements, we found that PCL has

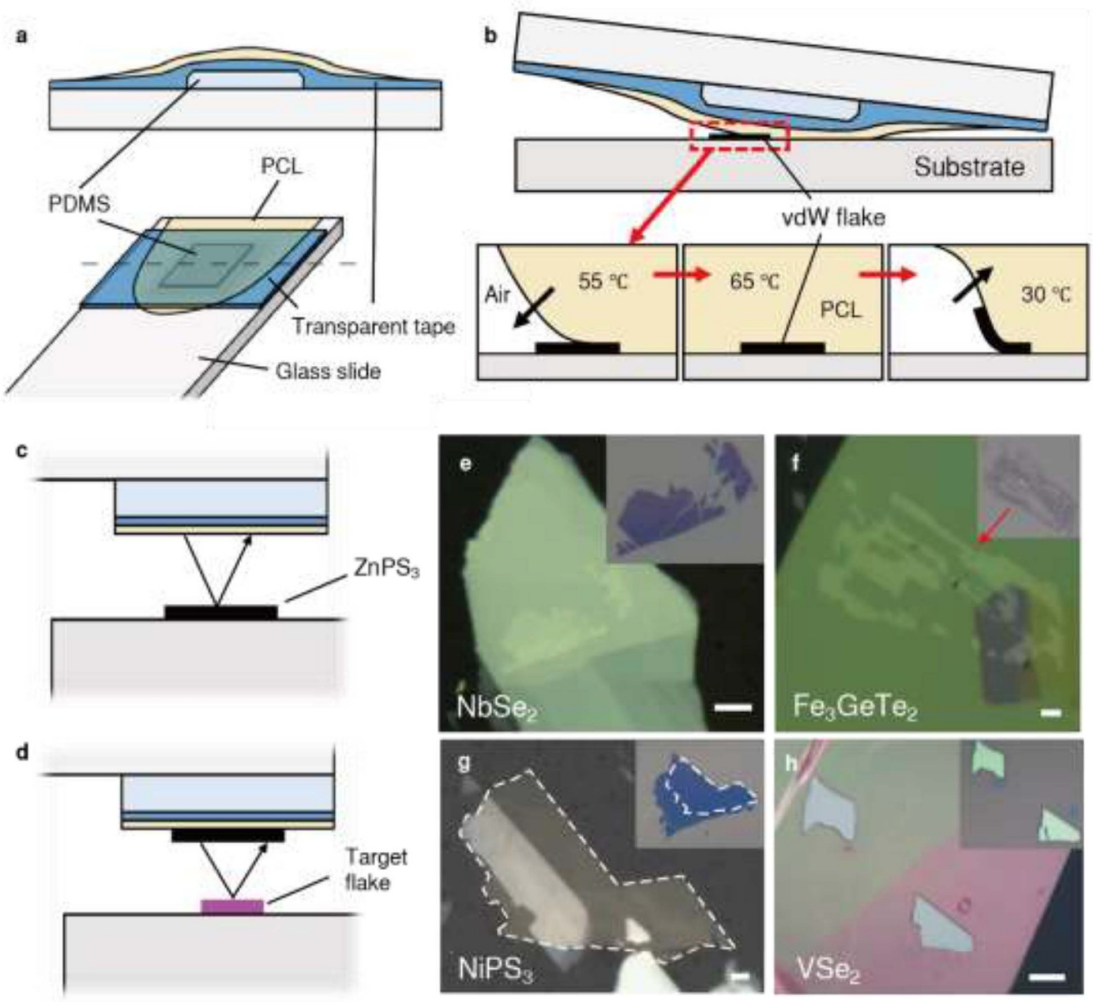

Figure 1. Schematics of dry transfer technique and its pick-up ability. (a) The structure of the PCL stamp for the fabrication. (b) Schematics of the pick-up process. (c) $ZnPS_3$ picked-up by PCL stamp. (d) Continuous pick-up of target flake followed by c (with $ZnPS_3$, here). (e)–(h) Optical images of PCL stamp after the pick-up process. Examples of $NbSe_2$, Fe_3GeTe_2, $NiPS_3$, and VSe_2 were shown, respectively. A bright color difference can recognize the shape of target flakes in each inset compared to the background of the $ZnPS_3$ flake in the image. All scale bars are for 5 μm. Insets: optical images of exfoliated target flakes on 285 nm SiO_2 substrate before the pick-up process.

the most robust adhesive strength than any other polymers known until now, at least 20 times larger than that of the most commonly used PPC [14] (see supplementary note 1 (available online at https://stacks.iop.org/2DM/7/041005/mmedia)). As a real test of the PCL stamp, we could successfully pick up all exfoliated graphite on oxygen plasma treated SiO_2 substrate and $CrPS_4$ (see supplementary note 1).

