Materials Research Express

PAPER

Photoresist-enabled assembly of BN/graphene/BN heterostructure and fabrication of one-dimensional contact electrode

Anjiang Cai¹2, Wang Yu¹, Guodong Zhang¹, Yulong Zhao¹, Jing Sun¹, Yuan Liu³ and Dongpeng Zhang¹²

¹ School of Mechanical and Electrical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, People’s Republic of China
² Shaanxi Key Laboratory of Nano Materials and Technology, Xi’an 710055, People’s Republic of China
³ The State Key Laboratory for Mechanical Manufacturing System Engineering, Xi’an liatong University, Xi’an 710049, People’s Republic of China

E-mail: cai_aj@163.com

Keywords: BN/graphene/BN heterostructure, PMMA substrates, photoresist, stacking transfer assembly, exposure on the back of surface substrate, one-dimensional contact

Abstract

A poly(methyl methacrylate) (PMMA) substrate is easily soluble in acetone and cannot withstand high temperatures, thereby restricting the application of graphene or boron nitride (BN) on it. Furthermore, the assembly mechanism of a BN/graphene/BN heterostructure directly determines the performance of a device. In this paper, we report the single-spin photoresist stacking transfer assembly (SPSTA) of a BN/graphene/BN heterostructure on a PMMA substrate using a photoresist as a support layer. The photoresist served as a protective layer for the retained BN/graphene/BN heterostructure. The excess BN/graphene/BN heterostructure was etched away by oxygen plasma, following which a metal was evaporated on the photoresist surface. As metal is impervious to light, the excellent light transmittance of the PMMA substrate could be utilized. After the photoresist was denatured by ultraviolet light exposure on the back of the substrate, it was dissolved by a sodium hydroxide (NaOH) solution, and a one-dimensional contact of the BN/graphene/BN heterostructure and metal was achieved. Finally, through different testing methods, we found that the SPSTA of the BN/graphene/BN heterostructure yields a smooth morphology and high electrical conductivity with a uniform sheet resistance. We examined the air failure of the BN/graphene/BN heterostructure and found that its SPSTA was stable. Our study realized the transfer of two-dimensional (2D) materials on PMMA substrates for the first time, overcome the membrane surface pollution caused by the traditional BN/graphene/BN heterostructure assembly process, realized the fabrication of BN/graphene/BN heterostructure devices on PMMA substrates for the first time, and offers important insights for the application of graphene and BN or other 2D materials on PMMA substrates.

1. Introduction

Graphene and boron nitride (BN) possess similar structural and mechanical properties [1, 2] and are combined to form heterostructures with electron mobilities up to 6000 cm²/(V × s) [3], an order of magnitude higher than that of other graphene-based heterostructures. In recent years, heterostructures comprising graphene and BN have been widely used in field-effect transistors, thermoelectric devices, and electrocatalysts, among other applications [4–6], due to the excellent electrical properties of the graphene/BN heterostructure [7, 8]. However, currently, graphene has not been applied in ultrahigh-pressure applications. Studies have found that BN/graphene/BN heterostructures can achieve gigapascal-scale pressure measurements [9]. However, it is extremely difficult to fabricate sensors for the same, and the substrate requirements are very unique. Traditional graphene device substrates are composed of silicon/silicon dioxide [8, 10]; the most significant drawback of such substrates is the low impact resistance. The impact resistance of poly(methyl methacrylate) (PMMA) substrate is 16 times higher than that of silicon and silicon dioxide [11]; hence, the former substrate is suitable for...
fabricating ultrahigh-pressure sensors. However, PMMA substrates have not been used in graphene and BN or with any other two-dimensional (2D) material substrate thus far due to the following reasons: (1) The glass-transition temperature of PMMA is 105 °C [12], whereas the epitaxial growth of a graphene or BN environment requires more than 800 °C [13, 14]; consequently, graphene or BN cannot be directly grown epitaxially on a PMMA substrate. (2) The support layer in a traditional 2D material transfer is a PMMA reagent [15]. The etched Cu foil of the 2D material transferred to the destination substrate needs acetone to dissolve the support-layer PMMA reagent; however, as our destination substrate is a PMMA substrate, a PMMA reagent cannot be used as a support layer in this transfer. Consequently, it has been challenging to identify a suitable method for transferring high-quality and large-area 2D materials on PMMA substrates.

