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Transfer-Print of Graphene, Boron Nitride and Gold Patterns onto Polymeric Materials

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14. ABSTRACT

In this work, we show a multi-step transfer approach that will provide a path towards realization of graphene (Gr)/boron nitride (BN) heterostructures on flexible substrates. First, we performed plasma treatment of the polymeric materials, followed by attachment of an additional molecular linker layer. Then, the polymers and the two dimensional (2D) materials (Gr, BN) were placed in a nanoimprinter at specified conditions (pressure, temperature and time) and mechanically separated after print. Similarly, gold patterns were transferred to polymers. We believe that this fabrication approach will allow for technological impact of 2D materials in flexible electronics applications.

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Abstract

Graphene (Gr) is a promising two-dimensional (2D) material due to its outstanding electrical properties, chemical stability and flexibility. Graphene's electrical properties are highly influenced by the substrates onto which it is placed, with typical electron mobility of 1000 V/cm^2*s when placed onto SiO*$_2$*/Si substrates. The latter increases by a factor of ten when graphene is placed on boron nitride (BN). However, Gr/BN heterostructures were demonstrated mainly only using Gr and BN flakes. The goal of this work is to produce cm-scale Gr/polymer and BN/polymer structures, which is challenging due to their atomic layer thickness and inert nature. In this work, we show a multistep transfer approach that will provide a path towards realization of 2D heterostructures on flexible substrates based on differential adhesion, meaning the adhesion between the 2D material and the polymer is stronger than the adhesion between the 2D material and its growth substrate. First, we performed plasma treatment of the polymeric materials, followed by attachment of an additional molecular linker layer. Then, the polymers and the 2D materials were placed in a nanoimprinter at specified conditions (pressure, temperature and time) and mechanically separated after print. Similarly, gold patterns were transferred to polymers. We believe that this fabrication approach will allow for technological impact of 2D materials in flexible electronics applications.*

Introduction

Polymers have unique physical and chemical properties, great thermal and chemical resistance and low manufacturing cost, that make them attractive in numerous biological, medical, automotive and flexible electronics applications[1,5, 6]. Polymers used in this study are thermoplastics and include ultra-high molecular weight polyethylene (UHMW PE), polyethylene naphthalate (PEN), polyethylene terephthalate (PET), polycarbonate (PC) and polystyrene (PS). However, these materials also have very poor adhesion and wettability[2,6,10], which makes their integration into structures difficult and thus application of surface treatments is typically needed.

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Many studies show that plasma treatments can be used for polymer surface modification[3] including RF, DC, microwave plasmas etc. [6,10]. The functional groups incorporated into the polymer surface depend on the plasma gas environment – for example oxygen is used for incorporation of hydroxyl, carbonyl, and carboxyl functionalities. Furthermore, processing conditions, including power and treatment time need to be finetuned for each polymer in order to achieve surfaces with high adhesion.

Graphene (Gr) is a promising two-dimensional (2D) material for flexible electronics applications, due to its outstanding properties including high electrical conductivity, high electron mobility, good thermal conductivity, chemical stability, strength and its flexibility[2, 4, 7-9]. Graphene's electrical properties are highly influenced by the substrates onto which it is placed, with typical experimental values for electron mobility of 1000 V/cm^{2}s. Only when Gr is placed onto boron nitride (BN), the graphene's mobility can reach 80,000 V/cm^{2}s [11]. However, these experiments were performed using Gr and BN flakes. The challenge of making these structures comes from the two-dimensional (2D) nature of Gr and BN films, which are less than 1 nanometer in thickness. This means that it is difficult to transfer such material without damaging its electrical and mechanical properties due to contamination, film tearing etc.

In this work, we show a multistep dry transfer approach towards realization of 2D heterostructures on flexible substrates. No polymeric stamps were applied to remove the 2D materials. No Cu foil etching was performed as well. Instead, mechanical peeling was applied to separate the 2D materials and their growth substrate Cu foil. Our approach was based on creating higher adhesion between Gr and BN and the polymer substrates compared to their adhesion to the Cu foil. To improve adhesion, first we performed plasma treatment of the polymeric materials. If needed, an additional linker layer of self-assembled chemical molecules was applied as well. Then, the polymers and the 2D materials, or the polymers and the gold patterned silicon wafers were placed in a nanoimprinter at specified conditions (pressure, temperature and time). Finally, the polymer was separated from the Cu foil or the silicon substrate by mechanical peeling. The 2D material or gold pattern transfer was verified by performing Raman and FTIR spectroscopies. We believe that this approach of 2D heterostructures fabrication will make a technological impact in flexible electronics applications.

1. Materials and Method

1.1 Materials

The organic materials used were polyethylene naphthalate (PEN) film (DuPont Teijin Q65), polyethylene terephthalate (PET) film (Terka) ST505 Melinex, heat stabilized film (DuPont Teijin Films), ultra-high molecular weight polyethylene (UHMW PE) film (Goodfellow), and polystyrene (PS) film Hi-impact (Terka), polycarbonate (PC) film (Goodfellow), polycarbonate (PC) film [b] and [c] was from Terka. Graphene (Gr)/Cu foil was purchased from Graphene supermarket. The inorganic material includes SiO_2/Si wafers (University Wafer).

1.2 Methods

1.2.1 Plasma System

Plasma treatment was performed using a RF plasma system (Plasma Etch, Inc.) that allows for computer-control of the RF power, the treatment time, and the gas flow. Typically, we created plasma in oxygen gas environment, however argon and nitrogen gases were available as well. The gas flow was kept constant at 5 sccm for most experiments. Only in some cases the flow rate was increased to 10 sccm. Depending on the substrate type, the plasma treatment time and the RF power were varied from 5 to 60 seconds and from 20 to 50 W respectively. The pressure in the plasma chamber was adjusted automatically.

The exact plasma experimental treatment procedure was as follows: First, the polymers or inorganic samples were taped to a glass slide using Kapton tape. Then, the samples were rinsed with isopropanol to remove surface contaminants, dried with nitrogen and placed inside the plasma treatment chamber. The plasma treatment began with chamber evacuated. Then, oxygen gas entered the chamber and samples were exposed to plasma at a specified RF power and a treatment time. Finally, the chamber was brought to atmosphere using nitrogen and the samples were taken out.

Figure 1: RF plasma system (Plasma Etch).

1.2.2 Surface characterization – water contact angle measurements

Contact angle measurements were performed using a goniometer (VCA 2500). 2 μl drops of milipore water were positioned on the surface using a micro-syringe. The contact angles of two drops were measurement for each sample and the average of the four angles was estimated.

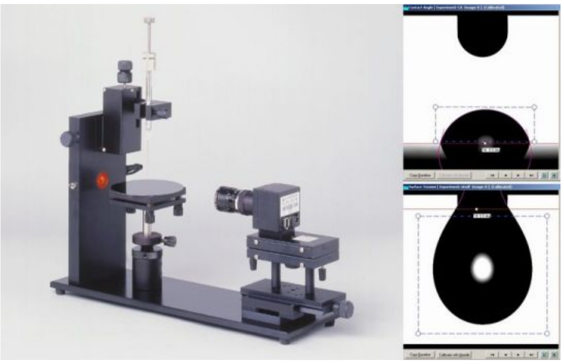


Figure 2: Goniometer for water contact angle measurements.

1.2.3 TFPA-NH_2 linker molecule deposition

First, a desired amount of TFPA-NH_2 molecule was dissolved in 10 mL of methanol (MeOH) to obtain molar concentrations from 4 to 12 mM. Then, the polymer of interest was submerged into the solution for about two hours. After that, the polymer was rinsed with MeOH and sonicated for 10 minutes in MeOH. Finally, the polymer was then rinsed again with MeOH and dried with nitrogen.

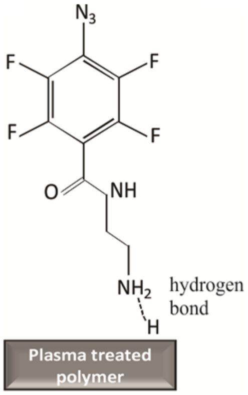


Figure 3: TFPA-NH_2 linker molecule attached to plasma treated polymer.

1.2.4 Transfer-print protocol

The transfer-print of 2D materials and gold patterns onto polymers was performed using a computer controlled nanoimprinter system (NX-2000). The used imprint procedure was as follows: first, polymer film/ wafers were placed on top of a wafer. Then, a thermally conductive Kapton tape was placed on top of the polymer/wafer stack. The latter was then placed in between two silicone sheets. Finally, the samples were introduced into the imprint chamber. When the imprint process began, the chamber was first evacuated. Then, the chamber was backfilled with nitrogen and the samples were imprinted at specified conditions (pressure, temperature and time). The typical imprint program includes three steps: pre-imprint step, imprint step, and cooling down. In the pre-imprint step, the pressure and temperature were 500 psi and 130 °C respectively. During the imprint step, the exact experimental pressure and temperature were specified. Finally, during the cooling step, the samples' temperatures were reduced to 55 °C. Consequently, the chamber was brought to atmospheric pressure using nitrogen. Finally, the samples were taken out of the chamber and graphene or BN on polymer substrates were separated from the Cu foil or the Si wafer by mechanical peeling with tweezers.

