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PMMA Dry Transfer of Graphene on *h*-BN using Heating/Cooling System

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Abstract

In this work, we present a PMMA dry transfer method which allows identification of clean interface area for high quality graphene/*h*-BN heterostructure fabrication. The mechanism lies in utilization of the large difference in thermal expansion coefficient between PMMA and graphene/*h*-BN substrate.

1. Introduction

Interfacial bubbles and wrinkles in graphene/*h*-BN van der Waals heterostructures are known to deteriorate the performance of the devices [1]. Therefore, identification of areas free of bubbles and wrinkles is essential before device fabrication. Dissolving PMMA after transferring graphene onto *h*-BN leaves PMMA residue even after annealing, making this method undesirable. Dry transfer method that does not require the dissolution of polymer is thus more desirable. Recently, a simple dry transfer method using PDMS has been reported [2]. Here, PMMA is more adhesive to graphene and harder than PDMS. Therefore, it was extremely difficult to obtain monolayer graphene with area as large as 100 μm^2 by mechanical exfoliation onto PDMS. On the other hand, large monolayer graphene can be obtained on PMMA, but the transfer process is more difficult because PMMA often picks up *h*-BN flakes instead of transferring graphene onto *h*-BN. In this study, we focus on the large difference in the thermal expansion coefficient of polymers and other inorganic materials, such as graphene, *h*-BN, and SiO_2 and have achieved dry PMMA transfer of graphene using the heating/cooling system. The transfer mechanism and transport characteristics are discussed.

2. PMMA Dry Transfer

h-BN was mechanically exfoliated onto n^+-Si/SiO_2 (90 nm) wafer, while graphene was separately exfoliated onto oxygen plasma treated PMMA/PDMS/glass slide substrate. Both substrates were then attached together in a micromanipulator alignment system, as shown in **Fig. 1**. Graphene and target *h*-BN were aligned under optical microscope and mechanically brought into contact and then peeled off by stepping motor. Peltier module was used to control the temperature of *h*-BN substrate during the transfer process.

To investigate the effect of contact temperature on the adhesion of PMMA to *h*-BN on SiO_2, the assemble was performed at different contact temperatures without graphene. As shown in **Fig. 2**, at contact temperature lower than 50°C, non-contact areas were observed around 100 nm-thick *h*-BN flakes. These areas become smaller when *h*-BN substrate is heated above 50°C due to the softening of PMMA and the thermal expansion of PDMS. This softening temperature is consistent with the glass transition temperature of PMMA measured by the differential thermal analysis. The thermal expansion of PDMS makes softened PMMA conform to the shape of thick *h*-BN flakes, thus ensuring the firm contact between graphene and target *h*-BN.

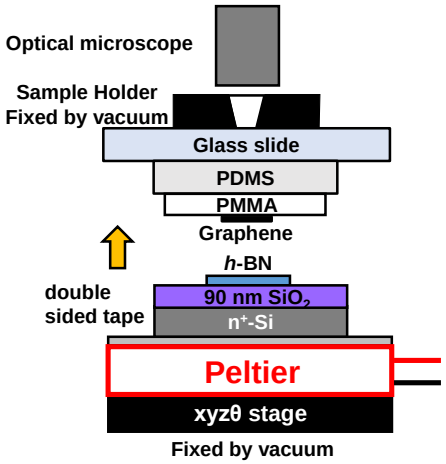

Fig. 1 Schematic of micromanipulator alignment system. The heating and cooling can be controlled by changing the current direction in Peltier module.

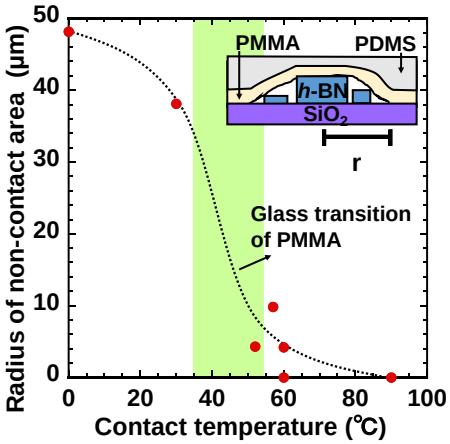

Fig. 2 Relationship between radius of non-contact area and contact temperature. Inset shows the definition of radius for non-contact area.

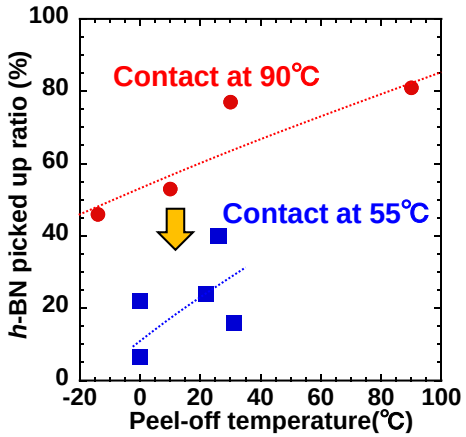

Fig. 3 Relationship between contact and peel-off temperatures, and ratio of *h*-BN flakes picked up by PMMA.