The residual polymer between graphene and BN during transfers will reduce the electron mobility between the heterostructure and electrode [16], which in turn affects the device performance. The assembly of a traditional 2D material heterostructure involves spinning the support material on each 2D material layer and then transferring the 2D material to the destination substrate [8, 10, 17]. However, this method significantly contaminates the heterostructure layers, and multiple transfers severely damage the thin films. Another challenge pertains to the assembly for obtaining a super-clean and polymer-free interlayer BN/graphene BN heterostructure. With a traditional silicon/silicon dioxide substrate, a one-dimensional (1D) contact is established between a 2D material and metal by evaporating the metal on the surface of the graphic photoresist and directly dissolving the photoresist with acetone [18, 19]. However, as explained above, PMMA substrates cannot employ acetone. Consequently, the photoresist can only be denatured by ultraviolet (UV) light exposure and dissolved in an NaOH solution. However, as metals are opaque, UV exposure cannot denature the photoresist, due to which the photoresist cannot dissolve in NaOH and, hence, cannot perform metal stripping. The final challenge pertains to achieving a 1D contact between the BN/graphene BN heterostructure and metal from the PMMA substrate. Based on the three challenges, we propose the use of a photoresist as the support layer for 2D material transfer, single-spin photoresist stacking transfer assembly (SPSTA) of a BN/graphene BN heterostructure on a PMMA substrate as the assembly process, and TPOTA of a BN/graphene BN heterostructure on a PMMA substrate as the control group. Initially, SPSTA is in the BN/Cu coating photoresist spin. After the removal of Cu, it is transferred to the graphene/Cu film to form a photoresist/BN/graphene/Cu substrate. After the second removal of Cu, it is transferred to the BN/Cu film to form a photoresist/BN/graphene/Cu/Cu substrate. Finally, after the last removal of Cu, it is transferred to the PMMA substrate to form a photoresist/BN/graphene BN/PMMA substrate. TPOTA is a spin on the BN/Cu photoresist. After the removal of Cu, it is transferred to the PMMA substrate. After removing the photoresist from the BN/PMMA substrate, it is spun on the graphene/Cu photoresist. After the second removal of Cu, it is transferred to the BN/PMMA substrate, and the photoresist from the graphene BN/PMMA substrate is removed and finally transferred to the BN/Cu spin-on photoresist. Finally, after the removal of Cu, it is transferred to the graphene BN/PMMA substrate, and the photoresist from the BN/graphene BN/PMMA substrate is removed. The difference between the two processes in assembling the BN/graphene BN heterostructure in a PMMA substrate is that SPSTA assembles the BN/graphene BN heterostructure on Cu and then transfers it to PMMA, whereas TPOTA assembles BN directly on PMMA. The BN/graphene BN heterostructure after the PMMA substrate assembly is completed, utilizing the excellent light transmittance of the PMMA substrate [20]. The 1D contact electrode was obtained by dissolving the denatured photoresist with the NaOH solution after UV exposure on the back of the PMMA substrate.

2. Results and discussion

2.1. SPSTA of a BN/graphene BN heterostructure on the PMMA substrate

The photoresist was selected as the support layer for the 2D material transfer because it cures with a certain adhesion to films. Furthermore, during curing, the photoresist will expand; the tensile membrane attached below maintains good flatness after curing and will not induce folding after the transfer. The photoresist was removed by dissolving it in the NaOH solution after the UV exposure, which ensures that the 2D material and PMMA substrate are not damaged. The ideal non-contaminating assembly condition for BN/graphene BN is that the middle-layer graphene and bottom-layer BN should not contact throughout the process. Figure 1 shows the SPSTA of the BN/graphene BN heterostructure. The photoresist was only spin-coated on the top-layer BN film, as shown in figure 1(b), followed by a transfer to the middle-layer graphene and bottom-layer BN, as shown in figure 1(c) and, finally, a transfer of the photoresist/BN/graphene BN heterostructure to the PMMA substrate treated by the hydrophilic treatment, as shown in figure 1(d). The PMMA underwent a hydrophilic treatment to enhance the van der Waals forces between the films and substrates [21].
2.2. Fabrication of a 1D contact electrode with the BN/graphene/BN heterostructure