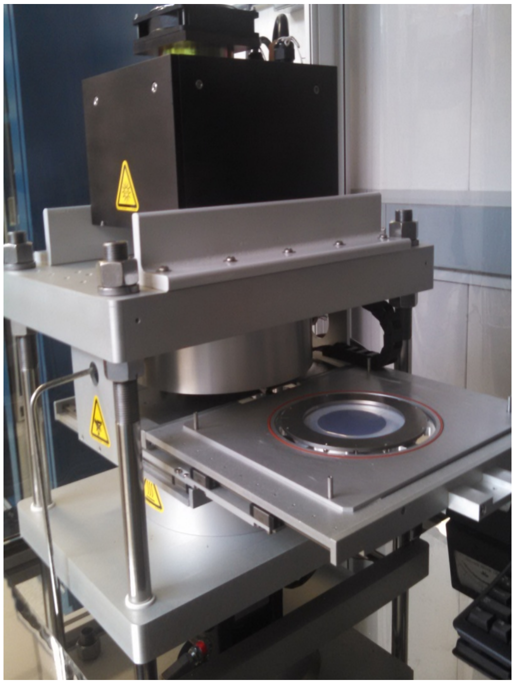


Figure 4: Nanoimprinter (NX-2000) system

1.2.5 Parylene coating of Si wafers

Samples were coated in a Specialty Coating Systems PDS 2010 Parylene Coater. A Silane-based adhesion promoter was used for Si samples before placing them into the Parylene Coater. Before using the coater, the Si samples were treated with a 0.5% Silane (A-174) in a 50:50=IPA:DIW mixture. Here, IPA and DIW denote isopropyl alcohol and deionized water respectively. At first, the Si samples were submerged in the adhesion promoter mixture for 30 minutes, then air-dried for 30 minutes, re-submerged in IPA and agitated until the residual silane solution is removed. The sample is removed from the IPA and then allowed to drain naturally. The samples must be dried completely and be coated with Parylene within 30 hours. Otherwise the adhesion promoter must be re-applied. The samples are loaded into the Parylene chamber where the powdered dimer (Parylene N) is heated and vaporized under vacuum to form a dimer gas. The gas is then pyrolized to cleave it into a monomer where it is then deposited as a transparent polymer film onto the sample at ambient temperature (~ 0.1 Torr). The parylene film thickness is typically 2 μm.

1.2.6 Gold coating and patterning of Si wafer

Gold film (~100 nm) was deposited on 75 cm diameter Si wafers by e-beam evaporation. Various patterns were prepared by a standard photolithographic process. At first, a positive photoresist (Shipley S1818) was coated on gold-coated Si wafers by spin coating (2000 rpm for 30 sec) and then baked on a hot plate at 115 C for 5 min. A frequency-tripled Nd:YVO4 (JDSU, Q301-HD) pulsed laser (355 nm, 30 ns FWHM) was used to directly write various patterns on these photoresist-coated wafers. The wafer was fixed on a vacuum chuck, while the laser beam was scanned in a raster pattern using a galvo scanner (SCANLAB, intelliSCAN 10). After laser writing step, the samples were developed in a MF 319 develop solution for 40 sec and then rinsed in a DIW for 1 min.

1.2.7 BN growth

Cu foils were loaded using a crucible into a home-built vertical atmospheric pressure chemical vapor deposition (APCVD) reactor and pumped down to a pressure of 10^{-2} Torr. The reactor had vertical configuration. The samples were first thermally annealed in a reducing environment at 1030°C under a flow of 180 standard cm^3/min (sccm) of N_2 and 20 sccm of H_2 for 5 hours to remove native oxide from the surface and to cause the Cu grain recrystallization. h-BN was then grown at atmospheric pressure (1.1psig using ammonia borane (H_3NBH_3, BoroScience International, Inc. 99.9% purity) as a precursor. The precursor was sublimated upstream at temperatures of 60-90°C and transported by 1.1 PSIG (816 Torr) of a carrier gas (mixture of 840 sccm of N_2 and 20 sccm of H_2) to the reactor. h-BN was grown for 30 minutes with a carrier gas flow rate of 860 sccm. After CVD growth, the samples were cooled down at 100°C/hr and removed from the furnace for further surface characterization.

2. Results and Discussion

2.1 Plasma functionalization of polymers and inorganics

2.1.1 Plasma treatment of PEN

Before plasma treatment polyethylene naphthalate (PEN) was hydrophobic as signified by a water contact angle (WCA)of approximately 90° (Table 1). RF plasma treatments in oxygen environment were performed by varying two key parameters RF power and treatment time. Figure 5a shows WCA dependence on RF power variation at a constant treatment time of 20 seconds, while Figure 5b shows WCA dependence on treatment time at constant RF power of 20W. We found that as the RF power was raised, the PEN surface became more hydrophilic until the power reached 40W. After that the hydrophilicity of PEN gradually decreased. Reduction of plasma treatment time was needed to produce hydrophilic surface. Based on the results, we determined that the optimal conditions for PEN were using RF power of 40 W and treatment time of 20 seconds. At these conditions, the hydrophobicity was reduced by approximately a factor of eleven (from 90° to 8°).

Table 1: Plasma functionalization conditions of PEN

Sample	Gas type	Flow rate (sccm)	Time (sec)	RF Power (W)	Contact Angle (°)
PEN ref.	N/A	N/A	N/A	N/A	90 ± 0.7
PEN1	O_2	5	20	30	28 ± 2.5
PEN2	O_2	5	20	35	22 ± 5.5
PEN3	O_2	5	20	40	8 ± 0.9
PEN4	O_2	5	20	45	17 ± 1.2
PEN5	O_2	5	20	50	23 ± 2.1
PEN6	O_2	5	20	20	30 ± 2.3
PEN7	O_2	5	30	20	29 ± 2.4
PEN8	O_2	5	60	20	66 ± 1.5

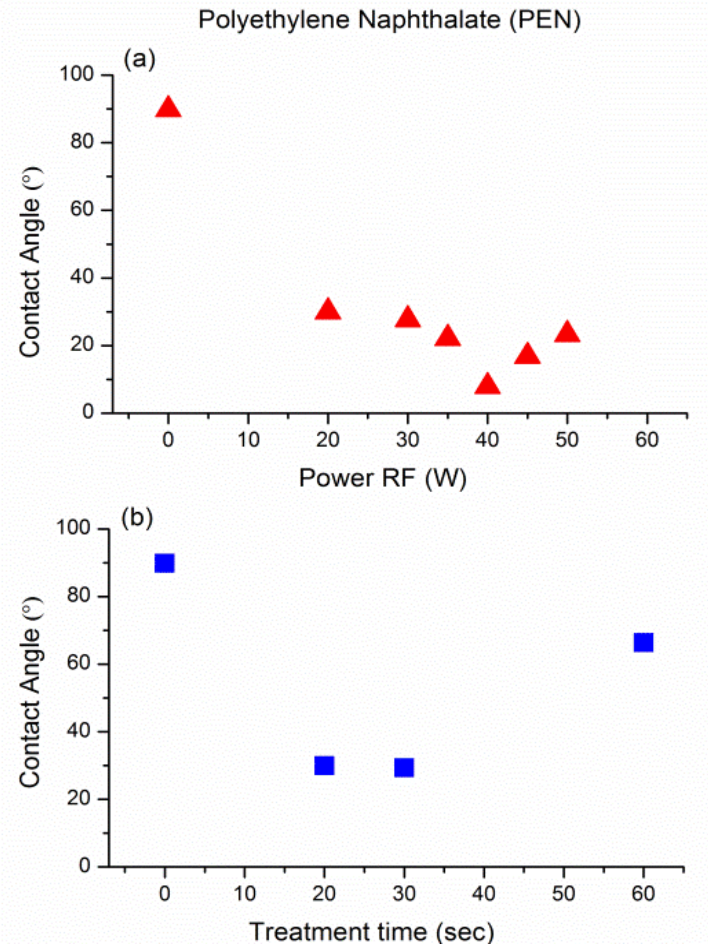


Figure 5: (a) Water contact angle measurement as a function of RF power for PEN at a constant treatment time of 20 seconds. (b) Water contact angle measurement as a function of treatment time for PEN at a constant RF power of 20 W.

