Pinpoint pick-up and bubble-free assembly of 2D materials using PDMS/PMMA polymers with lens shapes

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The key to achieving high-quality van der Waals heterostructure devices made by stacking 2D layered materials lies in having a clean interface without interfacial bubbles and wrinkles. In this study, the pinpoint pick-up and transfer system of 2D crystals is constructed using polymers with lens shapes. We report the bubble-free and clean interface assembly of 2D crystals in which unidirectional sweep of the transfer interface precisely controlled with the help of the inclined substrate pushes the bubbles away from the interface. © 2019 The Japan Society of Applied Physics

Van der Waals (vdW) heterostructure devices composed of 2D layered crystals provide a new fundamental platform for many device applications, such as high-performance transistors,1,2) light-emitting diodes3) and solar cells,4) because stacking various layers is possible without considering the lattice mismatch due to the dangling-bond-free layered structure, unlike the case for conventional 3D semiconductors. In the vdW research field, the rotation angle has been recognized as a new parameter for material design, since unconventional superconductivity was realized.5) The vdW heterostructures are generally fabricated from small exfoliated flakes by a manually controlled transfer process using polymers6–13) because the heteroepitaxial growth of vdW heterostructures by metal-organic chemical vapor deposition14) or molecular beam epitaxy15–17) is still under investigation. The fabrication techniques of vdW heterostructure by the transfer process have been improved by, for example, (i) deterministic transfer by viscoelastic stamping,18) (ii) dry transfer using the difference in the thermal expansion between polymers and inorganic materials,19) and (iii) pinpoint pick-up for precise position control.20)

Recently, a robotic system that automatically searches for exfoliated 2D crystals and assembles them into superlattices inside a glovebox was successfully constructed to overcome the practically impossible repetitive manual stacking of 29 layers.18) However, interfacial contaminants, such as hydrocarbon impurities, air, water and so on, are often incorporated as bubbles at the 2D/2D interface.19–22) Indeed, this kind of vdW heterostructure including interfacial bubbles is often utilized positively as cells for liquid in nanometer scale for transmission electron microscopy.23,24) However, when we consider the electron devices, the intrinsic transport properties of vdW heterostructures are expected to be blinded because bubbles work as trap sites or scattering centers. Therefore, bubble-free stacking is strongly required.25) For the pinpoint pick-up by the PMMA/PDMS lens, h-BN flakes were prepared on a SiO2/Si wafer by mechanical exfoliation. PMMA/PDMS lenses and target h-BN flakes on SiO2/Si wafers were assembled in the micromanipulator alignment system under laboratory air conditions and aligned under an optical microscope. Then, the substrate was heated by a Peltier module from the bottom. The heating and cooling by the Peltier module can be easily altered without removing the sample by changing the voltage direction from the DC power supply. The adhesion of PMMA improves at a substrate temperature above the glass transition temperature of PMMA (Tg = ~50 °C) because the viscosity is substantially decreased.26) Each PMMA/PDMS lens and target h-BN flake were mechanically brought into contact by the stepping motor with a resolution of 0.125 μm/pulse at the predetermined substrate temperature. Finally, the pick-up was carried out using the thermal shrinkage of PMMA by reducing the substrate temperature to RT. A typical example of the pinpoint pick-up of the target h-BN flake when the substrate temperature was reduced from 110 °C is shown in Supplementary movie-1.

Figure 2(a) shows the success ratio of the pinpoint pick-up of the h-BN flake as a function of the substrate temperature.