After the BN/graphene/BN heterostructure was transferred to the PMMA substrate in the first exposure, an electrode region pattern was developed, and an electrode channel was formed with an edge via plasma etching, as shown in figure 2(a). The etching diagram of the single electrode channel is shown in figure 2(g). The deposited electrode channel was well etched into an inverted trapezoidal structure with an edge contact using oxygen plasma technology. Figure 2(h) shows a good inverted trapezoidal structure in the electrode channel, as observed with a three-dimensional (3D) measuring laser microscope (OLS4000). The deposition of 100 nm Ti and 15 nm Au as edge-contact metal electrodes is shown in figure 2(b). Ti was chosen as the metal electrode because it adheres very well on PMMA substrates, enhancing the carbide formation between Ti and graphene, and has a lower contact resistance [22]. Au is convenient for testing lead wires. Because the PMMA substrate was easily dissolved in acetone and the light transmittance on the front side was low after the evaporation of Au and Ti, the excellent light transmittance of the PMMA substrate can be utilized. After the UV exposure of the rear of the PMMA substrate, the 1D contact between the BN/graphene/BN heterostructure and Au/Ti was achieved by stripping the metal with the NaOH solution, as shown in figures 2(c) and (d). The excess BN/graphene/BN heterostructure was exposed through photolithography and etched by oxygen plasma, as shown in figure 2(e). After etching the excess heterostructure and removing the photoresist, the BN/graphene/BN heterostructure was assembled on the PMMA substrate, and a 1D contact was achieved between the BN/graphene/BN heterostructure and Au/Ti, as shown in figure 2(f). The schematic of a single sensor is shown in figure 2(i). Figure 2(j) shows the 3D observation results for a 50 × 50 μm² device and how the BN/graphene/BN heterostructure film is sandwiched between the two edge-contact electrodes.