2.1.2 Plasma treatment of PET

Before plasma treatment polyethylene terephthalate (PET) was hydrophobic as signified by its high water contact angle of approximately 88° (Table 2). RF plasma treatments in oxygen environment were performed by varying the RF power only. Figure 6 shows WCA dependence on RF power variation at a constant treatment time of 20 seconds. We found that as the RF power was raised, the PET surface became more hydrophilic. Based on the results we determined that the optimal conditions for plasma treatment of PET were using RF power of 40 W and treatment time of 20 seconds. At these conditions, the hydrophobicity was reduced by approximately a factor of fourteen (from 88° to 6°).

Table 2: Plasma functionalization conditions of PET

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
PET ref.	N/A	N/A	N/A	N/A	N/A	88 ± 4.8
PET 1	O_2	5	20	30	0.103	13 ± 2.8
PET 2	O_2	5	20	35	0.105	15 ± 2.1
PET 3	O_2	5	20	40	0.106	6.1 ± 1.2

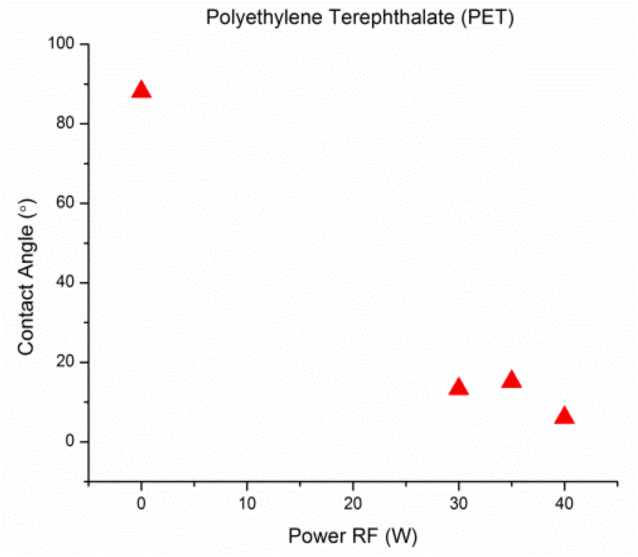


Figure 6: Water contact angle measurement as a function of plasma RF power for PET at a constant treatment time of 20s.

2.1.3 Plasma treatment of PE

Before plasma treatment polyethylene (PE) was hydrophobic, as signified by its high water contact angle of approximately 95° (Table 3). RF plasma treatments in oxygen environment were performed by varying two key parameters: RF power and treatment time. Figure 7a shows WCA dependence of RF power (20-40 W) at a constant treatment time of 10 seconds. We found that as the RF power was raised from 20 W to 30 W, the PE became hydrophilic, but further increase in power was not beneficial. Next, at a constant power of 20 W, the treatment time was varied from 10 to 30 seconds as shown in Figure 7 (b). A reduction of the plasma treatment time to 10 seconds was needed to produce a hydrophilic surface, longer plasma exposure yielded decreased hydrophilicity.

Some PE samples were exposed to plasma treatment in two cycle increments, allowing for independent adjustment of power and duration of each cycle. In the first cycle both power and treatment time were kept constant at 20 W and 30 seconds respectively. In the second cycle, as shown in Figure 7 (c), RF power was varied from 10 to 40 W at constant treatment time of 180 seconds. We found that as the RF power was raised to 40 W in the second cycle the hydrophilicity increased, lower power was not beneficial. Next, the treatment time was varied from 60 to 300 seconds, at constant power of 40 W as shown in Figure 7 (d). We found that reducing the treatment time to 60 seconds in the second cycle produced a hydrophilic surface; additional plasma exposure resulted in decreased hydrophilicity. Based on these results, we were able to reduce the hydrophobicity of the PE by a factor of four (from 95° to 23°).

Table 3: Plasma functionalization conditions of PE

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
PE (ref)	N/A	N/A	N/A	N/A	N/A	95 ± 1.9
PE 1	O_2	5	10	20	0.110	42 ± 3.0
PE 2	O_2	5	20	20	0.104	52 ± 4.3
PE 3	O_2	5	30	20	0.100	73 ± 4.9
PE 4	O_2	5	10	30	0.112	51 ± 4.9
PE 5	O_2	5	10	40	0.110	59± 17
PE 6	O_2	10	30/180	20/10	0.130	56 ± 4.4
PE 7	O_2	10	30/180	20/10	0.134	44 ± 10.6
PE 8	O_2	5	10	30	0.097	39 ± 1.2
PE 9	O_2	5	10	40	0.098	44 ± 4.2
PE 10	O_2	5	10	20	0.095	48 ± 2.7
PE 11	O_2	10	30/180	20/20	0.130	34 ± 1.1
PE 12	O_2	10	30/180	20/30	0.127	42 ± 6.9
PE 13	O_2	10	30/180	20/40	0.118	28 ± 6.2
PE 14	O_2	10	30/60	20/40	0.120	23 ± 6.1
PE 15	O_2	10	30/120	20/40	0.119	50 ± 2.8
PE 16	O_2	10	30/240	20/40	0.118	31 ± 2.9
PE 17	O_2	10	30/300	20/40	0.116	41 ± 3.5

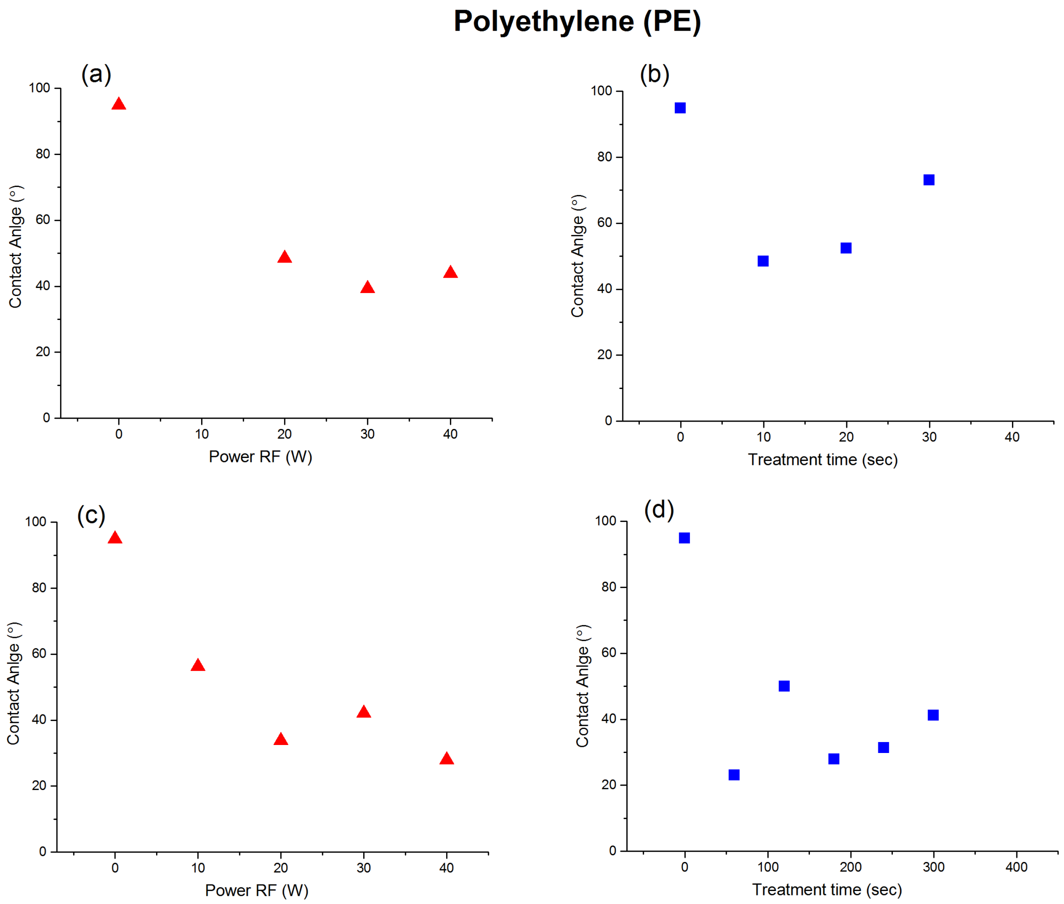


Figure 7: (a) Water contact angle measurement as a function of power for PE at constant treatment time of 10 seconds. (b) Water contact angle measurement as a function of treatment time for PE at constant power of 20 W. (c) Water contact angle measurement as a function of power for PE at constant treatment time of 180 seconds (d) Water contact angle measurement as a function of treatment time for PE at constant power of 40W.

2.1.4 Plasma treatment of PS

Before plasma treatment polystyrene (PS) was hydrophobic as signified by its high water contact angle of approximately 91° (Table 4). RF plasma treatments in oxygen environment were performed by varying the RF power. Figure 8 shows WCA dependence on RF power variation at a constant treatment time of 10 seconds. We found that as the RF power was increased, the PS surface became hydrophilic. We determined that the optimal condition for PS plasma treatment was a two-cycle process. In the first cycle, the RF power and the treatment time were 20 W and 30 seconds respectively. In the second cycle, the RF power and the treatment time were 10 W and 180 seconds respectively. At these conditions, the hydrophobicity was reduced by approximately a factor of nine (from 91° to 10°).