In the conventional vdW stacking method, the PPC or PC-based hBN pick-up method has been widely used as a top-most layer for the vdW heterostructure. Chemically inert hBN exhibits weak vdW interaction between hBN and substrate. This weak adhesion allows picking up hBN flakes from the SiO_2 substrate, where the flakes are initially deposited during the mechanical exfoliation process [14]. The PPC or PC polymer layers provide a rather weak adhesive strength, just enough to pick up hBN, making other vdW materials for the initial picking up layer for vdW heterostructure sub-optimal.

Once hBN is picked up, one can use the vdW force between hBN and the target flake to fabricate heterostructures. In this way, the PPC/hBN pick-up method has been able to cover many parts of the finally built vdW heterostructures. However, hBN is known to be bad at detaching some vdW materials from the substrate, making the PPC/hBN pick-up method more challenging and time-consuming for certain vdW materials [20]. To successfully pick up vdW flakes, the adhesive vdW force between the top-most material and the target flake must be significantly stronger than that between the substrate and the target flake. However, if the target flakes have strong adhesion with the deposited substrate, the PPC/hBN pick-up method fails. In particular, $NbSe_2$, a 2D vdW superconductor, is known extremely hard to pick up. Several innovative experimental techniques, including the via method, electrical contact with graphite, and PDMS drop down [20–23], have been performed to build vdW devices together with $NbSe_2$.

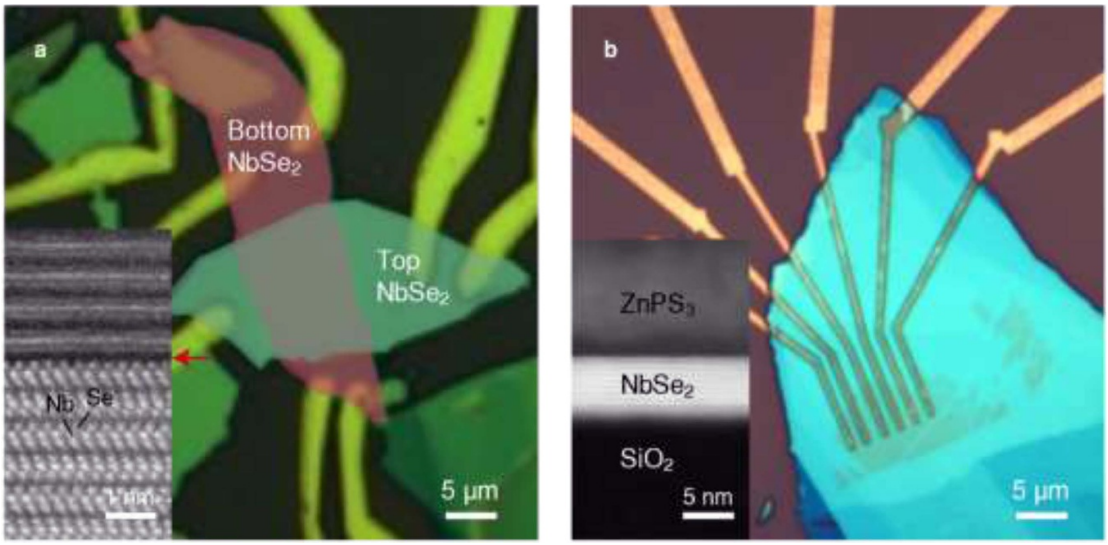

Figure 2. $NbSe_2$ heterostructures and its TEM images. (a) Optical microscope image of $NbSe_2/SiO_2/NbSe_2$ Josephson junction. Top $NbSe_2$ was directly detached from the SiO_2 substrate using a PCL stamp. Top and bottom $NbSe_2$ are depicted as the false-color for clarity. Inserted SiO_2 layer was 0.13 nm thick. (b) Optical microscope image of $ZnPS_3/NbSe_2$ flakes. It was dropped down on the pre-patterned electrode on 285 nm SiO_2 substrate after being picked up sequentially from the substrate. Insets: TEM images of each device showing a clean and sharp interface of the heterostructure.