We first observed the surface morphology of the BN/graphene/BN heterostructure under SPSTA and TPOTA using atomic force microscopy (AFM), as shown in figures 3(a) and (b). The BN/graphene/BN heterostructure fabricated by SPSTA was very smooth. However, the surface of the heterostructure fabricated by TPOTA was very rough due to the residual photoresist between the films. The Raman spectra of the substrate and heterostructure are shown in figure 3(c). The PMMA substrate presented distinct characteristic peaks at 1451, 1728, 2842, 2952, and 2999 cm⁻¹, whereas BN presented a Raman shift at 1366 cm⁻¹. In addition to the characteristic peaks of the PMMA substrate and BN, a G peak of graphene at 1582 cm⁻¹ and a 2D peak at 2700 cm⁻¹ were observed. However, the D peak corresponding to the defect at 1350 cm⁻¹ was not observed. The ratio of the 2D peak to the G peak was approximately 2, which indicates that graphene has an extremely high quality. Through Raman mapping, a 10 μm² area of the BN/graphene/BN heterostructure was scanned, and the mapping of the graphene G peak was selected to analyze the graphene monolayer [23]. SPSTA ensured good properties of the monolayer graphene, as shown in figure 3(d) (the illustration shows the scanned area). Meanwhile, TPOTA resulted in poor properties of the monolayer graphene, as shown in figure 3(e) (the illustration shows the scanned area), with the remaining contaminants causing graphene folds. Therefore, by
using a photoresist as a 2D material transfer support layer in SPSTA, a BN/graphene/BN heterostructure with extremely high quality was obtained on the PMMA substrate [23, 24]. We measured the sheet resistance of the BN/graphene/BN heterostructure via a four-probe test. The sheet resistances of the SPST-assembled BN/graphene/BN heterostructure were 1072, 1081, 1085, 1130, and 1176 $\Omega$, with an average of 1109 $\Omega$, (figure 3(f)). This finding implies that the SPST-assembled BN/graphene/BN heterostructure was very clean. The sheet resistances of the TPOT-assembled BN/graphene/BN heterostructures were 3881, 3976, 4453, 5652, and 6860 $\Omega$, with an average of 4965 $\Omega$, (figure 3(g)). This finding indicates that the TPOTA of the BN/graphene/BN heterostructure made it difficult to remove the photoresist between two heterostructures, which had a significant effect on the conductivity of graphene. The transfer length method is typically used for measuring the contact resistance ($R_C$) of a semiconductor [25, 26]. $R_C$ can be fitted by measuring the total resistance ($R_t$) over different transmission lengths. $R_t$ is composed of two ohmic contacts ($R_{c1}$) and a thin-film resistance in series, which can be written as $R_t = 2R_{c1} + \rho \times L/W$, where $R_{c1}$ is the contact resistance, $L$ is the device length, $W$ is the device width, and $\rho$ is the 2D channel resistivity. The SPSTA and TPOTA of the BN/graphene/BN heterostructure of the contact resistance $R_C$ with a 3-$\mu$m contact width are shown in figure 3(h); the magnified part near the axis origin highlights the intercept value (the illustration shows the TLM test structures). The $R_C$ value for the SPST-assembled BN/graphene/BN heterostructure edge contact was 139.5 $\Omega$, which is similar to the reported values of the edge-contact resistance [25, 26]. However, the $R_C$ of the TPOT-assembled BN/graphene/BN heterostructure edge contact was 370 $\Omega$. We employed a 50 $\times$ 50 $\mu$m$^2$ device for comparing the output currents from the two kinds of assembly processes (figure 3(i)). The total resistance of the SPST-assembled BN/graphene/BN heterostructure was 2270 $\Omega$; however, that of the TPOT-assembled heterostructure was higher (6850 $\Omega$) due to the photoresist residue between BN and graphene. The above results confirm that SPSTA provides an ultrahigh-quality BN/graphene/BN heterostructure.

**Figure 2.** (a) Using plasma technology for electrode groove etching. (b) Surface evaporation of photoresist under 100 nm Ti and 15 nm Au exposure. (c) Exposure of the back side of the PMMA substrate. (d) Stripping yields the metal to be retained as the edge-contact electrode of the BN/graphene/BN heterostructure. (e) O$_2$ plasma etches the excess BN/graphene/BN heterostructure. (f) Array of heterostructure devices on the PMMA substrate. (g) Schematic of a single inverted trapezoidal electrode groove. (h) Electrode channel observed using a 3D measuring laser microscope (OLS4000). (i) Schematic of the BN/graphene/BN heterostructure contact electrode edge. (j) 50 $\times$ 50 $\mu$m$^2$ sensor observed using a 3D measuring laser microscope (OLS4000).
To further determine the influence of air on BN/graphene/BN, we placed the two kinds of assembled BN/graphene/BN in an environment with a temperature of 292–298 K and relative humidity of 50%–60%. We compared the two kinds of process over 130 d of $R_t$ change, as shown in figure 3(j). In 20 d, the SPSTA resistance increased from 2.27 k to 2.57 k, a change of 13%. After 30 d, the total resistance drastically increased as graphene

Figure 3. (a) and (b) AFM images of the SPST- and TPOT-assembled BN/graphene/BN heterostructures. (c) Raman spectra of the BN/graphene/BN heterostructure transferred to the PMMA substrate. (d) and (e) Raman mapping showing the G peak strengths of $10 \times 10 \mu m^2$ graphene for the SPST- and TPOT-assembled BN/graphene/BN heterostructures. (f) and (g) Sheet resistances of five samples of the SPST- and TPOT-assembled BN/graphene/BN heterostructures. (h) Measurement curve in the rectangular transmission line model. (i) $U_{in}-I_{out}$ curves of the SPST- and TPOT-assembled BN/graphene/BN heterostructures. (j) Failure analysis of BN/graphene/BN heterostructures in air.
was mixed with air and water [27]. Due to the residual photoresist on the upper and lower surfaces of graphene, the resistance of TPOTA rapidly increased in the first 80 d and gradually stabilized after 80 d.

