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Research Article

Dry Transfer of van der Waals Junctions of Two-Dimensional Materials onto Patterned Substrates Using Plasticized Poly(vinyl chloride)/Kamaboko-Shaped Polydimethylsiloxane

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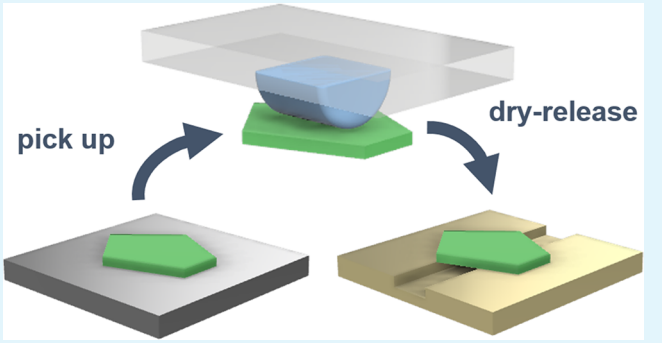
ABSTRACT: Two-dimensional (2D) materials can be transferred onto substrates with various surface structures, opening up multiple functions and applications for 2D materials in the form of suspended membranes. In this paper, we present a method for transferring exfoliated 2D crystal flakes from SiO_2 substrates onto patterned substrates using a poly(vinyl chloride) (PVC) layer mounted on a polydimethylsiloxane (PDMS) stamp structure. 2D crystal flakes can be transferred onto various patterned structures such as grooves, round holes, and periodic hole or groove patterns. Our method can also be used to fabricate suspended van der Waals (vdW) heterostructures by assembling 2D crystal flakes on the PVC/PDMS stamp and then transferring them onto patterned substrates. The adhesiveness and curvature of the PVC/PDMS stamp were tuned, and a high successful transfer rate was realized due to the use of kamaboko-shaped (semicylindrical) PDMS and the addition of an appropriate amount of a high-viscosity plasticizer to the PVC layer. Taking advantage of this method, we demonstrate the facile fabrication, simply by transferring a vdW heterostructure onto an Au-coated groove substrate, of a suspended vdW field-effect transistor device with the carrier density tuned using ionic gating. This method enables the transfer of 2D crystal flakes and vdW heterostructures onto various patterned substrates, and hence it should help to advance suspended 2D materials research.



KEYWORDS: *2D materials, van der Waals heterostructures, poly(vinyl chloride), suspended 2D crystal flakes, kamaboko-shaped PDMS, liquid-gate graphene FET*

1. INTRODUCTION

Two-dimensional (2D) crystal flakes such as graphene and transition-metal dichalcogenides (TMDs) are thin and flexible, unlike conventional materials. Because they deform flexibly under stress, 2D crystal flakes can be mechanically picked up from one substrate and transferred to another using thermoplastic polymers.[1] 2D crystal flakes can be transferred not only to flat substrates but also to patterned ones,[2−7] and hence these materials have greater applicability.[7−9] For example, by transferring 2D crystal flakes onto holey substrates, we can fabricate a structure consisting of a 2D crystal flake suspended over a hole. Such suspended membranes have been used to study the mechanical strength,[10] vibration frequency,[11] and strain-dependent properties of 2D materials.[3] Suspended 2D materials are also used to minimize the effects of thermal conduction and optical absorption by the underlying substrate during, for example, transmission electron microscopy (TEM)[12] and thermal measurements.[13] The transfer of 2D crystal flakes onto patterned substrates is also effective for combining 2D crystal flakes with functional substrates. By transferring a 2D crystal flake onto a photonic crystal, a typical example of a structure with a periodic surface pattern, the light-emission intensity of the 2D crystal flake can be increased owing to the cavity effect.[14] Periodic surface patterns can also be used to introduce periodic potential modulation to the 2D crystal flake.[15] Furthermore, 2D crystal flakes can be combined with microelectromechanical system devices, which can perform mechanical movements on the microscopic scale,[16] to fabricate 2D material devices such as flow and pressure sensors.[17]