Table 4: Plasma functionalization conditions of PS

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
PS (ref)	N/A	N/A	N/A	N/A	N/A	91 ± 3.2
PS 1	O_2	5	10	30	0.112	29 ± 1.9
PS 2	O_2	5	10	40	0.110	26 ± 1.5
PS 3	O_2	10	30/180	20 /10	0.130	10 ± 1.3

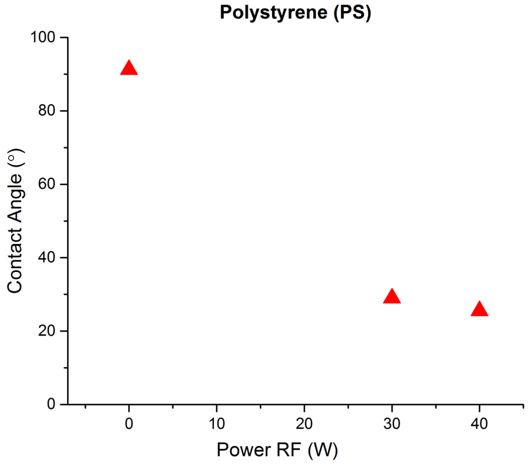


Figure 8: Contact angle measurement as a function of RF power for PS at constant treatment time of 10s.

2.1.5 Plasma treatment of PC

Polycarbonate (PC) films from three different sources were used in this study. First, we are going to present data for plasma treatment of PC purchased from Goodfellow. Next, we are going to discuss plasma treatment of PC films purchased from Tekra [PC (b)] and [PC (c)].

a) Plasma treatment of PC films from Goodfellow [PC (a)]

Before plasma treatment polycarbonate (PC) was hydrophobic as signified by its high water contact angle of approximately 96° (see Table 5). RF plasma treatments in oxygen environment were performed by varying the RF power and treatment time. Figure 9a shows WCA dependence on RF power variation (from 30 W to 50 W) at a constant treatment time of 20 seconds. The Figure 9b shows WCA change as function of treatment time (from 5 to 40 seconds) while the RF power of 20 W was held constant and finally Figure 9c shows WCA dependence on treatment time at a constant RF power of 40 W. We found that as the RF power was raised, the PC surface became more hydrophilic until the power reached 40W. After that the hydrophilicity of PC gradually decreased. For a constant power of 20W, the treatment time variation did not change the water contact angle of 50°. For a constant power of 40W, the treatment time from 5 to 20 seconds improved the hydrophilicity of PC surface; further increase however was not beneficial. Thus, the optimal plasma treatment conditions for PC were using a RF power of 40 W and a treatment time of 20 seconds. At these conditions, the hydrophobicity was reduced by approximately a factor of four (from 96° to 27°).

Table 5: Plasma functionalization conditions of PC

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Contact Angle (°)
PC ref.	N/A	N/A	N/A	N/A	96 ± 1.9
PC 1	O_2	5	20	30	48 ± 3.0
PC 2	O_2	5	20	35	27 ± 4.4
PC 3	O_2	5	10	20	45 ± 3.8
PC 4	O_2	5	30	20	53 ± 4.1
PC 5	O_2	5	60	20	47 ± 0.6
PC 6	O_2	5	20	40	27 ± 0.8
PC 7	O_2	5	20	45	29 ± 1.7
PC 8	O_2	5	20	50	34 ± 0.8
PC 9	O_2	5	5	40	42 ± 0.9
PC 10	O_2	5	25	40	47 ± 2.0
PC 11	O_2	5	30	40	36 ± 0.8
PC 12	O_2	5	40	40	51 ± 2.4
PC 13	O_2	5	10	40	42 ± 1.5

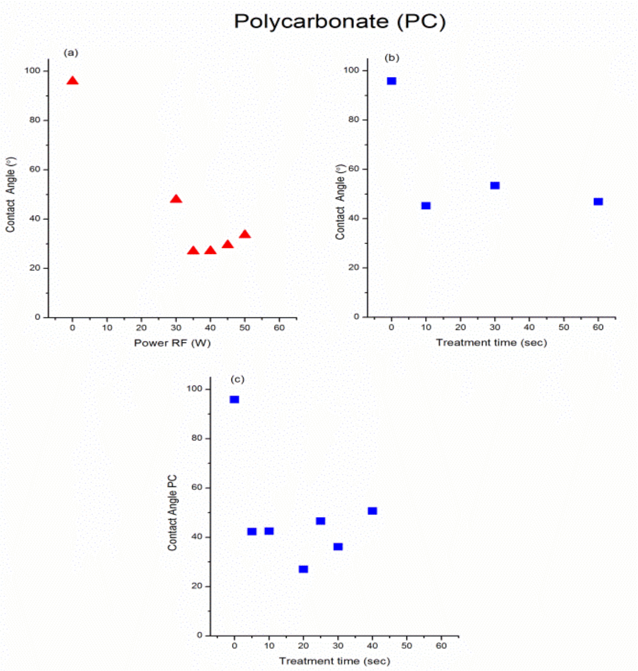


Figure 9: (a) Water contact angle measurement as a function of RF power for PC at a constant treatment time of 20 seconds. (b) Water contact angle measurement as a function of treatment time for PC at a constant RF power of 20 W. (c) Water contact angle measurement as a function of treatment time for PC at a constant RF power of 40 W.

b) Plasma treatment of PC from Tekra [PC (b)]

Before plasma treatment polycarbonate [PC (b)] was hydrophobic as signified by its high water contact angle of approximately 95° (see Table 6). RF plasma treatments in oxygen environment were performed by varying the RF power only. At a constant treatment time of 20 seconds, RF power was varied from 40 to 50 W as shown in Figure 10. We found that lower RF power provided for a better hydrophilic surface. Thus, we determined that the optimal conditions for plasma treatment of PC (b) were using RF power of 40 W and treatment time of 20 seconds. At these conditions, the hydrophobicity was reduced by approximately a factor of eight (from 96° to 12°).

Table 6: Plasma functionalization conditions of PC (b)

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
PC ref.	N/A	N/A	N/A	N/A	N/A	96 ± 2.3
PC 1 (b)	O_2	5	20	40	0.097	12 ± 1.6
PC 2 (b)	O_2	5	20	45	0.095	21 ± 7.1
PC 3 (b)	O_2	5	20	50	0.096	39 ± 3.9

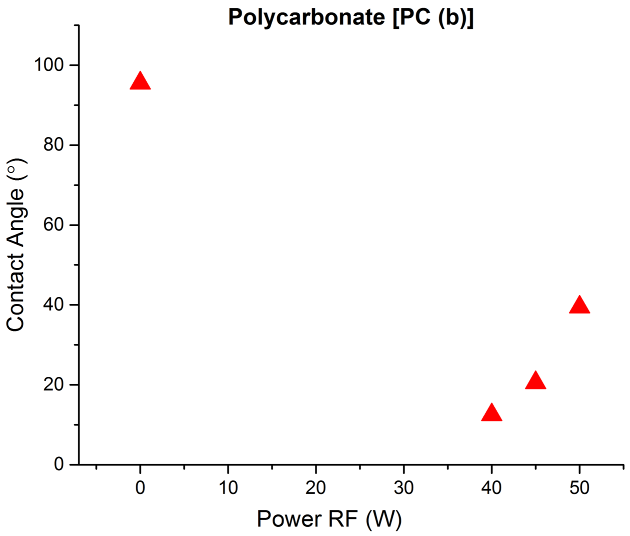


Figure 10: Contact angle measurement as a function of power RF for PC (b) at constant treatment time of 20s.

c) Plasma treatment of PC from Tekra [PC (c)]

Before plasma treatment polycarbonate [PC (c)] was hydrophobic as signified by its high water contact angle of approximately 97° (see Table 7). RF plasma treatments in oxygen environment were performed by varying the RF power only. At a constant treatment time of 20 seconds, RF power was varied from 40 to 50 W as shown in Figure 11. We found that as the power was increased to 50 W, the surface of PC (c) became more hydrophilic, lower power was not beneficial. Based on the results we determined that the optimal conditions for PC (c) were using RF power of 50 W and treatment time of 20 seconds. At these conditions, the hydrophobicity of PC was reduced by approximately a factor of fourteen (from 97° to 7°).

