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Site-specific stamping of graphene micro-patterns over large areas using flexible stamps

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Abstract
Site-specific stamping has the potential of becoming a low-cost, high-throughput method for depositing specific-shaped graphene micro-patterns over large areas on a wide variety of substrates. The use of an approach involving flexible stamps presented here represents an important advance towards reaching that potential. This approach entails lithographic creation (dry etching) of high-quality micro-pillar arrays of highly oriented pyrolytic graphite (HOPG) over large areas. This is followed by embedding the micro-pillar arrays in polydimethylsiloxane (PDMS), and detaching them from the HOPG base. This results in flexible stamps containing embedded HOPG micro-pillar arrays with freshly cleaved stamping surfaces. The flexible HOPG/PDMS stamps are then brought into contact with substrate surfaces to site-specifically stamp graphene or few-layer graphene (FLG) arrays over large areas. The freshly cleaved nature of the micro-pillar surfaces in the flexible stamps, the low elastic modulus of the flexible stamps and the elimination of sidewall deposits on the micro-pillars allow for more uniform stamping, relative to the use of stiff HOPG stamps from earlier studies. This approach has the potential to expand the substrate choice for graphene or FLG stamping to include curved and/or flexible substrates that could have an impact on the burgeoning field of flexible/stretchable electronics.

(Some figures may appear in colour only in the online journal)

1. Introduction

An unusual combination of tunable properties possessed by graphene makes this remarkable 2D crystal of carbon an attractive material for a wide range of potential applications [1–5]. Isolating graphene or few-layer graphene (FLG) by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) crystals remains the most popular and successful method for fabricating high-quality graphene-based devices [1, 2, 5, 6]. The resulting individual graphene sheets are then dispersed randomly onto oxidized Si substrates, followed by deposition of metal electrodes to make contacts [1, 2, 5–7]. This approach, although highly successful for making fundamental measurements and discoveries, may not be amenable to high-throughput fabrication of graphene-based devices. The latter will require new methods for producing large arrays of specific-shaped graphene deposited site-specifically over large areas on substrates made of a wide variety of materials.

Other competing methods include volatilization of Si from single-crystal SiC substrates to form graphene [8, 9]. However, in that graphene synthesis method the underlying substrate is generally limited to SiC. More recently, chemical vapor deposition (CVD) of large-area graphene on polycrystalline Cu foils, followed by transfer of the graphene onto a variety of substrates, is emerging as an attractive, low-cost method [10–16]. However, the quality of CVD graphene is inferior for high-end applications, but the importance of using Cu(111) surfaces for improving the quality of CVD graphene is being recognized [17–19].

In this context, in an earlier study [20] we demonstrated the feasibility of, and provided the scientific basis for, a new method for creating graphene-based devices: site-specific stamping of graphene or FLG micro-patterns. The site-specific stamping method, inspired by the work of Lu *et al* [21, 22], Zhang *et al* [23] and Liang *et al* [24], entails lithographic creation (dry etching) of micro-pillar arrays in HOPG over large areas, which constitutes the stamp. The stamps are then brought into contact with different types of substrates in a controlled manner. The stamp surface/substrate interactions screen the cohesion between graphene sheets near the stamp/substrate interface, leaving graphene or FLG stamped on predetermined sites on the substrates [20]. This method allows the site-specific placement of numerous, specific-shaped graphene or FLG micro-patterns over large areas, on an expanded choice of substrate materials beyond oxidized Si and SiC. The stamps can be reused repeatedly, making site-specific stamping a potentially low-cost, high-throughput method for depositing graphene or FLG. Furthermore, site-specific placement of graphene or FLG, in principle, allows high-throughput metal-contact deposition for making devices. Variations of the site-specific stamping method have since been reported in the literature [25–29].

Although the site-specific stamping method is attractive, and it has the potential for broad impact, three important issues have been identified that are precluding the successful use of this method. First, the vertical sidewalls of the stamp micro-pillars appear to have carbon deposits formed on them during the inductively coupled plasma (ICP) reactive-ion etching (RIE) of HOPG to etch out the micro-pillars. The presence of such deposits is not conducive to stamping because they constrain the peeling of the graphene sheet during stamping. Second, the top surfaces of the micro-pillars are unacceptably rough due to the extensive processing needed to fabricate the stamps [20]. There is a need to obtain micro-pillar top surfaces that are as smooth as freshly cleaved HOPG. Finally, the HOPG stamps ($\sim$5 $\times$ 5 mm^2; $\sim$2 mm thickness), with the arrays of etched-out micro-pillars (individual pillars $\sim$10 μm diameter, $\sim$5 μm tall), are stiff. Therefore, any unevenness in the pillar heights and/or slight non-parallel alignment between the stamp surface and the substrate exaggerates the disparity in stamping force experienced by the individual micro-pillars. This can lead to uneven stamping coverage, shearing and stamped micro-patterns with vastly different numbers of graphene layers [20].