Still, very limited device fabrication yields have so far been reported due to strong adhesion of $NbSe_2$ to the SiO_2 substrates. We found that the strong adhesive force of PCL provides enough adhesion to pick up several new vdW flakes directly from the substrate. Therefore, there is no need to restrict the top-most vdW layer to hBN in the PCL-based pick-up method.

The strong adhesion using PCL allows us to apply this polymer layer to pick up other designed vdW materials as the top-most layer for vdW heterostructures. Using this method, we first tested the insulating vdW material, $ZnPS_3$ (see supplementary note 2), as the top-most layer. The PCL stamp was used to pick up $ZnPS_3$ from the substrate in figure 1(c).

We also found that the PCL/$ZnPS_3$ can pick up the other target vdW flakes with high yield (figure 1(d)). Figures 1(e)–(g) showcase the successful examples of several vdW target flakes, which we tried with this method with the following success rate: 12 success/14 trials, 2/2, 2/3, and 1/2 for $NbSe_2$, Fe_3GeTe_2, $NiPS_3$, and VSe_2, respectively. In contrast, when we used the PPC/hBN pick-up method, it produced significantly smaller yields: 0 success/7 trials, 0/4, 1/4, and 0/1 for $NbSe_2$, Fe_3GeTe_2, $NiPS_3$, and VSe_2, respectively. With this new method reported here, we succeeded in all the van der Waals materials we tested: $NbSe_2$, Fe_3GeTe_2, $NiPS_3$, and VSe_2. Furthermore, we also found in this study that $ZnPS_3$ is a right candidate as an alternative top-most capping layer, aspects of which provides the adhesion force enough to target material under fabrication and the material as the protecting layer for underlying flakes (see supplementary note 3). Using PCL, we also demonstrated a direct pick-up method successfully without any top-most capping layer, as shown in figures 2(a) and 3(a). In this case, the functionalized van der Waals materials were used as the self-defined top-most capping layer.

A clean interface also demonstrates the strength of this new pick-up method. Among the all vdW heterostructure assembly methods, the vdW pick-up method by hBN shows the cleanest interface [12]. It is because vdW flakes are sequentially picked up, which makes their interfaces, not in direct contact with the polymer. Therefore, underneath flakes and its interfaces remain free of the polymer residue. We demonstrate that it is also the case with the PCL pick-up method. We checked the interface in the test samples of $NbSe_2/SiO_2/NbSe_2$ and $ZnPS_3/NbSe_2$ heterostructures (see figure 2) with the TEM images (insets of figures 2(a) and (b)) showing a very sharp and clean interface.

Moreover, there is no artificial effect in the transport data originating from the fabrication method (see supplementary note 3). All these observations validate the clean interface achieved by the PCL pick-up method. A clean interface between two different materials is crucial to attaining new emergent phenomena [24–27]. Thanks to its clean interfaces by the pick-up method, we can now explore the intriguing phenomena that could otherwise be more difficult, if not impossible, to realize and thereby investigate novel physics like proximity effect at the interface of the vdW heterostructure system.

As another test, we fabricated the $CrPS_4/NbSe_2/CrPS_4$ heterostructure (figures 3(a) and (b)). It not only introduces the magnetic proximity effect to the superconducting system in vdW heterostructure [28] but also demonstrates the novel aspect of the PCL method further. Here we could expect the additional