Table 7: Plasma functionalization conditions of PC (c)

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
PC ref.	N/A	N/A	N/A	N/A	N/A	97 ± 1.9
PC 1 (c)	O_2	5	20	40	0.097	12 ± 2.4
PC 2 (c)	O_2	5	20	45	0.095	28 ± 2.9
PC 3 (c)	O_2	5	20	50	0.096	7 ± 1.6

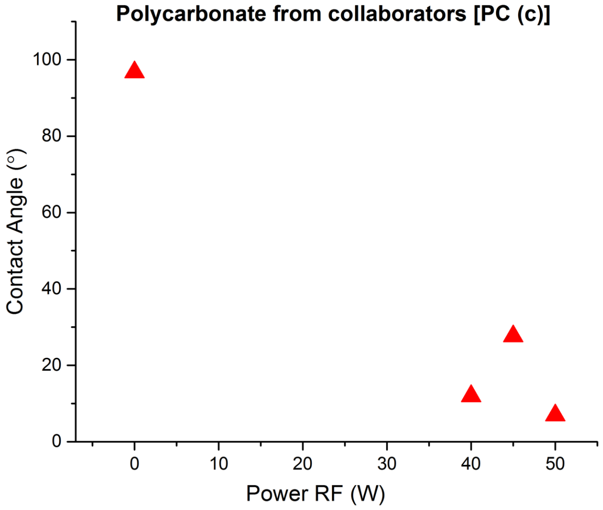


Figure 11: Contact angle measurement as a function of power RF for PC (c) at constant treatment time of 20s.

2.1.8 Plasma treatment of SiO_2/Si wafers

Before plasma treatment SiO_2/Si was hydrophilic as signified by its water contact angle of 57° (see Table 8). RF plasma treatments in oxygen environment were performed by varying the RF power and treatment time. Figure 12a shows WCA dependence on RF power variation (from 30 to 50 W) at a constant treatment time of 60 seconds. Figure 12b shows WCA dependence on treatment time (from 20 to 60 seconds). at a constant RF power of 50 W. We found that as the RF power of the plasma treatment was raised, the SiO_2/Si surface became more hydrophilic. All treatment times used produced hydrophilic surface, but the best result was achieved at 20 seconds. Based on the results we determined that the optimal conditions for SiO_2 were using a RF power of

50 W and a treatment time of 20 seconds. At these conditions, the hydrophilicity was increased by approximately a factor of twenty-four (from 57° to 3°).

Table 8: Plasma functionalization conditions of SiO_2/Si wafers

Sample name	Gas Type	Flow rate (sccm)	Time (sec)	RF Power (W)	Vacuum	Contact Angle (°)
SIC ref.	N/A	N/A	N/A	N/A	N/A	57 ± 2.9
SIC 2	O_2	5	60	30	0.101	16 ± 1.3
SIC 3	O_2	5	60	40	0.109	4.2 ± 0.9
SIC 4	O_2	5	60	50	0.102	4.3 ± 0.7
SIC 5	O_2	5	20	50	0.100	2.8 ± 0.4
SIC 6	O_2	5	30	50	0.100	4.5 ± 0.8

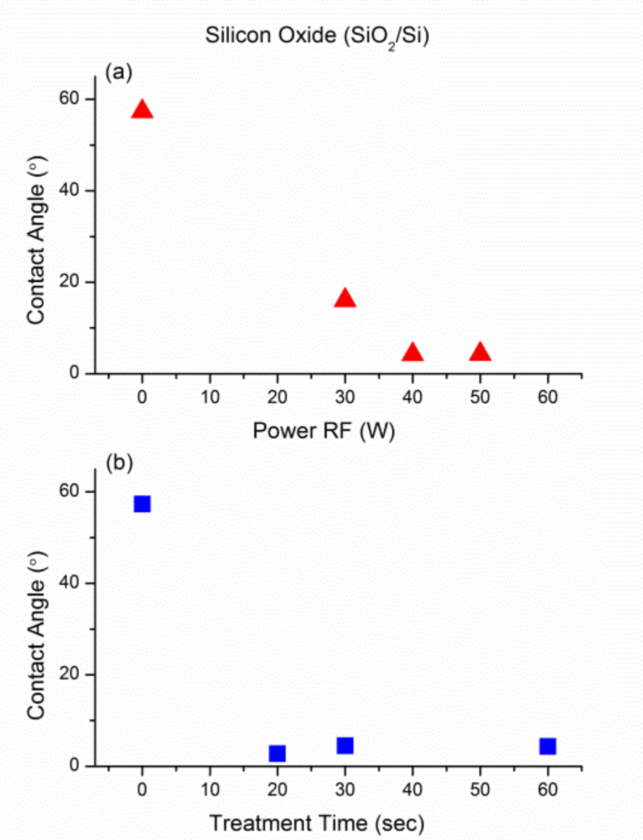
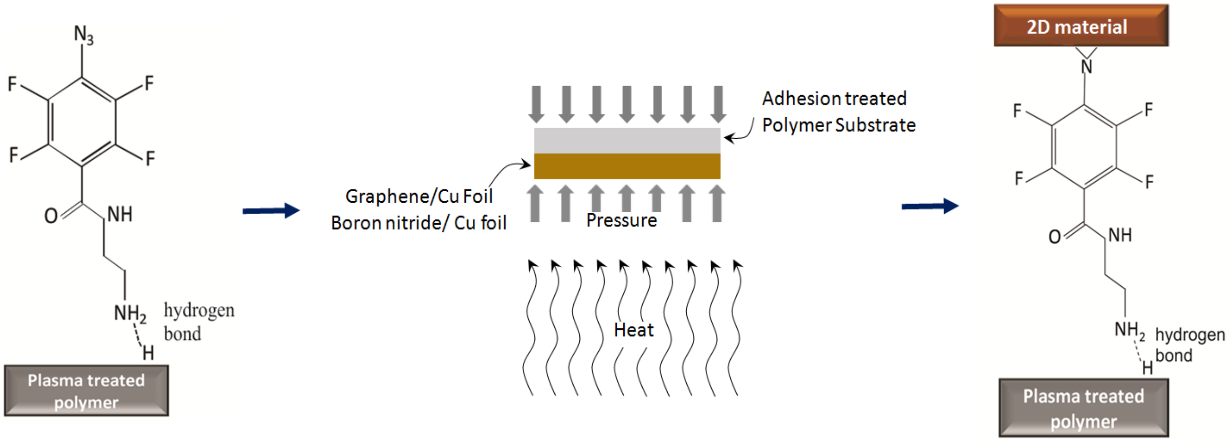


Figure 12: (a) Water contact angle measurement as a function of RF power for SiO_2/Si wafers at constant treatment time of 60 seconds. (b) Water contact angle measurement as a function of treatment time for SiO_2/Si wafers at a constant RF power of 50 W.

Plasma treatment in oxygen gas environment yielded substrates with increased hydrophilicity. All of the inorganic substrates, PEN, PET, PS, PC (b) and PC (c) were completely wettable at best plasma processing conditions. The WCAs of PEN and PET were reduced by a factor of eleven (from 90° to 8°) and fourteen (from 88° to 6°) respectively. The WCAs of PS was reduced by a factor of nine (from 91° to 10°). The hydrophobicity of PC (a) and PE were reduced by approximately a factor of three (from 95° to 27°) and by a factor of four (from 95° to 23°) respectively.

2.2 Two-dimensional material transfer

After plasma treatments, the polymer surfaces were highly wettable and reactive and had better adhesion properties. Next, these "activated" polymers were further functionalized with a chemical linker molecule (TFPA-NH_2) to enhance adhesion. Gr/Cu and BN/Cu foils were used without further modification. Both, the adhesion treated polymers and the 2D materials were placed inside the Nanoimprinter. There they were heated and pressed at a specific temperature and pressure, and formation of carbene (C-N) bonds between TFPA-NH_2/polymer and graphene were achieved. This covalent bond strength was much higher than the van der Waals interactions between the graphene and the Cu foil and thus, the 2D material was transferred from the Cu foil to the polymer. Similar results were achieved with BN/Cu as well. It should be noted that this work is an extension of previously conducted experiments[1, 12]. First the results from graphene transfer to PS and PE will be discussed, followed by BN transfer to PS and PEN.



Schematic 1: Imprint process of 2D materials transfer.

2.2.1 Graphene transfer-print

Table 10 shows a summary of the imprint conditions used for graphene transfer to PS and PE. Two major parameters were varied: pressure and temperature. Surprisingly, the print conditions used in our previous work[1, 12] of 500 psi and 130 C did not yield successful transfer. After extensive trouble shooting, we determined that the actual pressure in the chamber varies widely from the set experimental pressure in the software by approximately 50 psi. Thus, additional pressure gauges were installed to ensure more accurate measurement of this parameter. We found that temperature variation was also critical. There was only one thermocouple at the bottom of the print stack that provides the temperature for the software. No additional work was devoted on further modification of the hardware of this parameter.

Figure 14 and 15 show Raman spectra of the Cu foil before and after imprint to polystyrene and polyethylene respectively. Three peaks signify the presence of graphene - D peak at 1350 cm^{-1}, the G peak at 1600 cm^{-1} and the 2D peak at 2700 cm^{-1}. For polystyrene, as the pressure decreased from 540 to 530 psi and temperature decreased from 130 to 120 °C, the D, G and 2D peaks were not detected suggesting a complete graphene transfer. For polyethylene, complete graphene transfer was achieved when pressure was increased from 520 to 540 psi and temperature increased from 120 to 130 ℃ as shown in Figure 15. The print time was 20 minutes in all cases.