The objective of this work is to address all three issues simultaneously in improving the site-specific graphene stamping method. In order to address the first issue, reduced radio-frequency (RF) power is used for RIE (no ICP) etching out the micro-pillars, minimizing deposition of carbon on the sidewalls. In order to address the second and third issues, a new flexible-stamp approach is used here, which is shown in figure 1 schematically. The basic idea is to embed the HOPG micro-pillars in polydimethylsiloxane (PDMS), with a very low elastic modulus, creating a flexible HOPG/PDMS stamp with freshly cleaved micro-pillar stamping surfaces.

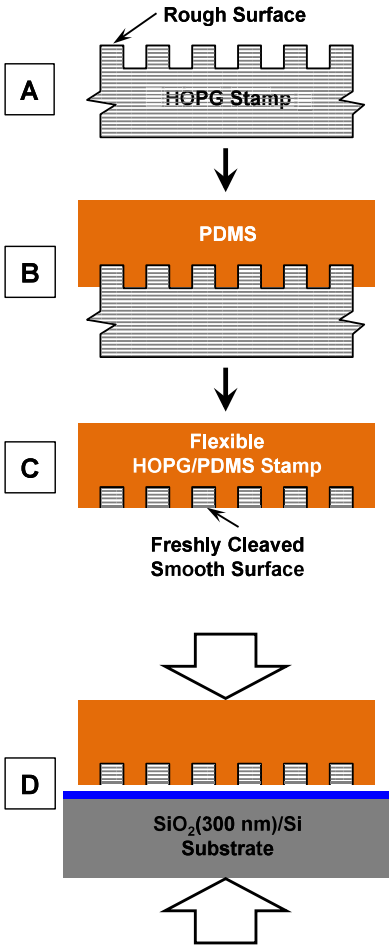

Figure 1. Schematic diagram (cross section) depicting the flowchart for the flexible-stamp fabrication ((A)–(C)) and the stamping process (D). (Not to scale.)

It is demonstrated that graphene or FLG stamping using HOPG/PDMS flexible stamps is significantly improved relative to the original stamping method using stiff HOPG stamps [20].

2. Experimental details

2.1. Stamp preparation

Figure 1(A) is the schematic (cross section) of the stiff HOPG stamp with micro-pillar arrays, where the graphene sheets run horizontally. These stamps were fabricated using a variation of the procedure described by Li *et al* [20]. Briefly, commercially obtained HOPG (SPI-1 Grade, SPI Supplies, West Chester, PA) samples were cut into small square plates ($\sim$5 $\times$ 5 mm^2; $\sim$2 mm thickness) with a razor blade. One face of the entire HOPG plates was coated with amorphous silica films of $\sim$500 nm thickness using sputtering (ATC Orion Series, AJA International, N Scituate, MA). Positive photoresist (1813 Grade, Rohm and Hass, Marlborough, MA) was then spin-coated onto the surface of the silica film. An aligner (Model 620, EV Group, Albany, NY), in conjunction with a mask, was used to produce

photoresist circles (∼10 μm diameter) on the silica surface. The exposed silica film was etched for 4 min using CF_4 (5 mTorr) RIE (Plasma-Therm® SLR 770, Plasma-Therm Inc., N St Petersburg, FL) with RF power of 100 W. The photoresist mask and other organics were removed using acetone, and the exposed graphite was then dry-etched for a total of 30 min (10 min etching followed by 5 min off, repeated three times) using O_2 (5 mTorr) RIE with RF power of 100 W. Unlike in the previous study [20] it is not necessary to remove the silica masking layer by HF because that layer ends up being embedded in the PDMS, and also this eliminates any additional processing steps involving corrosive acids.