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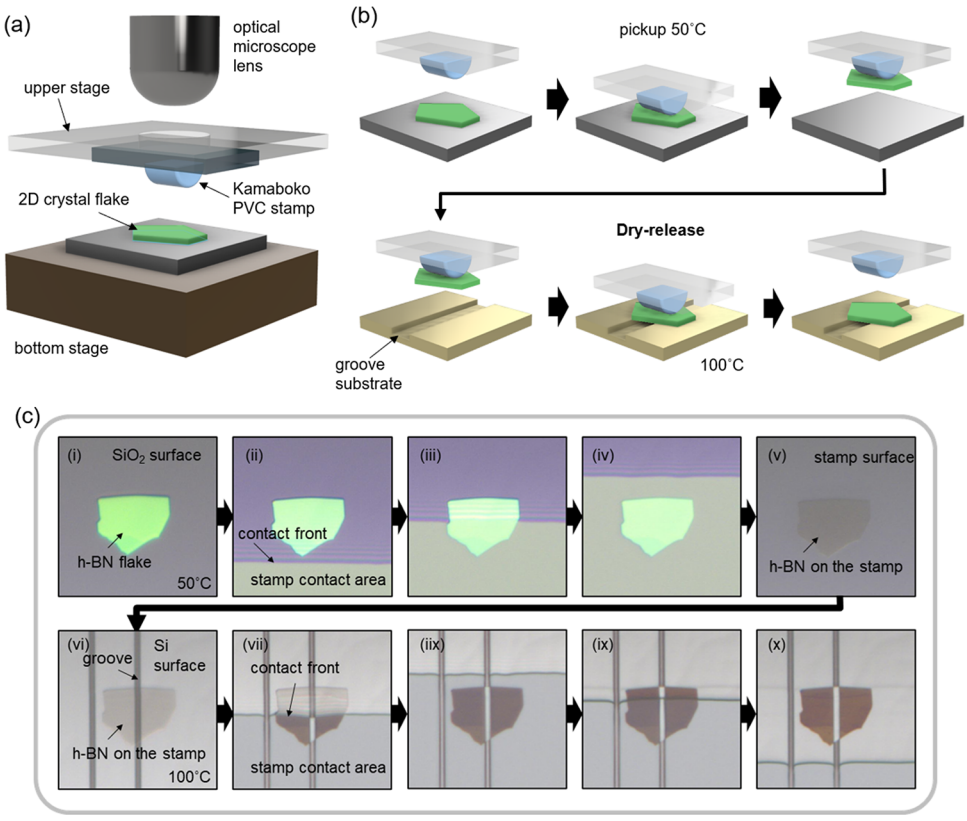

Figure 1. (a) Schematic of the 2D crystal flake transfer apparatus. (b) Schematic of the transfer process. (c) Photographic flowchart showing the transfer of a h-BN flake from a SiO_2/Si substrate to a groove-patterned Si substrate.

Although the combination of 2D crystal flakes and patterned substrates has produced a wide range of potential applications, research progress in this field depends on the development of transfer techniques.[18−24] The transfer of 2D crystal flakes onto a patterned substrate is challenging because of the risk of destroying the suspended layer during the transfer process. In particular, immersion in a solvent after transfer is very damaging to the suspended layer and reduces the transfer yield. Such low yields may not be crucial for the transfer of large-area 2D crystal flakes synthesized by chemical vapor deposition,[25−34] which can be transferred onto a large number of device arrays simultaneously. By contrast, 2D crystal flakes fabricated by mechanical exfoliation, which are of higher quality, are smaller in size (~10−100 μm in length). Therefore, to fabricate high-quality devices based on suspended 2D crystal flakes created by exfoliation, improved transfer yields and positioning accuracy, using methods that do not feature solvent immersion, are required.

In this study, we demonstrated a method for transferring exfoliated 2D crystal flakes onto a patterned substrate with high positioning accuracy and without postimmersion in solvents. 2D crystal flakes were picked up from SiO_2/Si substrates and dry-released to a targeted spot on the patterned substrate using a stamp consisting of plasticized poly(vinyl chloride) (PVC) on kamaboko-shaped polydimethylsiloxane (PDMS). We demonstrated that our technique is capable of fabricating suspended van der Waals (vdW) heterostructures via the assembly of 2D crystal flakes on the kamaboko-shaped stamp and their transferal to a patterned substrate. Our method facilitates the fabrication of suspended 2D crystal flake and their vdW heterostructure devices, promoting the advancement of suspended 2D materials research.