Table 10: Imprint conditions for graphene to PS and PE

Sample Name	Polymer Type	2D material	Print Conditions				Analysis
			Pressure (psi)	Actual pressure (psi)	Temperature (°C)	Time (min)	Raman
07112017A	PS	Gr 1L	540	490	125	20	Not Successful
07112017B	PS	Gr 1L	540	490	120	20	Not Successful
07112017C	PS	Gr 1L	530	480	120	20	Successful
07112017D	PS	Gr 1L	520	470	120	20	Partially Successful
07132017A	PE	Gr 1L	530	480	120	20	Successful
07132017B	PE	Gr 1L	520	470	120	20	Not Successful
07132017C	PE	Gr 1L	540	490	130	20	Successful
07142017A	PS	Gr 1L	530	480	120	30	N/A
07142017B	PS	Gr 1L	530	480	120	25	N/A

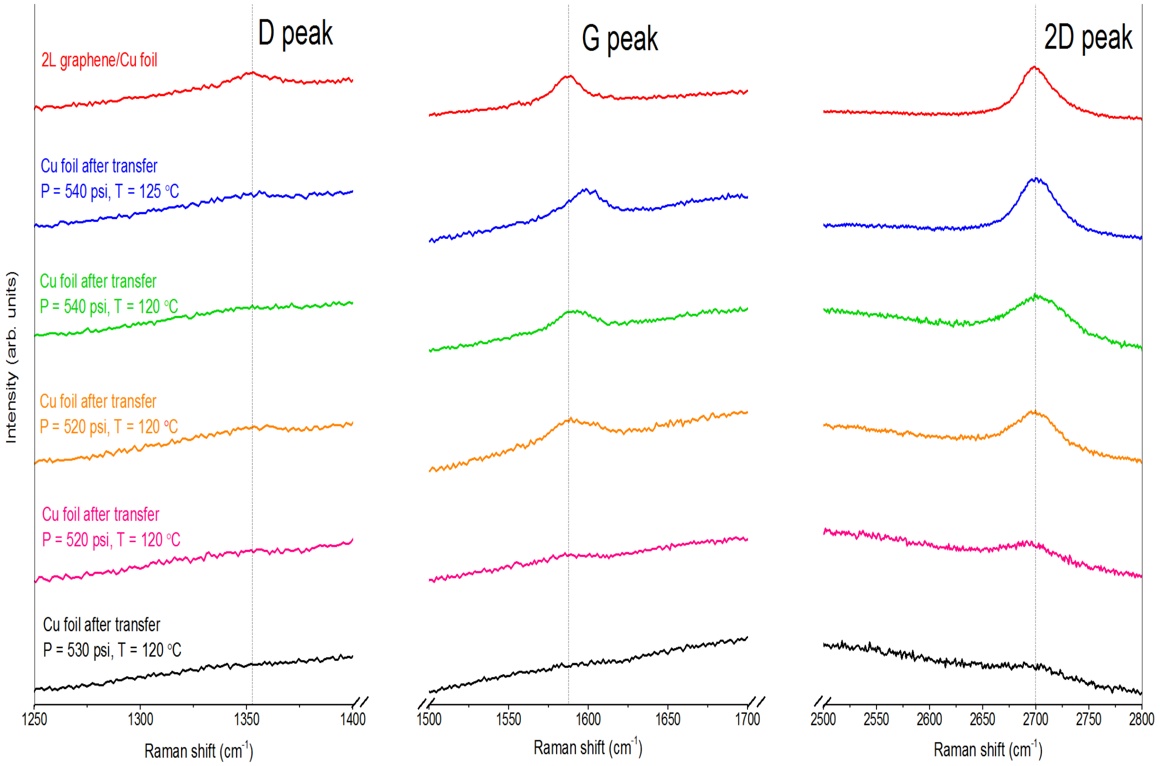


Figure 14: Raman spectra of the copper foil with 2L graphene before and after transfer to PS.

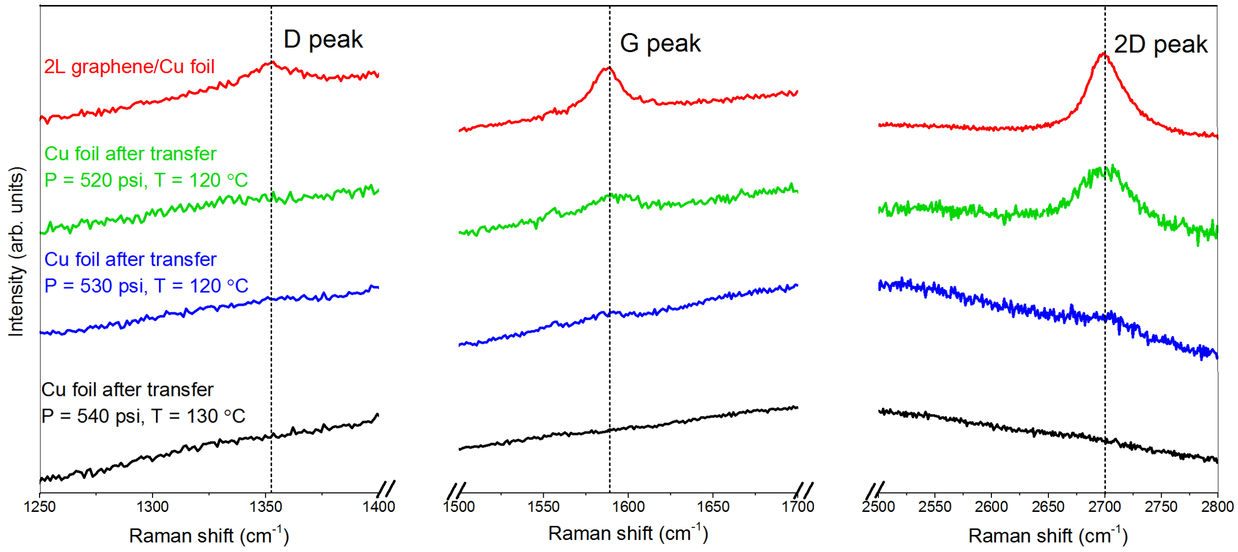


Figure 15: Raman spectra of the copper foil with 2L graphene before and after transfer to PE.

2.2.2 Boron nitride transfer-print

A summary of the imprint conditions used for the transfer of boron nitride to polystyrene is shown in Table 11. Similar to the graphene transfer shown above, the two main parameters varied in the transfer print process were pressure and temperature. Figures 16 and 17 show Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) analysis[13] of the Cu foil before and after BN transfer. Figure 16 shows raw FT-IRRAS spectra of the best transfer. To estimate the transferred amount, area under each peak was calculated - the peaks are shown in Figure 17. Then, using the following formula

$$\%\,transferred = \left(1 - \frac{Peak\ Area\ before}{Peak\ Area\ after}\right) * 100\ \%$$

the amount of transferred BN to PS was calculated. The best transfer-print conditions for boron nitride to PS (Figure 16) were at pressure, temperature and processing time of 530 psi, 120 °C and 25 minutes, respectively. We were able to transfer about 70% of the boron nitride to the PS at those conditions. XPS analysis of transferred BN to PS indeed confirm the presence of boron and nitrogen elements (Table 12, Figure 18). Even though BN was not completely transferred onto PS, we determined that increasing the printing time at a pressure of 480 psi could result in complete BN transfer.