The PDMS matrix was prepared using the Sylgard 184 Silicone Elastomer kit (Dow Corning Corp., Midland, MI). The base and curing agent were mixed in the weight ratio of 10:1, and were stirred for several minutes to form a transparent viscous mixture which was allowed to rest for ∼30 min to remove any bubbles. The stiff HOPG stamp was placed in the mixture and cured in an oven at 110 °C for 12 h (figure 1(B)). The stiff HOPG stamp base was peeled away by hand from the cured PDMS containing embedded HOPG micro-pillars to obtain the flexible HOPG/PDMS stamps (figure 1(C)).

Stiff HOPG stamps from the previous study [20] were obtained for comparative studies. Those stamps were dry-etched using higher ICP-RIE etching powers: RF(RIE) = 200 W and ICP = 500 W. In that previous study [20] the silica masking layer was removed with dilute HF to expose the HOPG micro-pillar surfaces for stamping.

2.2. Stamping

Stamping was carried out following the same procedure used in the earlier study [20]. Briefly, a single-crystal Si wafer with a thermally grown silica layer of ∼300 nm thickness was used as the substrate. The SiO_2 (300 nm)/Si substrate was thoroughly cleaned prior to stamping. The flexible HOPG/PDMS stamp or the stiff HOPG stamp was attached to the top platen of the aligner (Model 620, EV Group, Phoenix, AZ) and the substrate to the bottom platen. Both were brought into light contact and then separated (figure 1(D)). The stamped substrates were cleaned successively using acetone, *N*-methyl-2-pyrrolidone and isopropyl alcohol to remove any organic residue from the stamping process.

2.3. Characterization

The stiff HOPG stamps were observed in scanning electron microscopes (SEM; Ultra 55 Plus, Carl Zeiss International, Thornwood, NY or Sirion, FEI Company, Hillsboro, OR), the latter equipped with an energy dispersive spectrometer (EDS; EDAX, Mahwah, NJ). The micro-pillar sidewalls were characterized using micro-Raman spectroscopy (InVia Raman Microscope, Renishaw, Gloucestershire, UK) using a 514 nm wavelength laser (∼2 μm spot size) at 1 mW power. The flexible HOPG/PDMS stamps were observed in an optical microscope (Olympus, Center Valley, PA).

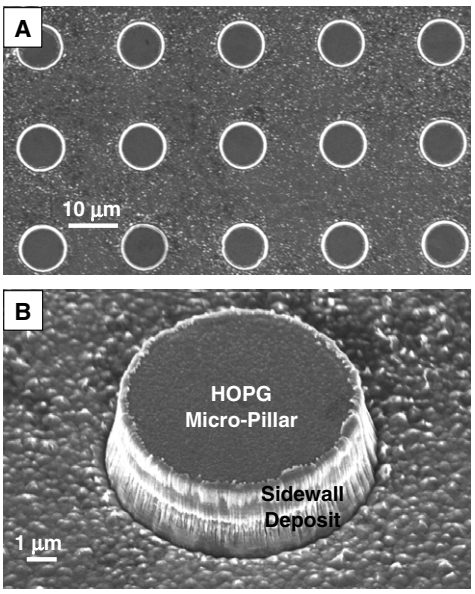

Figure 2. SEM micrographs of as-fabricated stiff HOPG stamps from the previous study [20] showing the sidewall carbon deposits on the micro-pillars: (A) plan view at low magnification and (B) angled view at higher magnification.

The stamping top surfaces of the micro-pillars in both the stiff HOPG stamps and the flexible HOPG/PDMS stamps were characterized using an atomic force microscope (AFM; NanoMan Dimension 3100, Veeco, Santa Barbara, CA). The stamped impressions on the SiO_2 (300 nm)/Si substrates were observed using the optical microscope and the SEM, and they were characterized using the micro-Raman spectrometer (514 nm wavelength laser; ∼2 μm spot size; 1 mW power).

3. Results and discussion

A low magnification SEM image of a stiff HOPG stamp from the previous study [20] is shown in figure 2(A). The light contrast at the circular micro-pillar edges is from the sidewall carbon deposits, which are shown clearly in the high magnification SEM image in figure 2(B). The EDS of the sidewall region (not shown here) confirmed that those deposits are made of pure carbon. Micro-Raman spectroscopy of the sidewall deposits shows the presence of disordered graphitic carbon, as indicated by the presence of the characteristic peak at ∼1350 cm^{-1} in figure 3 (arrow) [30], which is absent in the spectrum from the center of the same micro-pillar. While the exact genesis of these deposits is not known, reducing the RIE power with no ICP and removing organic impurities can eliminate these deposits, resulting in clean sidewalls, as seen in figures 4(A) and (B).