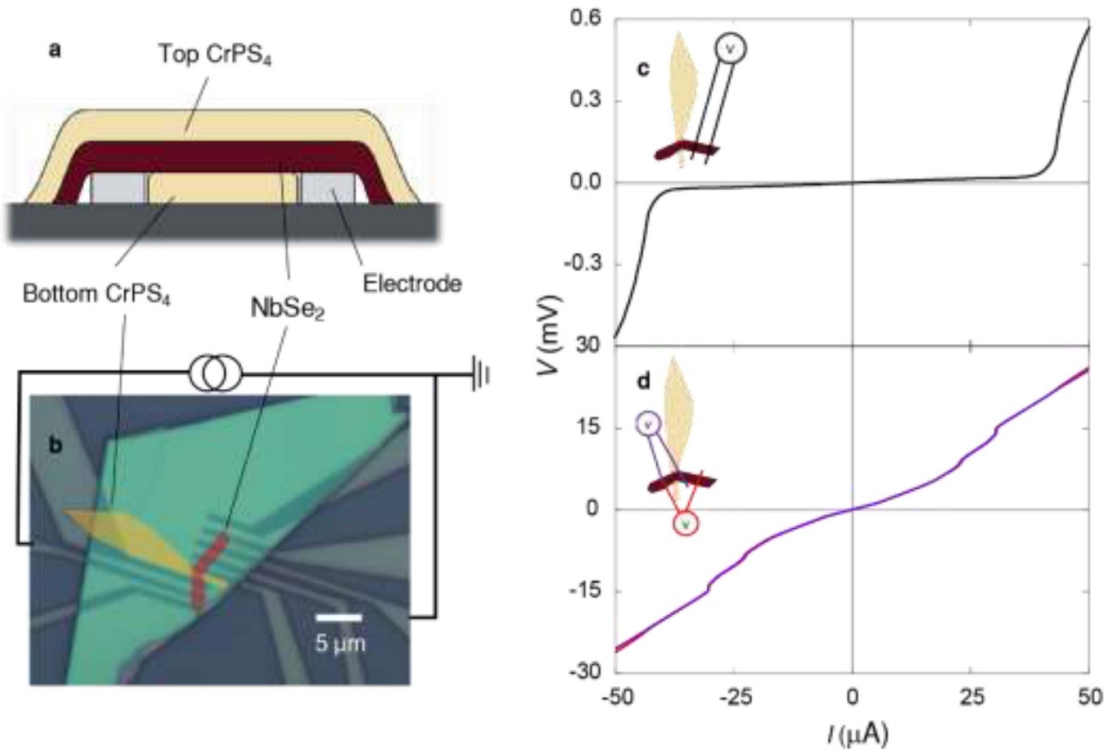

Figure 3. Transport measurement of $CrPS_4/NbSe_2/CrPS_4$ heterostructure. (a) Schematics of the device. (b) Optical microscope image of the device (False color). Bottom $CrPS_4$ and $NbSe_2$ are colored to the same color to the corresponding layer of a for clarity. (c) and (d) V–I characteristics at 1.5 K. Voltage drop was measured at different parts. Each colored data indicates the same colored wire configuration drawn at the schematics in the inset.

magnetic exchange interaction to $NbSe_2$ due to the nearby A-type antiferromagnetic vdW $CrPS_4$, which is different from the case of non-magnetic insulator $ZnPS_3$ described in figure 2(b) (see supplementary note 2). And the $NbSe_2$ superconductivity is expected to be affected dramatically by the magnetic moments of $CrPS_4$ [26]. We note that because the clean interface is crucial and ferromagnetic insulators are quite rare, this kind of experiment has remained limited only to a handful of cases [29].

For the fabrication of the heterostructure (figures 3(a) and (b)), we sequentially picked up the three key materials from the SiO_2 substrates: the top $CrPS_4$, the middle $NbSe_2$, and the bottom $CrPS_4$ (see Methods). Note that we were able to pick up $NbSe_2$ using $CrPS_4$. We emphasize that during the whole process, the middle $NbSe_2$ layer was never exposed to the PCL polymer, unlike the previously known methods [12].

The quality of $CrPS_4/NbSe_2$ interfaces can further be tested by carrying out electrical transport measurements, as shown in figure 3(b). In this heterostructure, the electrical current flows only through $NbSe_2$ since $CrPS_4$ is insulating [30]. All the measurements were performed at 1.5 K, well below the T_C of $NbSe_2$. Figure 3(c) shows the typical superconducting behavior of $NbSe_2$ across the region, where a single side of $NbSe_2$ is in contact with $CrPS_4$. Interestingly, we find that the superconducting behavior of $NbSe_2$ destroyed across the part where both sides of $NbSe_2$ are sandwiched by $CrPS_4$ (figure 3(d)), exhibiting metallic V–I characteristics (non-zero slope near zero-current). Assuming the quality of $NbSe_2$ is similar in both regions, the observation of non-superconducting behavior in the $CrPS_4$-sandwiched part of the $NbSe_2$ sample suggests that superconductivity of $NbSe_2$ was significantly weakened by the spin alignment nearby from the magnetic material. Similar destruction of superconductivity was reported in the thin films of ferromagnet and superconductor [31].