Table 11: Imprint conditions for boron nitride to PS

2D material	**Print Condition**				**Analysis**
	Pressure (psi)	Actual pressure (psi)	Temperature (°C)	Time (min)	FTIR
BN F1026-1	540	490	125	20	20%
BN F1026-2	540	490	120	20	15%
BN F1026-3	530	480	120	20	50%
BN F1026-4	520	470	120	20	30%
BN F1026-5	530	480	120	30	60%
BN F1026-6	530	480	120	25	70%
BN F1026-7	530	450	120	35	10%

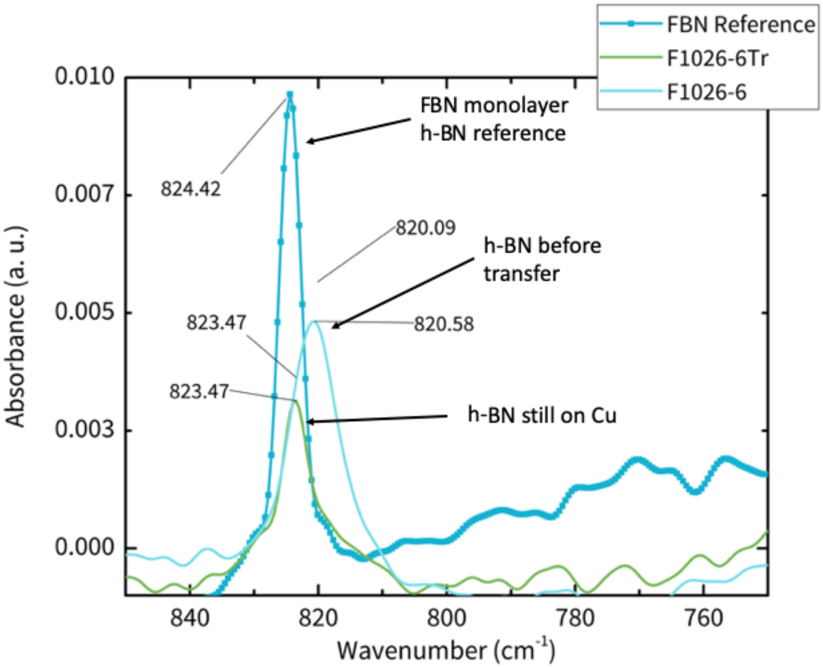


Figure 16. FTIR of BN/Cu foil before and after transfer print F1026-6 (p = 530 psi, t = 25 min)

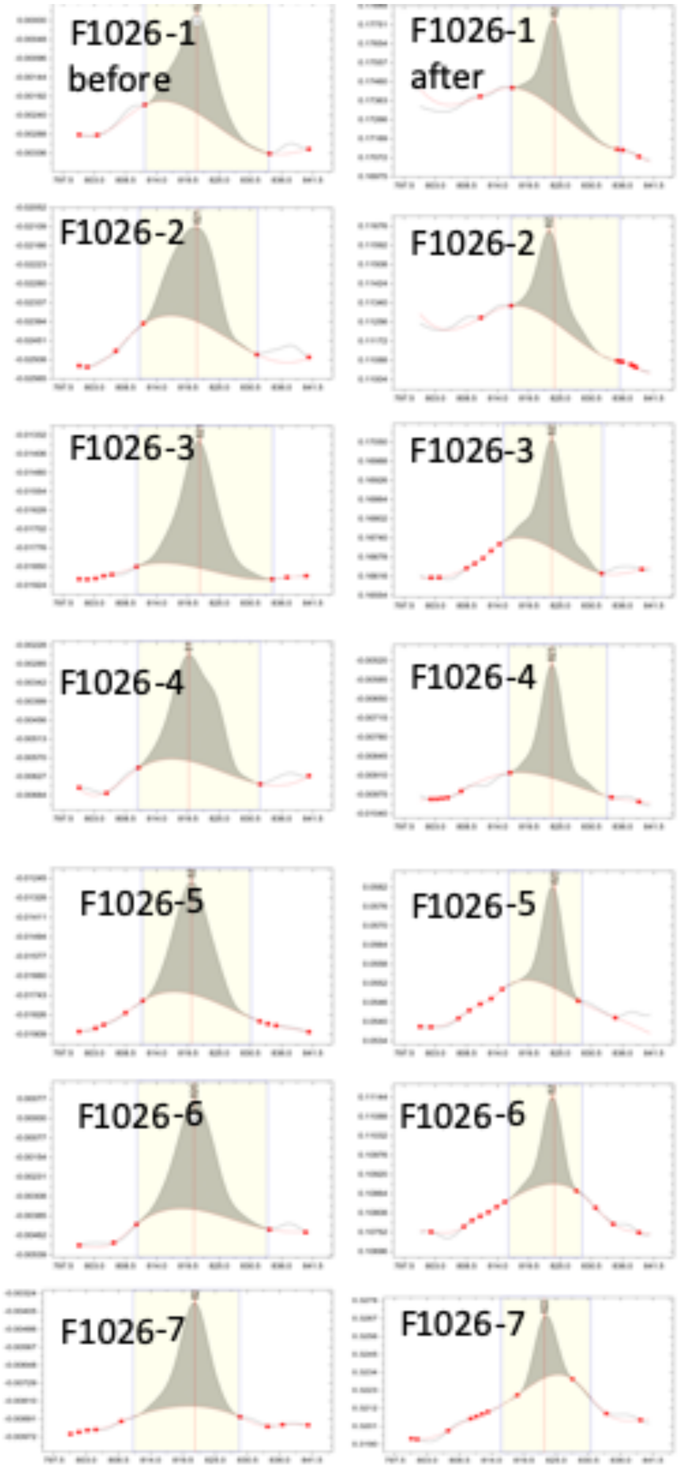


Figure 17. BN/Cu peak areas from FTIR analysis before and after transfer used for estimation of amount of BN transferred shown in Tables 11 and 12.

Table 12: XPS and FTIR analysis of BN/PS samples after transfer-print

Sample Name	Polymer type	2D material	XPS analysis of PS								FTIR analysis Of Cu foil after print
			B1s	C1s	F1s	N1s	O1s	Si2p	Cu2p	Zn2p	
07112017A	PS	BN F1026-1	0.69	77.39	2.52	4.09	13.79	1.14	0.52	0.11	20%
07112017B	PS	BN F1026-2	7.12	66.07	2.41	9.33	13.19	1.38	0.31	0.21	15 %
07112017C	PS	BN F1026-3	6.91	69.77	1.35	8.36	12.28	1.31	0	0.04	50 %
07112017D	PS	BN F1026-4	8.25	66.54	1.77	9.84	13	0.63	0	0	30 %
07142017A	PS	BN F1026-5	5.85	73.18	0.8	6.43	11.11	2.38	0.18	0.07	60 %
07142017B	PS	BN F1026-6	8.61	65.62	1.19	8.96	12.62	2.85	0.17	0	70 %
07192017A	PS	BN F1026-7	5.21	69.28	2.53	6.65	13.65	2.17	0.34	0.19	10 %

2.3 Gold patterns transfer-print

Figure 19 shows a schematic of the gold pattern transfer. The plasma treated polymer and the gold patterned Si wafer were placed inside the nanoimprinter. There they were heated and pressed at a specific temperature and pressure. This yielded gold pattern attachment to the polymer. Finally, after the imprint is done, polymer/Au/Si wafer stack was taken out of the nanoimprinter and the polymer substrates were mechanically separated from the Si wafer by peeling with tweezers.

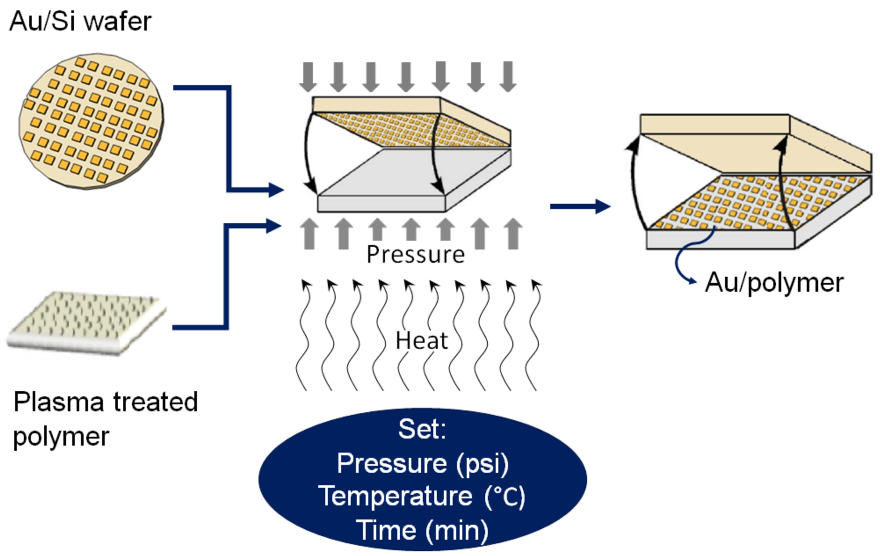


Figure 19: Transfer-print process of gold patterns from Si wafer onto polymers

Complete gold patterns were transferred onto PE, PET and PEN substrates. The best gold pattern transfer PEN (Figure 20) was achieved using a three-step process as shown in Table 13 and Figure 20c. The pattern transfer was improved as the imprint conditions were changed as follows: pressure and temperature in the first step were increased from 250 psi to 280 psi and from 150 °C to 170 °C respectively, and the pressure was increased from 20 psi to 40 psi in the second and third steps. For PE, the best gold pattern transfer produced was using wafer one, where the pressure, temperature and time for the first step of 520 psi, 140 °C and 15 minutes, respectively; while the pressure, temperature and time conditions for the second step were 40 psi, 140 °C and 5 minutes (Figure 21). For PET, the best gold pattern transfer produced was using wafer one (Figure 22), where the pressure, temperature and time conditions for the first step were 520 psi, 175 °C and 15 minutes, respectively; and the pressure, temperature and time conditions for the second step were 50 psi, 140 °C and 5 minutes. It has to be noted, that some of the parylene was also transferred onto the samples, when wafer 2 (Figure 23) was used. Best results were obtained using the gold patterning of wafer 1 (Figure 23) - this might be due to the resist used for patterning. For the fabrication of for wafer 1, a negative resist was used and the resist was completely removed after the lithographic patterning; for wafer 2 a positive resist was used, and some of the resist maybe covering the gold pattern and affecting the transfer print.