Based on this series of study, it is realized that once graphene and *h*-BN are brought into contact, the adhesion between them is strong enough to either cause *h*-BN to be picked up by graphene on PMMA or cause graphene to be transferred to *h*-BN on SiO_2. In order to successfully transfer graphene onto *h*-BN, *h*-BN must not be picked up by PMMA. After the contact at two different temperatures of T_{cont} = 55 and 90°C, the effect of peel-off temperature on the ratio of *h*-BN flakes picked up by PMMA was investigated. As shown in **Fig. 3**, the data at T_{cont} = 90°C shows higher ratio of *h*-BN flakes picked up by PMMA than that at T_{cont} = 55°C for all peel-off temperature, due to firm contact around the edge of *h*-BN flake. At lower peel-off temperature, PMMA can be peeled off using only thermal shrinkage of PDMS and PMMA without moving the stage down, allowing smoother peeling than using the stepping motor. It was found that contact temperature around 55°C and peel-off temperature around 15°C are desirable condition because of lower ratio of *h*-BN picked up by PMMA as well as ensured contact between graphene and *h*-BN. The success rate is more than 80 %.

Unlike graphene transferred onto *h*-BN by dissolving PMMA, wrinkles and bubbles can be clearly seen without PMMA residue on graphene transferred onto *h*-BN in case of PMMA dry transfer, as shown in **Fig. 4**. After annealing the stack in Ar/H_2 gas at 200°C for 3 hours, small bubbles aggregated into larger bubble to reduce the total surface energy, so called Ostwald ripening. This allows identification of clean interface area for device fabrication.

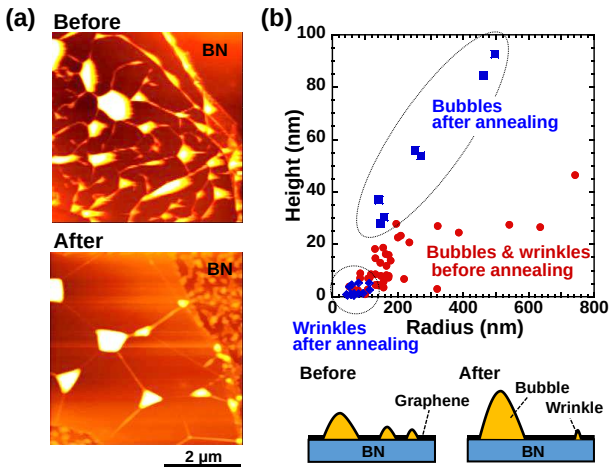

Fig. 4 (a) AFM images and schematics of bubbles and wrinkles before and after annealing. **(b)** Height and radius of bubbles and wrinkles estimated from (a). The number of bubbles decreased, while the size and height of bubble increased. The clean area is widened. Interestingly, the total volume of hydrocarbon inside of bubbles seems to be unchanged for this sample.

3. Demonstration of high mobility of Graphene/*h*-BN

The bubble region of graphene on *h*-BN was removed by oxygen plasma and the device was fabricated using the clean interface region. Finally, the device was annealed in Ar/H_2 gas at 300°C for 3 hours. Transport characteristics in graphene on *h*-BN are shown in **Fig. 5**. The thickness of *h*-BN was 47 nm as measured by AFM. The carrier density is estimated by assuming dielectric constant of 4 for *h*-BN. The carrier mobility is 20,000 $cm^2V^{-1}s^{-1}$ at n = 2×10^{11} cm^{-2} at 20K. The resistivity of Dirac point increases as the temperature decreases, in contrast to that of graphene on SiO_2 [3], indicating less charged impurities at the graphene/*h*-BN interface.

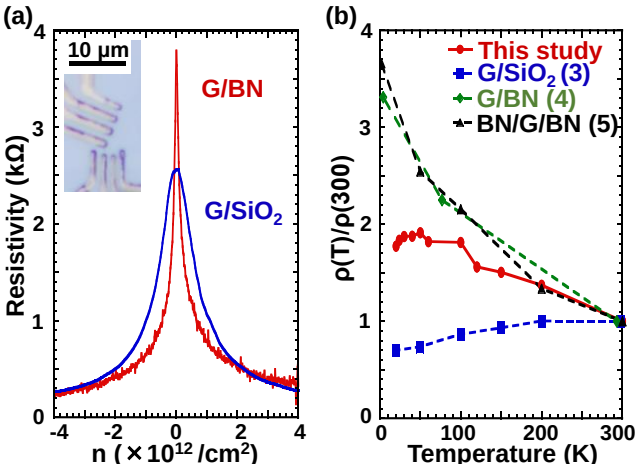

Fig. 5 (a) Resistivity as a function of carrier density at 20K. **(b)** Temperature dependence of the normalized resistivity at Dirac point. The literature data is also included for comparison.

4. Conclusions

Using the heating/cooling system, PMMA dry transfer of graphene onto *h*-BN allowed identification of clean interface area for the device fabrication. Transport data shows superior characteristics unable to achieve in graphene/SiO_2 devices.

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