4. Conclusions

In conclusion, our new PCL-based pick-up method, together with $ZnPS_3$ and $CrPS_4$, can be used for several vdW flakes that have been known difficult to handle thanks to its strong adhesive strength. By using this method, several new vdW heterostructures, otherwise challenging to fabricate, could be achieved with a unique combination and an increased yield. Furthermore, we could also show that this original pick-up method ensures a polymer-residue-free and clean interface by TEM measurement and transport measurements. Finally, we succeeded in fabricating $NbSe_2$ heterostructure sandwiched by magnetic $CrPS_4$, showing an apparent magnetic proximity effect. The PCL pick-up method presented here will be proven invaluable to the much more extensive efforts towards the fabrication of clean-interfaced

vdW heterostructure boosting the related research field.

Acknowledgments

The authors would like to thank Jonghyeon Kim, Inho Hwang, Youjin Lee, and Junghyun Kim for their generous help and discussion. Work at CQM was supported by the Leading Researcher Program of the National Research Foundation of Korea (Grant No. 2020R1A3B2079375). Work at IBS CCES was supported by the Institute for Basic Science of the Republic of Korea (Grant Nos. IBS-R009-G1); work at Harvard Univ. was supported by Global Research Laboratory Program (2015K1A1A2033332) through the National Research Foundation of Korea (NRF) for sample preparation and DOE QPRESS (DE-SC0019300) for device fabrication and characterization; work by Y.J.S. used resources at the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, and at Brookhaven National Laboratory under Contract No. DE-SC0012704; work at Yonsei Univ. was supported by the National Research Foundation of Korea (NRF) grants funded by the Ministry of Science, ICT (SRC Program No. NRF-2017R1A5A1014862); work of M.K. was supported by the National Research Foundation of Korea (NRF) grants funded by the Ministry of Science and ICT (MSIT) [No. 2015R1A5A1037627]; work of D.K. was supported by Basic Science Research Program, Quantum Computing Technology Development Program (Grant No. 2018R1A2A3075438 and No. 2019M3E4A1080145) through the National Research Foundation of Korea (NRF) funded by the Korean government (MSIT) and Creative-Pioneering Researchers Program through Seoul National University (SNU).

Author contributions

SS and YJS contributed equally. J-GP and PK supervised the project. SS, YJS, and SL prepared devices and single crystals, and YJS developed the PCL polymer. SS, JS, HI, and DK measured transport properties. HK & MK performed Cs-TEM measurement, and JK & JHK carried out optical absorption measurement. SS, YJS, KZ, MJC, PK, and J-GP designed the experiments, and SS and YJS analyzed the data. All authors discussed the results, and SS, KZ, PK, and JGP wrote the manuscript with comments from all authors.

Additional information

Supplementary information is available in the online version of the paper.

Competing financial interests

The authors declare no competing financial interest.