Table 13: Gold pattern transfer to organic substrates.

Sample Name	Polymer Type	Wafer	Pressure (psi)	Actual pressure (psi)	Temperature (°C)	Time (min)	Results
PEN15	PEN	1	250	N/A	150	3	Partial gold Pattern transfer
			20	N/A	150	0.33	
			20	N/A	180	3	
PEN16	PEN	1	280	N/A	170	3	Partial gold pattern transfer
			20	N/A	170	3	
PEN17	PEN	1	280	N/A	170	3	Complete gold Pattern transfer
			40	N/A	150	0.33	
			40	N/A	180	3	
PEN18	PEN	2	280	250	170	3	No gold pattern transfer
			40	40	150	0.33	
			40	40	180	3	
PEN18	PEN	2	540	490	175	10	No gold pattern transfer
			50	50	120	5	
GPE01	PE	1	500	450	130	3	No gold pattern transfer
GPE02	PE	1	520	470	140	15	Complete gold pattern transfer
			40	40	140	5	
GPE03	PE	2	520	470	140	15	Complete transfer with paralyn
			40	40	140	5	
GPE04	PE	2	520	470	140	15	Half gold pattern transfer
			40	40	120	5	
GPET01	PET	1	520	470	175	15	Complete gold pattern transfer
			50	50	140	5	
GPET02	PET	2	520	470	175	15	No gold pattern transfer
			50	50	140	5	

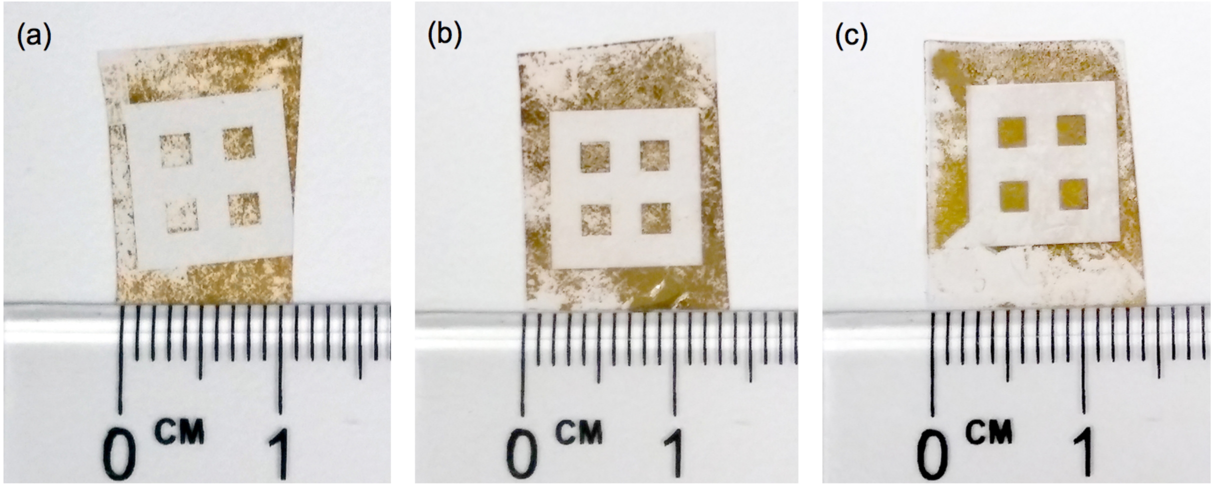


Figure 20: (a) Gold pattern transferred onto PEN (PEN15, Table 12) using wafer 1. (b) Gold pattern transfer onto PEN (PEN16, Table 12) using wafer 1. (c) Gold pattern transfer onto PEN (PEN17, Table 12) using wafer 1.

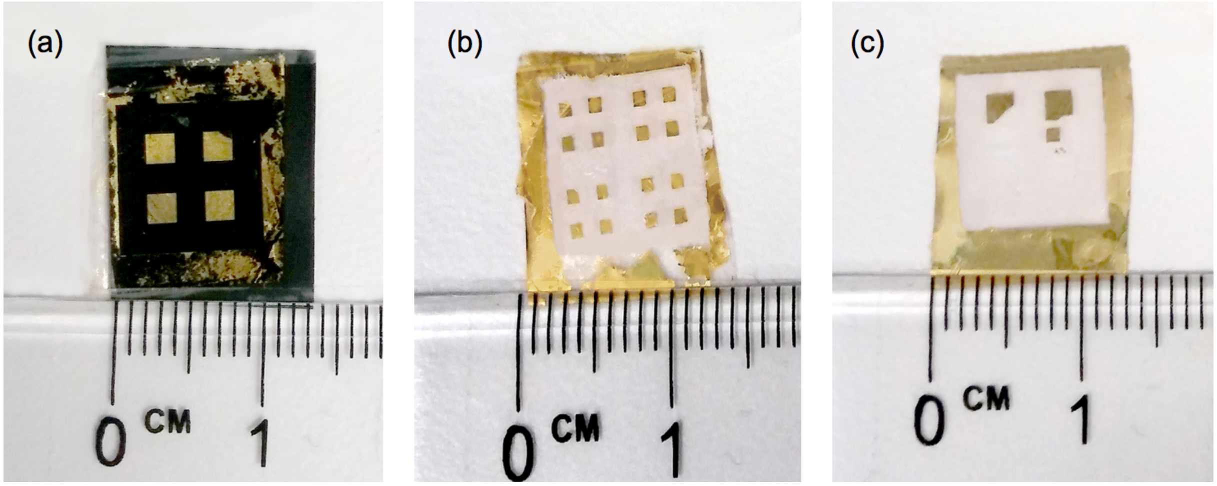


Figure 21: (a) Gold pattern transferred onto PE (GPE02, Table 12) using wafer 1, (b) Gold pattern transfer onto PE (GPE03, Table 12) using wafer 2 (c) Gold pattern transfer onto PE (GPE04, Table 12) using wafer 2.

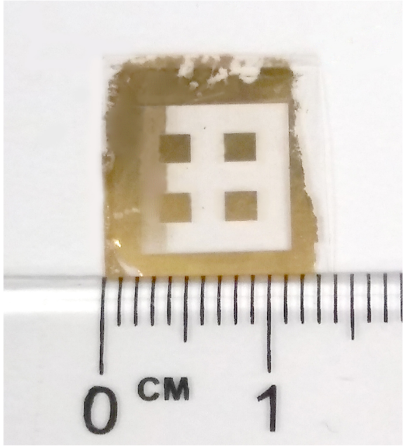


Figure 22: Gold pattern transfer onto PET (GPET01, Table 12) using wafer 1.

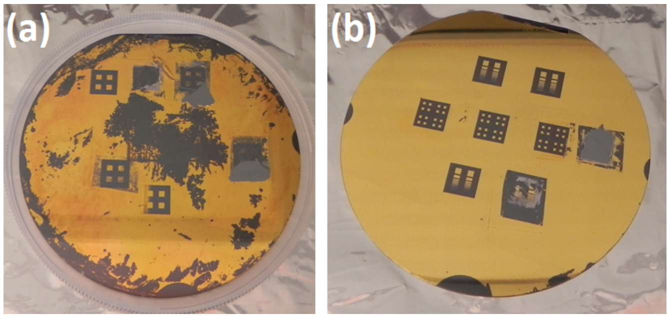


Figure 23: (a) Wafer 1, the gold was patterned using negative resist, the photoresist was completely removed, many successful transfer-prints were achieved. (b) Wafer 2, the gold was patterned using positive resist, the photoresist may be not completely removed; transfer-print success was affected.

3. Summary

In this report, we showed a general approach for transfer printing two dimensional materials including graphene and boron nitride, as well as gold patterns onto polymers. Special attention was given to improve adhesion of the polymers using RF plasma. Indeed, plasma treatment in oxygen gas environment yielded substrates with increased hydrophilicity - SiO_2/Si PEN, PET, PS, PC (b) and PC (c) were completely wettable at best plasma processing conditions. The hydrophobicity of PC(a) was reduced by approximately a factor of three (from 95° to 27°) and of PE was reduced by approximately a factor of 4 (from 95° to 23°). We were able to completely transfer graphene onto PS and PE. Partial transfer of boron nitride to PS was achieved as well. Complete gold pattern transfer onto PE, PET and PEN substrates was demonstrated as well. Even though there is enormous amount of future work needed to bring this project to flourishion, this report shows the potential of the nanoimprint technology for large-scale two-dimensional materials and pattern transfer.

4. Reference

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