2. RESULTS AND DISCUSSION

Figure 1a shows a schematic of the setup used for the 2D crystal flake transfer process. The apparatus consisted of a lower stage, an upper stage, and an optical microscope. A mechanically exfoliated 2D crystal flake on a SiO_2/Si substrate was placed on the lower stage, and a polymer stamp on a glass slide was fixed onto the lower surface of the upper stage using vacuum chucks. The stamp consists of a plasticized PVC layer mounted on a piece of soft PDMS for mechanical support. The details of the stamp preparation are shown in Figures S1−S3. The *XYZ* position and movement speed of the lower stage can be accurately controlled using an electric motor, and the stamp is made to contact or separated from the 2D crystal flake by moving the lower stage. The 2D crystal flakes were observed through the (transparent) polymer stamp by optical microscopy. The temperature of the PVC stamp and 2D crystal flake were controlled using a heater attached to the underside of the lower stage.

Figure 1b shows a schematic of the process of transferring a 2D crystal flake from SiO_2/Si to a groove-patterned substrate. The PVC stamp is in contact with the 2D crystal flake on the SiO_2/Si substrate and then detached at 50 °C, at which temperature the adhesion of PVC is strong, and the 2D crystal flake is picked up by the polymer stamp. Next, the SiO_2/Si substrate on the lower stage is removed, and a groove-patterned substrate is put in its place. The 2D crystal flake on the PVC stamp is aligned with the desired position on the groove-patterned substrate and then contacted with the

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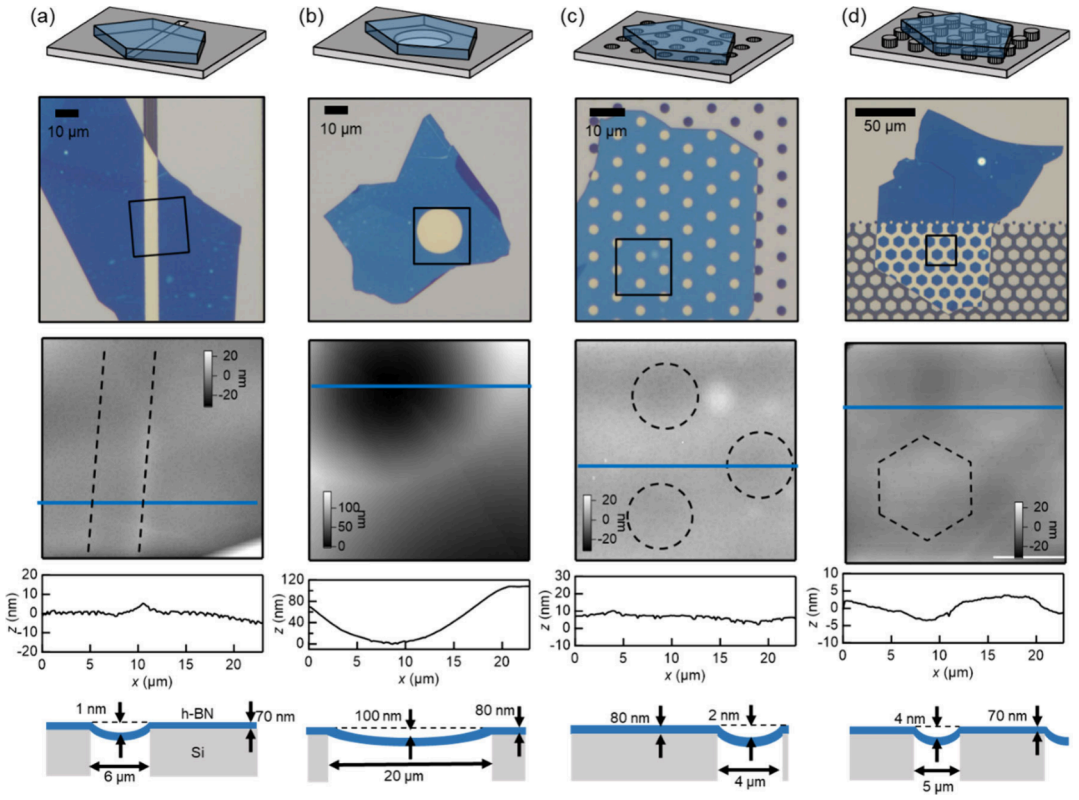

Figure 2. Transfer of h-BN flakes onto Si substrates with (a) groove, (b) hole, (c) periodic hole, and (d) hexagonal-hole-patterned structures: schematics (first row), micrographs (second row), AFM images of the area highlighted by the overlaid black rectangular outline in the micrograph (third row), and cross-sectional AFM profiles (fourth row) with schematics (fifth row) corresponding to the position marked by the blue lines in the AFM maps.