ORCID iD

Je-Geun Park https://orcid.org/0000-0002-3930-4226

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films *Science* **306** 666–9
[2] Ajayan P, Kim P and Banerjee K 2016 Two-dimensional van der Waals materials *Phys. Today* **69** 38–44
[3] Son S *et al* 2019 Bulk properties of the van der Waals hard ferromagnet VI_3 *Phys. Rev.* B **99** 041402
[4] Park J G 2016 Opportunities and challenges of 2D magnetic van der Waals materials: magnetic graphene? *J. Phys. Condens. Matter* **28** 301001
[5] Gibertini M, Koperski M, Morpurgo A F and Novoselov K S 2019 Magnetic 2D materials and heterostructures *Nat. Nanotechnol.* **14** 408–19
[6] Manzeli S, Ovchinnikov D, Pasquier D, Yazyev O V and Kis A 2017 2D transition metal dichalcogenides *Nat. Rev. Mater.* **2** 17033
[7] Carvalho A, Wang M, Zhu X, Rodin A S, Su H and Castro Neto A H 2016 Phosphorene: from theory to applications *Nat. Rev. Mater.* **1** 16061
[8] Burch K S, Mandrus D and Park J G 2018 Magnetism in two-dimensional van der Waals materials *Nature* **563** 47–52
[9] Huang B *et al* 2017 Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit *Nature* **546** 270–3
[10] León-Brito N, Bauer E D, Ronning F, Thompson J D and Movshovich R 2016 Magnetic microstructure and magnetic properties of uniaxial itinerant ferromagnet Fe_3GeTe_2 *J. Phys. D: Appl. Phys.* **120** 083903
[11] McGuire M 2017 Crystal and magnetic structures in layered, transition metal dihalides and trihalides *Crystals* **7** 121
[12] Frisenda R, Navarro-Moratalla E, Gant P, Pérez De Lara D, Jarillo-Herrero P, Gorbachev R V and Castellanos-Gomez A 2018 Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials *Chem. Soc. Rev.* **47** 53–68
[13] Dean C R *et al* 2010 Boron nitride substrates for high-quality graphene electronics *Nat. Nanotechnol.* **5** 722–6
[14] Wang L, Dean C R, Meric I, Shepard K L, Hone J, Kim P, Watanabe K and Taniguchi T 2013 One-dimensional electrical contact to a two-dimensional material *Science* **342** 1–12
[15] Castellanos-Gomez A, Buscema M, Molenaar R, Singh V, Janssen L, Van Der Zant H S J and Steele G A 2014 Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping *2D Mater.* **1** 011002
[16] Pizzocchero F, Gammelgaard L, Jessen B S, Caridad J M, Wang L, Hone J, Bøggild P and Booth T J 2016 The hot pick-up technique for batch assembly of van der Waals heterostructures *Nat. Commun.* **7** 11894
[17] Brec R 1986 Review on structural and chemical properties of transition metal phosphorous trisulfides MPS_3 *Solid State Ion.* **22** 3–30
[18] Mayorga-Martinez C C, Sofer Z, Sedmidubský D, Huber Š, Eng A Y S and Pumera M 2017 Layered metal thiophosphite materials: magnetic, electrochemical, and electronic properties *ACS Appl. Mater. Interfaces* **9** 12563–73
[19] Pei Q L *et al* 2016 Spin dynamics, electronic, and thermal transport properties of two-dimensional $CrPS_4$ single crystal *J. Phys. D: Appl. Phys.* **119** 043902
[20] Kim M, Park G-H, Lee J, Lee J H, Park J, Lee H, Lee G-H and Lee H-J 2017 Strong proximity Josephson coupling in vertically stacked $NbSe_2$–Graphene–$NbSe_2$ van der Waals Junctions *Nano Lett.* **17** 6125–30

[21] Xi X, Wang Z, Zhao W, Park J H, Law K T, Berger H, Forró L, Shan J and Mak K F 2016 Ising pairing in superconducting $NbSe_2$ atomic layers *Nat. Phys.* **12** 139–43
[22] Telford E J *et al* 2018 Via method for lithography free contact and preservation of 2D materials *Nano Lett.* **18** 1416–20
[23] Tsen A W, Hunt B, Kim Y D, Yuan Z J, Jia S, Cava R J, Hone J, Kim P, Dean C R and Pasupathy A N 2016 Nature of the quantum metal in a two-dimensional crystalline superconductor *Nat. Phys.* **12** 208–12
[24] Nadj-Perge S, Drozdov I K, Li J, Chen H, Jeon S, Seo J, MacDonald A H, Bernevig B A and Yazdani A 2014 Observation of Majorana fermions in ferromagnetic atomic chains on a superconductor *Science* **346** 602–7
[25] Buzdin A I 2005 Proximity effects in superconductor-ferromagnet heterostructures *Rev. Mod. Phys.* **77** 935–76
[26] Linder J and Robinson J W A 2015 Superconducting spintronics *Nat. Phys.* **11** 307–15
[27] Yankowitz M, Chen S, Polshyn H, Zhang Y, Watanabe K, Taniguchi T, Graf D, Young A F and Dean C R 2019 Tuning superconductivity in twisted bilayer graphene *Science* **363** 1059–64
[28] Cardoso C, Soriano D, García-Martínez N A and Fernández-Rossier J 2018 Van der Waals spin valves *Phys. Rev. Lett.* **121** 067701
[29] Senapati K, Blamire M G and Barber Z H 2011 Spin-filter Josephson junctions *Nat. Mater.* **10** 849–52
[30] Lee J, Ko T Y, Kim J H, Bark H, Kang B, Jung S-G, Park T, Lee Z, Ryu S and Lee C 2017 Structural and optical properties of single-and few-layer magnetic semiconductor $CrPS_4$ *ACS Nano* **11** 10935–44
[31] Li B, Roschewsky N, Assaf B A, Eich M, Epstein-Martin M, Heiman D, Münzenberg M and Moodera J S 2013 Superconducting spin switch with infinite magnetoresistance induced by an internal exchange field *Phys. Rev. Lett.* **110** 097001