3. Methods

3.1. SPSTA of a BN/graphene/BN heterostructure on a PMMA substrate

First, the photoresist was spun on the surface of the Cu/BN film (parameters of the spin-coating photoresist: low speed = 500 m s\(^{-1}\), 9 s; high speed = 1500 m s\(^{-1}\), 30 s), as shown in figure 1 (b). The volume of the photoresist significantly changed before and after curing conducted at 25 °C for 30 min. Figure 1 (c) illustrates the assembly process of the BN/graphene/BN heterostructure, in which the film cleaned after each etching was transferred to the adjacent Cu substrate film. The etching solutions were FeCl\(_3\) (20 g), H\(_2\)O (150 ml; 4 h), and cleaning fluid.
The cleaning contact resistance for the 1D contact between the BN and metal edges reported elsewhere. This (PMMA substrates were subjected to UV light for 30 s to denature the photoresist in the electrode area, the oxygen plasma to remove the excess BN photoresist was removed from the 0.5% NaOH solution to obtain BN/PMMA substrates. The second step was to transfer the intermediate layer of graphene. First, the photoresist was spun on the surface of the graphene/Cu film, the first etching step was repeated to acquire the photoresist/graphene, the BN/PMMA substrate was transferred to form photoresist/graphene/BN/PMMA substrates, and the photoresist was removed to acquire the graphene/BN/PMMA substrate. The third step was to transfer the top layer of BN. First, the photoresist was spun on the surface of the BN/Cu film, the first etching step was repeated to acquire the photoresist/graphene, and it was transferred to the graphene/BN/PMMA substrate to form photoresist/BN/graphene/BN/PMMA substrates. This process refers to the BN/graphene/BN assembly method with PMMA as the transfer support layer [8, 10, 17].

3.3. Fabrication of 1D contact electrode with the BN/graphene/BN heterostructure
The first step, as shown in figure 2(a), used the blocking effect of the mask. The photoresist/BN/graphene/BN/PMMA substrates were subjected to UV light for 30 s to denature the photoresist in the electrode area, the modified photoresist was dissolved in the 0.5% NaOH solution, and the exposed area was bombarded with oxygen plasma to remove the excess BN/graphene/BN. The second step was to prepare 100 nm Ti/50 nm Au on the entire substrate surface via electron beam evaporation technology, as shown in figure 2(b). The third step was to denature all photoresists by shining UV light on the back of PMMA substrates for 40 s, as shown in figure 2(c). The fourth step was to dissolve the photoresist with the 0.5% NaOH solution to remove the excess metal, as shown in figure 2(d). The fifth step was to rotate a photoresist layer again and dry it at 75 °C for 20 min and make use of the blocking effect of mask and irradiation under UV for 30 s to denature the photoresist except the sensitive element. The denatured photoresist was dissolved with the 0.5% NaOH solution, and then the excess BN/graphene/BN was removed with oxygen plasma, as shown in figure 2(e). The sixth step was to denature all photoresists using UV light and dissolve the denatured photoresist with the 0.5% NaOH solution, as shown in figure 2(f). The etching parameters of oxygen plasmas were as follows: gas flow rate: 70 sccm; etching power: 50 W; etching time: 90 s.

4. Conclusion
The SPST-assembled BN/graphene/BN heterostructure on the PMMA substrate was very clean and highly smooth with a high electrical conductivity, first, because the photoresist support layer was very flat after curing and, second, because only the top-layer BN came into contact with the photoresist throughout the process. Neither the middle-layer graphene nor the bottom-layer BN was in contact with the photoresist. In addition, the contact resistance for the 1D contact between the BN/graphene/BN heterostructure and metal achieved by us was similar to that for the 1D contact between graphene and metal edges reported elsewhere. This finding indicates that the contact between a BN/graphene/BN heterostructure and metal edge can be realized on a PMMA substrate. Finally, our results confirm that photoresist materials can be used as a support layer to transfer other 2D materials and that the SPST-assembled BN/graphene/BN heterostructures can be applied to other 2D material heterostructure assemblies. The method of achieving a 1D contact between the BN/graphene/BN heterostructure and metal by denaturing the photoresist with a UV exposure on the back of the PMMA substrate is more suitable for organic substrates with excellent light transmittance.
Acknowledgments