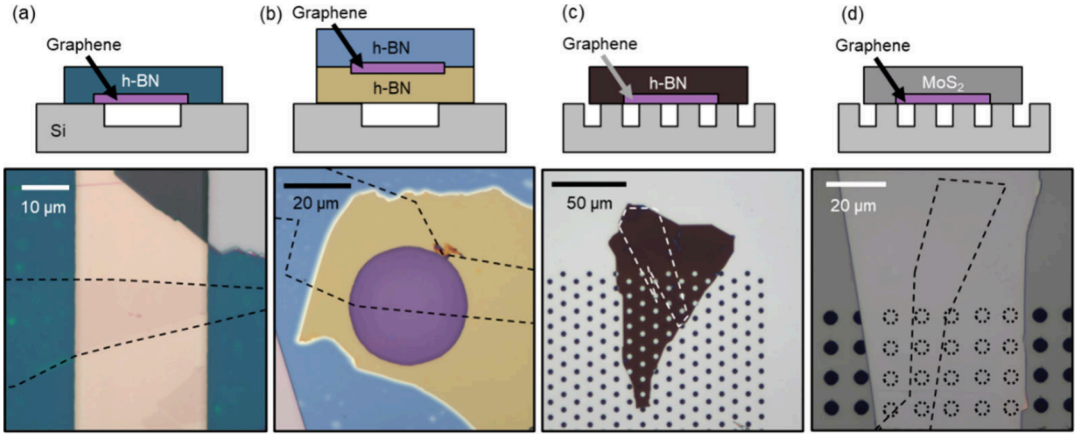

Figure 3. Fabrication of vdW heterostructures on patterned Si substrates: schematics (first row) and micrographs (second row) of (a) h-BN/graphene on a groove, (b) h-BN/graphene/h-BN on a hole, (c) h-BN/graphene on a hole pattern, and (d) MoS_2/graphene on a hole pattern. The overlaid dashed lines indicate the position of the graphene.

substrate at 100 °C, at which temperature the adhesion of PVC is weak, and the stamp is slowly peeled off. If the adhesion force between the 2D crystal flake and the substrate is greater than that between the 2D crystal flake and the stamp, the 2D crystal flake is transferred to the substrate. Figure 1c shows photographs of the transfer process in which a hexagonal boron nitride (h-BN) flake (~40-nm-thick) is transferred onto a grooved Si substrate such that it spans the groove. The details of the experimental conditions are presented in Figure S4. The key advantage of our technique is that there is no need for solvent immersion after transfer. Thus, this technique is termed a "dry-release" process. As the risk of sample destruction is significantly reduced owing to the lack of solvent immersion, 2D flakes can be transferred to groove-patterned substrates with a high success rate. In Figure S5, we illustrate the tips for the optimal transfer of a 2D crystal flake onto the groove.

This method can be used to transfer 2D crystal flakes onto Si substrates with various surface structures. Figure 2 shows schematics, photographs, atomic force microscopy (AFM) images, cross-sectional profiles, and cross-sectional structure schematics of h-BN flakes transferred to surfaces with various