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The pick-up of the $h$-BN flake was quite difficult at temperatures below 70 °C, whereas the success ratio was almost 100% at temperatures above 110 °C. However, the success ratio for crack-free pick-up of the $h$-BN flake became very low at high temperatures, as shown in Figs. 2(a) and 2(b). Although 2D layered flakes showed excellent flexible properties below ten layers, kinks were formed for 20 or more layers during bending.\(^{20}\) Since a thickness of $\sim$20 nm...
is required for h-BN flakes to achieve atomically flat surfaces,\(^1\) crack formation is a critical issue for pinpoint pick-up. As the substrate temperature increased beyond the \(T_g\), the PMMA became softer and the adhesion between the PMMA and SiO\(_2\) increased. When the PMMA detached from the substrate, it was substantially deformed, resulting in severe cracking in the h-BN, as schematically shown in Fig. 2(c). This situation was the same for the pick-up by moving down the stage at a constant substrate temperature. The key point to overcoming this issue is that PMMA becomes hard at temperatures lower than \(T_g\). Therefore, after the PMMA/PDMS lenses are attached to the target h-BN and the SiO\(_2\) substrate at a temperature above \(T_g\), at which they are kept for a while, the substrate temperature is reduced to 55 °C below the \(T_g\), while the contact is maintained. Then, h-BN can be picked up by moving down the stage because PMMA is too hard to deform, as schematically shown in Fig. 2(c). By this procedure, the success ratio of the h-BN flake target pick-up without any cracks is close to 90%, as shown by arrows. To achieve a bubble-free interface, two kinds of processes can be categorized: one in which the bubbles incorporated are removed from the interface “after the transfer” and the other in which the bubble-free interface is obtained “during the transfer”. In our previous study involving the isothermal annealing of a graphene/h-BN heterostructure at 200 °C after the transfer,\(^10\) the smaller bubbles aggregated into larger bubbles to reduce the surface energy (Ostwald ripening), which increased the clean interface area. Although the number of bubbles was reduced, the total volume of bubbles was almost the same even after aggregation. Therefore, a completely bubble-free interface was not achieved. Moreover, since the migration of bubbles incorporated at the interface of the two sets of thick 2D crystals is quite limited, obtaining a wide and clean interface area is rather difficult. Therefore, as in the former case, a thermal gradient was produced by local laser heating to enhance

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Fig. 3. (Color online) (a) Typical image of the h-BN/h-BN heterostructure obtained by pinpoint pick-up and transfer technique. Many bubbles are observed, as shown by arrows. (b) Typical image of the bubble-free transfer of the h-BN/h-BN heterostructure. Thicknesses of the top and bottom h-BN flakes are 38 and 35 nm, respectively, as determined by atomic force microscopy (AFM). Inset shows the AFM image at the red broken rectangular region. (c) Schematic illustration of the inclined substrate and PMMA/PDMS lens. (d) Successive images during the unidirectional transfer using the inclined substrate. Sample is shown in (b).
bubble migration. As shown in Supplementary Fig. S1, which is available online at stacks.iop.org/APEX/12/055008/mmedia, two bubbles heated by the Ar laser (red arrows) became large, whereas almost no change was observed for the local heating at the bubble-free region (blue arrows). It was hard to control the migration of bubbles by local laser heating. Another trial was undertaken involving cyclic annealing, which is known to be effective in removing dislocations from the crystals.27) As shown in Supplementary Fig. S2, an unidirectional sweep of the transfer interface using the inclined substrate, as shown in Fig. 3(c). Aluminum was used because of its high thermal conductivity. When the h-BN flake on the PMMA/PDMS lens contacted the h-BN crystal on the SiO₂ substrate at 120 °C, the contact interface swept from one side to another side, as shown in Fig. 3(d) and Supplementary movie-3. This unidirectional sweep of the transfer interface pushed the hydrocarbon contaminants, resulting in a bubble-free interface, as shown in Fig. 3(b). The inset image measured by AFM indicates a bubble-free interface. The double lens structure was important again because the relatively large angle (≈3°–5°), which cannot be used for planar PDMS stamping, enabled unidirectional sweeping.

In conclusion, pinpoint and bubble-free transfer is achieved by precisely controlling both the hardness of PMMA through the substrate temperature and the sweep direction of the transfer interface using the inclined substrate. This method can be applied to all kinds of 2D crystals.

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