Figure 5(A) is an AFM image of the top surface of an as-processed stiff HOPG stamp micro-pillar from the previous study [20] showing high peak-to-peak roughness (∼10 nm). The source of this roughness is the extensive processing involved in stiff HOPG stamps fabrication, including the various silica deposition and HF etching steps described by Li *et al* [20]. This type of roughness is an obstacle in the

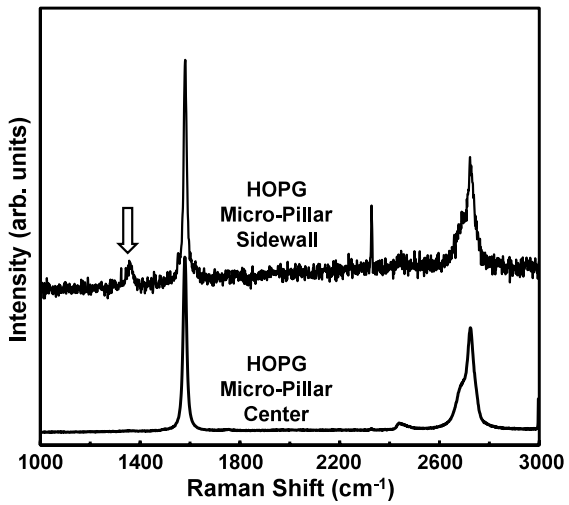

Figure 3. Micro-Raman spectra (514 nm laser) from sidewall and center of a micro-pillar from figure 2. Arrow indicates peak centered around 1350 cm^{-1}, indicative of disordered graphite in the sidewall.

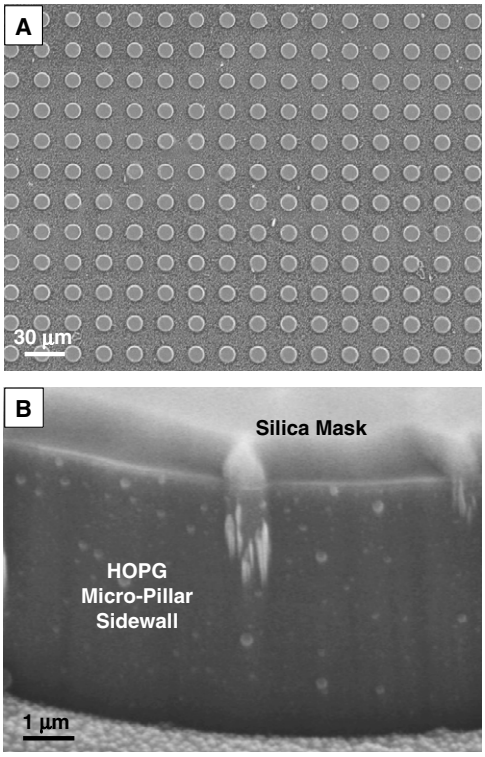

Figure 4. SEM micrographs of stiff HOPG stamps fabricated at lower ICP-RIE power showing a lack of significant sidewall deposits: (A) low magnification plan view and (B) high magnification angled view. The silica mask layer on top is still present, which does not need to be removed for flexible stamp fabrication.

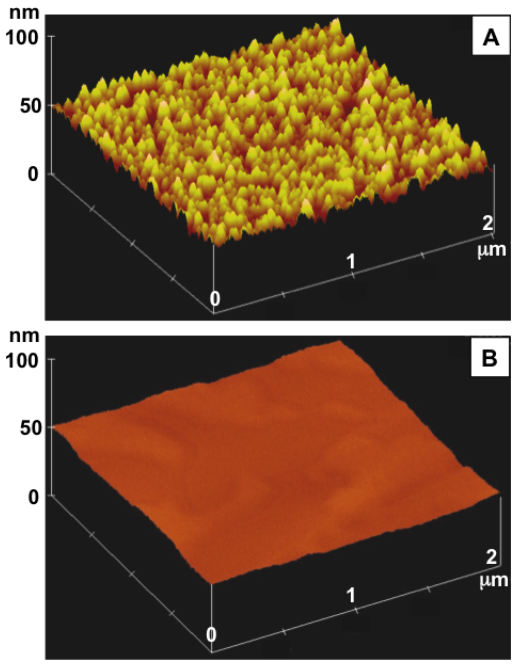

Figure 5. AFM images of the top surfaces of as-processed HOPG stamp micro-pillars: (A) stiff HOPG stamp from the previous study [20] and (B) flexible HOPG/PDMS stamp fabricated in this study. Same lateral and vertical scales, as indicated.