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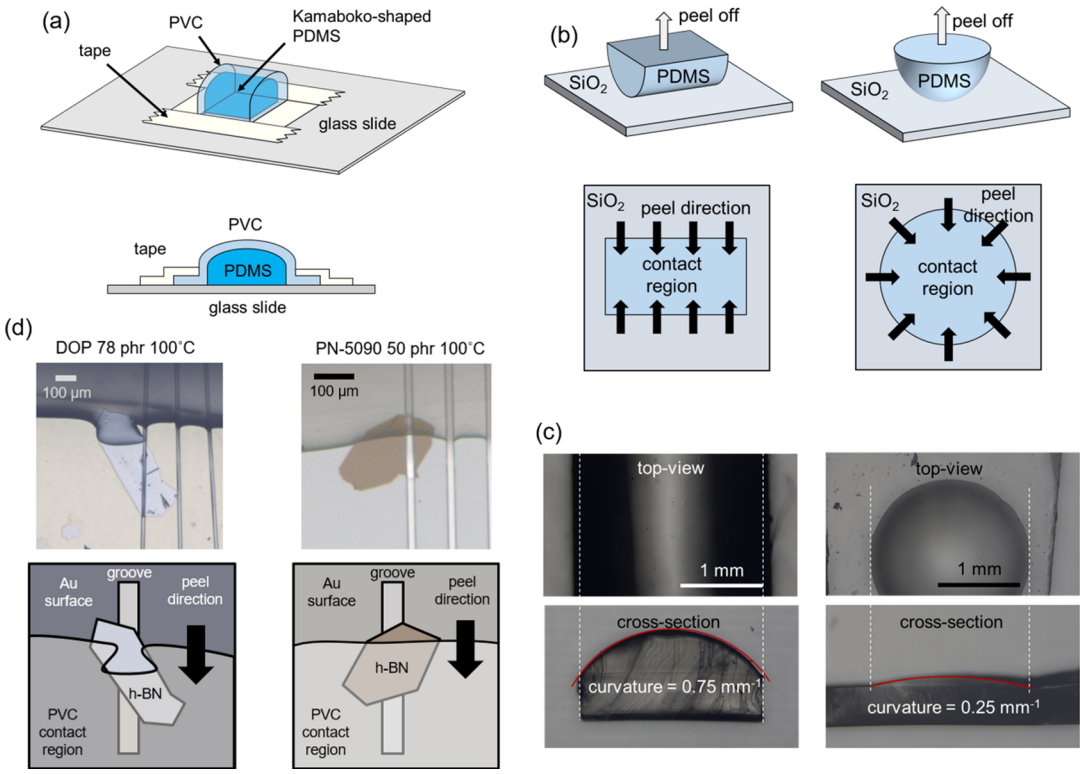

Figure 4. (a) Schematic of PVC/PDMS stamp. (b) Direction of the force applied during the dry-release processes using the kamaboko-shaped (left) and dome-shaped (right) PDMS. (c) Micrographs showing top views and cross sections of kamaboko-shaped (left) and dome-shaped (right) PDMS. The red lines are fits of the surface arcs overlaid on the images to highlight the different curvatures. (d) Differences in the peel interfaces between the PVC film and substrate during dry release depending on the plasticizer type: PVC film with 78 phr DOP (left) and PVC film with 50 phr PN-5090 (right).

structures: grooves, holes, a periodic hole pattern, and a periodic hexagonal-hole pattern. The transferred h-BN flakes were 70−80 nm thick and appeared blue on the Si substrate. The slightly indented shape of the transferred h-BN suggests the presence of strain in the suspended region. As discussed in the introduction, suspended 2D crystal flakes are important for studying mechanical properties, such as fracture strength[10] and vibration frequency,[11] as well as the strain-dependent properties of 2D materials.[3] In addition, 2D materials must be suspended for TEM measurements, and our method is capable of transferring h-BN onto a TEM grid, as demonstrated in Figure S6. Furthermore, this method can be widely applied to the fabrication of experimental devices combining 2D crystal flakes and periodic surface patterns, such as photonic crystals.[14]

Our dry-release method is unique in that the 2D crystal flakes exfoliated onto SiO_2/Si are picked up using PVC and then transferred to a patterned substrate. This approach means that multiple 2D crystal flakes can be sequentially stacked on the PVC stamp before they are transferred to a patterned substrate, facilitating the fabrication of suspended vdW heterostructures on patterned substrates. Figure 3 shows suspended vdW heterostructures fabricated using our method: h-BN/graphene on a groove, h-BN/graphene/h-BN on an isolated hole, h-BN/graphene on a periodic hole pattern, and MoS_2/graphene on a periodic hole pattern. To fabricate these suspended vdW heterostructures, h-BN, graphene, and MoS_2 were first mechanically exfoliated onto SiO_2/Si substrates using tape. These 2D crystal flakes were successively picked up using the PVC stamp to assemble a vdW heterostructure on the stamp. The stacked structure was then dry-released onto the patterned substrate. This contrasts with a previously reported dry-transfer method using PDMS,[8] which requires repetition of the transfer process to fabricate a stacked structure because only one layer can be stacked at a time owing to the weak adhesion of PDMS. The method outlined in the present paper is also compatible with the tear-and-stack method,[35,36] which enables precise control of the twist angles between 2D crystal flakes. The facile fabrication of suspended vdW heterostructures will provide more possibilities for device applications.