This work was supported by the Pre-research Key Laboratory Fund for Equipment (No. 614260290408), Equipment Pre-Research Fund Major Project (No. 61406190501), and Science Foundation of Shaanxi Provincial Department of Education (No. 20JS063).

ORCID iDs

Anjiang Cai  https://orcid.org/0000-0001-7175-609X

References

[1] Zhao S and Xue J 2013 *Journal of Physics D Applied Physics*. 46 135303
[2] Eshkalak K E, Sadeghzadeh S and Jalaly M 2018 *Computational Materials Science* 149 170–81
[3] Dean C R et al 2010 *Nature Nanotechnology* 5 723–6
[4] Kim E, Jain N, Jacobs-Gedrim R, Xu Y and Yu B 2012 *Nanotechnology* 23 125706
[5] Tran V T, Saint-Martin J and Dollfus P 2015 *Nanotechnology* 26 495202
[6] Huang Y, Yang T, Yang L, Liu R and Tang S 2019 *Journal of Materials Chemistry A* 7 15173–80
[7] Iqbal M Z and Faisal M M 2019 *Journal of Applied Physics* 125 084902
[8] Li M, Wu C, Zhao S, Deng T, Wang J and Li Z 2018 *Applied Physics Letters* 112 143502
[9] Xu Y, Guo Z, Chen H, Yuan Y, Lou J and Lin X 2011 *Applied Physics Letters* 99 133109
[10] Li M, Zhang T, Wang P, Li M and Liu Z 2019 *Sensors* 19 22223
[11] Al-Kawaz A, Hadi N J and Hamzah A F 2017 *International Journal of Applied Engineering Research* 12 6176–81
[12] Eriksson M, Groossens H and Peijs T 2013 *Nanocomposites* 1 36–45
[13] Summersfield A, Davies A, Cheng T S, Korolkov V, Cho Y J and Mellor C J 2016 *Scientific Reports* 6 22440
[14] Liu Z, Song L, Zhao S, Huang J, Ma L and Zhang J 2011 *Nano Letters* 11 2032–7
[15] Reina A, Son H, Jiao L, Fan B, Dresselhaus M S and Liu Z F 2008 *Journal of Physical Chemistry C* 112 17741–4
[16] Lindvall N, Kalabukhov A and Yurgens A 2012 *Journal of Applied Physics* 111 666
[17] Wang L, Meric I, Huang P Y, Gao Q and Gao Y 2013 *Science* 342 614–7
[18] Robinson J A, Labela M, Zhu M and Hughes Z 2011 *Applied Physics Letters* 98 611–568
[19] Gong C, Zhang C, Oh Y J, Wang W, Lee G and Shan B 2017 *2D Materials* 4 025033
[20] Chen S, Ye F, Tang G and Wang X 2014 *Journal of Macromolecular Science Part A* 51 173–9
[21] Calado V E, Schneider G F, Theulings A M M G, Dekker C and Vandersypen L M K 2012 *Applied Physics Letters* 101 103116
[22] Cheng G and Stephen M 2014 *ACS Nano* 8 642–9
[23] Lui C H, Li Z, Chen Z, Klimov P V, Brus L E and Heinz T F 2010 *Nano Letters* 11 164–9
[24] Ni Z, Wang Y, Yu T and Shen Z 2008 *Nano Research* 1 273–91
[25] Li Q, Liu W, Cao G, Li X and Wang X 2016 *Applied Physics Letters* 108 652
[26] Gahoi A, Wagner S, Bablich A, Kataria S, Passi V and Lemme M C 2016 *Solid-State Electronics* 125 234–9
[27] Yang Y, Brenner K and Murali R 2012 *Carbon* 50 1727–33