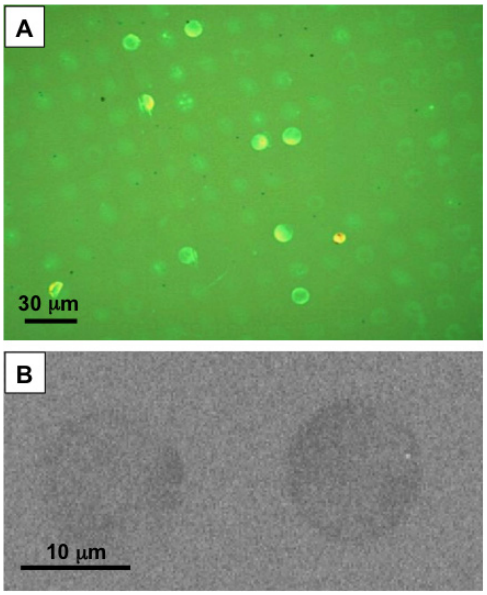

Figure 6. Images of representative stamped impression on a SiO_2 (300 nm)/Si substrate using a flexible HOPG/PDMS stamp: (A) low magnification optical and (B) higher magnification SEM.

path towards stamping of graphene or FLG using stiff HOPG stamps. The fabrication of flexible HOPG/PDMS stamps (figure 1) sidesteps this issue by embedding the rough surfaces and creating freshly cleaved, smooth HOPG surfaces that are used for stamping. Figure 5(B) is an AFM image (same scale as figure 5(A)) of the surface of a HOPG micro-pillar in the flexible HOPG/PDMS stamp showing a significantly smoother surface (<1 nm).

An optical micrograph of stamped impression on SiO_2 (300 nm)/Si substrate is shown in figure 6(A). Faithful reproduction of the micro-pillar array pattern from the flexible HOPG/PDMS stamp onto the substrate over a large area can be seen in figure 6(A). Overall, the uniformity of the impressions is significantly improved compared to stamping

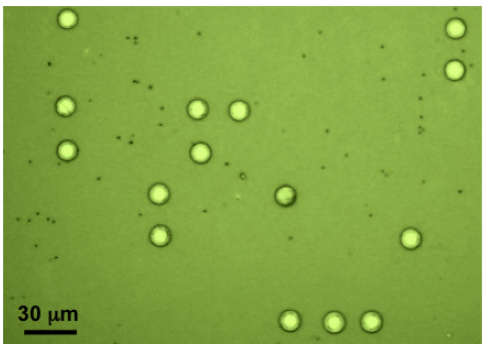

Figure 7. Low magnification optical image of a typical stamped impression on a SiO_2 (300 nm)/Si substrate using a stiff HOPG stamp.

by stiff HOPG stamps as shown in figure 7. Figure 6(B) is a higher-magnification SEM image showing two impressions of single-layer graphene. However, there is some non-uniformity in the contrast in figure 6(A), where the bright contrast in some of the impressions is due to the higher number of graphene layers present in those impressions.

Figure 8 shows examples of micro-Raman spectra obtained from five different stamped impression circles. These spectra reveal the presence of single-layer graphene (SLG), bi-layer graphene (BLG) and few-layer graphene (FLG). The SLG spectra are characterized by a sharp, symmetric 2D-band peak and a G-band peak of lower intensity [31]. Defect D- and D′-band peaks are also observed, which is typical of graphene on SiO_2 (300 nm)/Si [31]. The BLG spectra are characterized by slight broadening and blueshift of the 2D band and higher intensity of the G-band peak. The FLG spectrum shows blueshifted, asymmetric 2D band and a significantly stronger G-band peak. The number of graphene layers from that spectrum could not be determined accurately. Stamped impression circles with different numbers of graphene layers (3, 4, 5, . . .) are also present but they are not shown here.