So far, in this paper, we have reported our demonstration of the transfer of exfoliated 2D crystal flakes onto silicon substrates with various surface structures. Four aspects of our method are critical to the realization of a high transfer yield: (1) the kamaboko shape of the PDMS, (2) the use of PVC, (3) the high viscosity of the plasticizer, and (4) optimization of the plasticizer content of the PVC. Each of these aspects is now expanded upon.

(1) Kamaboko-shaped PDMS: We used a semicylindrical PDMS structure as a mechanical support for the PVC layer (Figure 4a), which we refer to as kamaboko-shaped PDMS (Figure S7). Previously reported polymer-based transfer methods used polymer films on flat[37,38] or dome-shaped[36] PDMS. Dome-shaped PDMS has the advantage of limiting the contact area with the substrate. However, the stress at the peeling front of the stamp is directed toward the center of the circle (it is not uniaxial), as illustrated in the right half of Figure 4b. As a result, the 2D crystal flake is more likely to be distorted and detached from the substrate. In the case of the

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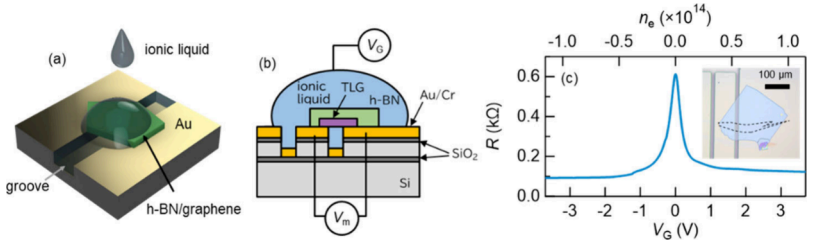

Figure 5. (a) Schematic of a suspended h-BN/graphene FET device with split Au/Cr electrodes. The ionic liquid is poured into the groove and used as a liquid gate to modulate the carrier concentration. (b) Cross-sectional structure of the device. (c) Two-terminal resistance at room temperature as a function of the gate voltage (lower axis) and carrier concentration (upper axis). Inset: Micrograph of the device. The overlaid dashed outline indicates the TLG.

kamaboko-shaped PDMS used in this study, the peeling direction is uniaxial, as illustrated in the left half of Figure 4b, and hence the distortion of the 2D crystal flake is minimized. This results in a greater success rate for the dry-release process. Another important point is that the curvature of the kamaboko-shaped PDMS can be greater than that of a PDMS dome, as shown in the micrographs in Figure 4c. We observed that a larger curvature positively correlated with the probability of successful dry transfer onto the patterned substrate (Figure S8).

(2) Use of PVC: PVC is an excellent polymer material that can be used for the all-dry pickup and release of 2D crystal flakes.[39−41] Immersion in organic solvents should be avoided during the transfer of crystal flakes onto a patterned substrate to prevent damage to the crystal flakes. Therefore, we selected PVC as the material for the stamp in this study.

(3) High-viscosity plasticizer: In general, the flexibility of PVC can be tuned by incorporating plasticizers. A plasticizer is a liquid material at room temperature that is added to PVC to increase its flexibility. In this study, a high-viscosity polyester plasticizer (PN-5090, Adeka) was used. The viscosity of PN-5090 is 10,000 mPa·s, which is more than 100 times larger than that of dioctyl phthalate (DOP; 80 mPa·s), the most commonly used plasticizer for PVC. The viscosity of the plasticizer is very important in the present method, especially when transferring 2D materials onto an Au-coated substrate. The rate of successful transfer to an Au-coated substrate was extremely low when PVC containing DOP was used. The DOP-containing PVC adhered very strongly to the Au, and the peeling interface was significantly distorted (Figure 4d, left). In contrast, the peeling interface of PN-5090-containing PVC was not distorted during peel-off (Figure 4d, right), and the rate of successful dry transfer was very high. One possible reason for this is that the DOP-containing PVC film is more stretchable than the PN-5090-containing PVC film. Because PN-5090 has a high viscosity, the PN-5090-containing film is less likely to be stretched while it is being peeled off from the Au surface. It is very important to minimize the distortion of crystal flakes during dry-release transfer onto structured surfaces. We also note that the plasticizer migration is suppressed with the high-viscosity plasticizer PN-5090 than with DOP, preventing the surface contamination of the transferred 2D materials due to the plasticizer. The details of the plasticizers are presented in Table S1. Characterization of the plasticizer residual on 2D crystal flakes is presented in Figure S9.

(4) Adjustment of the plasticizer content: PVC films with a plasticizer content of 50 phr (per hundred resin) were used. In general, the glass transition temperature T_g of PVC decreased with the addition of plasticizers.[42−44] In addition, based on our experience, the adhesion force between PVC and the 2D crystal flake tended to decrease as the plasticizer content was increased. Strong adhesion with reduced plasticizer content is advantageous for the pickup of 2D crystal flakes, whereas strong adhesion at high temperatures is disadvantageous for dry release. The pickup probability was more than 90% for PVC with low plasticizer content (<60 phr), whereas it dropped to approximately 70−80% when the plasticizer content was 80 phr. Therefore, we set the plasticizer content to 50 phr, above which we assumed that the pickup probability of PVC started to decrease. By reducing the adhesion of PVC to the bare minimum, the dry-release rate of the 2D crystal flakes on the patterned substrates significantly increased.

As illustrated in Figure 3, our method enables the facile fabrication of vdW heterostructures by assembling 2D crystal flakes on a PVC stamp and then transferring them to a patterned substrate. Taking advantage of this capability, we devised the device geometry shown in Figure 5a. The device is fabricated by transferring a stacked h-BN/graphene heterostructure to an Au-coated groove-patterned Si substrate using the PVC stamp. Because graphene has no band gap (or a small band gap), ohmic contact between graphene and Au can be achieved simply by placing the graphene on the Au layer, allowing electrical conduction measurements to be performed. Furthermore, by covering the suspended 2D crystal flake with an ionic liquid, the carrier concentration can be tuned using a liquid gate to enable field-effect transistor (FET) operation. Ionic liquids are often used to effectively inject carriers into 2D materials and can achieve carrier concentrations 2 orders of magnitude greater than those achieved using a conventional doped Si or metal back gate.[45,46]

As a model suspended vdW heterostructure device, we fabricated a suspended h-BN/trilayer graphene (TLG) device with a liquid gate (see Figure S10 for sample preparation details). Figure 5b shows a cross-sectional schematic of the device structure. h-BN and TLG were picked up and stacked on the PVC stamp, and the stacked structure was released at a position corresponding to the TLG straddling the groove. The Si substrate surface was coated with Au, which functioned as metal electrodes (see Figure S11 for the substrate fabrication details). The TLG was capped by h-BN and was in contact with Au across the groove, making it possible to measure the two-terminal conduction in the TLG. The ionic liquid was poured into the groove such that it covered the h-BN/TLG and entire gate electrode (Figure S10). The inset of Figure 5c shows an optical microscopy image of the device, and the overlaid dashed outline indicates the TLG. Figure 5c shows the two-terminal resistance as a function of the carrier density n_e and back-gate bias voltage V_G at room temperature and under

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ACS Appl. Mater. Interfaces 2024, 16, 62481−62488

vacuum conditions. Carriers were injected to obtain a carrier concentration exceeding 1.0×10^{14} cm^{-1} (assuming a capacitance of 5 $\mu F/cm^2$). The resistance peak observed near zero bias corresponds to the charge-neutral point of TLG.[46] The contact resistivity was approximately 6×10^{-5} $\Omega \cdot cm^2$, indicating that good Ohmic contact was realized between the TLG and Au simply by placing the h-BN/TLG vdW stack on the Au-coated substrate using our method.