While smoother HOPG micro-pillar stamp surfaces (figure 5(B)) and the elimination of constraining sidewall deposits on the micro-pillars (figure 4(B)) benefit the stamping process, the uniformity of stamping observed in figure 6(A) can be attributed to the low elastic modulus of the flexible HOPG/PDMS stamps, compared to a stiff HOPG stamp (figure 7). First consider the case of the stiff HOPG stamp, which has a compressive *c*-axis elastic modulus of ∼35 GPa [32]. It is known that the heights of all the micro-pillars are never exactly the same, and there is bound to be slight misalignment between the stamping surface and the substrate during stamping. This combined with the very high elastic modulus of stiff HOPG stamp can lead to individual micro-pillars experiencing vastly different stamping forces. Since the number of graphene layers stamped depends on the stamping force, the use of stiff HOPG stamps results in highly non-uniform stamping [20]. In contrast, in the case of the flexible HOPG/PDMS stamp the elastic modulus of the PDMS matrix is only ∼1 MPa [33]. The nearly 4.5 orders of magnitude lower elastic modulus of the PDMS

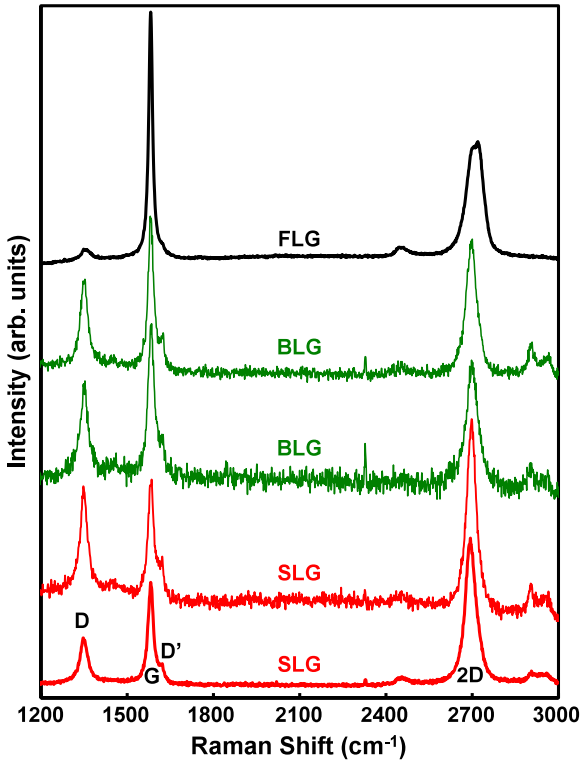

Figure 8. Raman spectra (514 nm laser) from different regions of stamped impressions in figure 6 showing the presence of SLG, BLG and FLG. The 2D, G, D and D′ bands are marked.

matrix alleviates significantly any stamping-force disparity among individual micro-pillars during stamping, resulting in the improved stamping uniformity observed. Quantitative stamping force measurements and solid mechanics analysis of the stamping process are being explored.

While the site-specific impressions on substrates produced by such a stamping process are still not all SLGs, one could perform other possible post-stamping steps with the possibility of achieving SLGs. One such step is ultrasonic agitation, which has the potential of removing the extra layers from the FLG impressions, leaving the SLG in contact with the substrate. Another step is the use of adhesive tape to remove gently peel off extra layers from the FLG impressions. This latter step is reminiscent of the original 'scotch tape' method [6], but with the advantages of: (i) the impression shapes being predetermined by the stamp and (ii) having the impression placed over large areas of the substrate site-specifically. The feasibility of these post-stamping steps is being investigated.

The results from this work show that stamping of graphene or FLG can be improved significantly by using the flexible HOPG/PDMS stamp approach relative to the stiff HOPG stamps used in the previous study [20]. Also, this approach has the potential to expand the substrate choice even further, where the ability to stamp graphene or FLG on curved and/or flexible substrates could have an impact on the burgeoning field of flexible/stretchable electronics [34, 35].

4. Conclusions

Flexible PDMS stamps containing embedded HOPG micro-pillar arrays with freshly cleaved stamping surfaces can be fabricated using simple methods. The freshly cleaved nature of the micro-pillar surfaces in the flexible HOPG/PDMS stamps, the low elastic modulus of such stamps and the elimination of sidewall deposits on the micro-pillars allow for more uniform stamping compared to the use of stiff HOPG stamps from earlier studies.

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