This model device illustrates the facility with which a h-BN/TLG device can be fabricated using our method, and it is expected that the same technique can be used for systems based on other materials. The fabrication of a FET structure by placing 2D crystal flakes on an Au-coated groove-patterned substrate and pouring an ionic liquid into the groove is very convenient because it means that electrode fabrication processes such as electron-beam lithography and metal deposition can be avoided. In addition, the use of a liquid gate has the advantage that a large number of carriers can be injected, allowing us to explore the physical phenomena of 2D materials at high carrier concentrations, such as superconductivity in TMDs.

3. CONCLUSIONS

This study demonstrated the fabrication of structures featuring suspended 2D crystal flakes based on the pickup of exfoliated flakes from SiO_2/Si substrates and their transfer to patterned substrates using a plasticized PVC/kamaboko-shaped PDMS stamp. The plasticized PVC stamp was demonstrated to be capable of realizing the dry release of 2D crystal flakes with a high success rate, eliminating the requirement for solvent immersion and hence preventing the possible destruction of the suspended 2D crystal flake. To achieve the dry release of 2D flakes onto a patterned substrate with a high success rate, we tuned the adhesiveness and curvature of the PVC/kamaboko-shaped PDMS stamp by optimizing the amount of high-viscosity plasticizer added to the PVC layer. This method is distinct from previously reported dry-transfer methods in that multiple exfoliated 2D crystal flakes on SiO_2/Si can be sequentially picked up by the PVC/PDMS stamp and then together transferred to the patterned substrate. In other words, using our method, it is possible to pick up 2D crystal flakes multiple times and assemble a stacked structure on the PVC before transferring them to the patterned substrate. Taking advantage of this possibility, we demonstrated the fabrication of a suspended vdW heterostructure device by simply placing a stacked h-BN/graphene structure on an Au-coated groove-patterned substrate, and electrical conduction measurements were performed by tuning the carrier concentration using an ionic liquid. We expect that this method will facilitate 2D crystal flake transfer onto substrates with various surface structures, thereby expanding the application scope of 2D materials.

4. MATERIALS AND METHODS

Fabrication of the Plasticized PVC Film. PVC powder (1.0 g; degree of polymerization, 700), the plasticizer (0.5 g; PN-5090, Adeka), and cyclohexanone (8 mL) were mixed to prepare a PVC solution. The PVC solution was spin-coated onto a 1.5 cm square SiO_2/Si substrate at 1000 rpm for 30 s, and the coated substrate was then heated on a hot plate at 160 °C for 1.5 min to evaporate the solvent.

Fabrication of Kamaboko-Shaped PDMS. The base and curing agents of a commercial PDMS kit (SYLGARD184, Dow Corning) were mixed in a weight ratio of 10:1, and then the liquid mixture was deaired in a vacuum desiccator. The commercially available PDMS sheet was cut into 2 mm widths, which were then laid on a glass slide, and the un-cross-linked PDMS was dropped to form a kamaboko shape. The mixture was baked at 130 °C for 10 min.

Fabrication of the PVC/PDMS Stamp. The PVC films on SiO_2 and the kamaboko-shaped PDMS on a glass slide were treated with air plasma for 1 min. The four sides of the PVC film were taped to form a frame and the film was peeled from the substrate, which is then turned upside down, placed over the PDMS, and fixed with tape to the glass slide around the PDMS. The PVC film was heated on a hot plate at 160 °C for 1 min to increase adhesion between the film and PDMS. See the Supporting Information for more details.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c05972.

Fabrication of the plasticized PVC film, fabrication of kamaboko-shaped PDMS, fabrication of the PVC/PDMS stamp, conditions of h-BN transfer, tips for transferring 2D crystal flake onto grooves, transfer of h-BN flake to a TEM grid, kamaboko—traditional Japanese food, curvature of kamaboko-shaped PDMS, properties of PN-5090 h-BN/TLG sample preparation, characterization of plasticizer residues by AFM, h-BN/TLG sample preparation, and patterned substrate fabrication (PDF)

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Author Contributions

M.O. and T.M. conceived and designed the experiments; M.O. performed the experiments with the help of H.T., M.A., Y.Z.,

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and R.M.; H.T. fabricated the patterned substrates; K.W. and T.T. grew the h-BN crystals; M.O. and T.M. wrote the manuscript with contributions from all authors.

Notes

The authors declare no competing financial interest.

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