

# Pyrolysis-assisted Graphene Exfoliation from Graphite Particles Deposited on Photoresist Pillars

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**Abstract**—A simple and cost-effective route is described to exfoliate graphene through deposition of graphite particles on SU-8 pattern followed by the high-temperature pyrolysis process. During the pyrolysis process, the SU-8 photoresist pillars were slowly converted to desired glassy-like carbon posts and various gases were released such as carbon oxides, water vapor, methane and hydrogen. The splitting phenomenon of graphite into graphene sheets was observed. The rapid ramping rate of temperature and the released gases intercalated inside the graphite are thought to be the predominant mechanism driving the exfoliation. The introduced approach can be applied to fabricate graphene-integrated carbon MEMS for a variety of electrochemical applications.

**Index Terms** – graphene, C-MEMS, pyrolysis, exfoliation

## I. INTRODUCTION

ELEMENTAL carbon in its chemical allotropes occurs in a great variety of forms such as diamond, graphite, graphene, amorphous carbon, fullerenes and carbon nanotubes (CNTs) [1-3]. Those structural and functional carbon related materials have shown remarkable differences in properties and hence potential applications [4-7]. Among them, graphene with superior performance continues to be a hot research area since the extremely strong and thin carbon material was discovered in 2004 [8-13].

Just one atom thick, the two-dimensional (2D) honeycomb-shaped material has several remarkable properties combining mechanical toughness with superior electrical and thermal conductivity [13-15]. Those properties make graphene very promising in various applications such as field effect transistors, lithium ion batteries, hydrogen storage, molecular sensors and reinforcing fillers in high performance polymer composites [10, 11, 14]. There are several methods for produce individual graphene sheets. Chemical vapor deposition (CVD) [16], mechanical exfoliation [17] and epitaxial growth [18] are generally used to produce graphene sheets. However, the synthesis of large amount of graphene and its transfer into functional structures still remain challenging [11, 14]. Recently, graphene has been

synthesized from thermal exfoliation in which, graphite oxide as starting materials readily exfoliates by the expansion of CO<sub>2</sub> evolved into the interstices between the graphene sheets during rapid heating [19].

In this study, we report our efforts to produce graphene through thermal exfoliation using a C-MEMS process together with the deposition of graphite particles. The fabrication process mainly includes photolithography, deposition of graphite film and pyrolysis. Splitting graphite into graphene sheets happens on the photoresist pillars through controlled pyrolysis process. During the pyrolysis process, rapid heating and intercalated recursive gases released by the carbonization of SU-8 splitte graphite oxide into single graphene sheets.

## II. EXPERIMENTAL DETAILS

The typical process flow we used to produce graphene is schematically shown in Fig. 1. Graphite deposited in the wafer before pyrolysis was used as the material to produce graphene. A negative photoresist, SU-8 (GM1075), was spin coated and patterned by UV photolithography and pyrolyzed into a patterned carbon structure at 1100 °C, as illustrated in Fig. 1.

### A. Photolithography

First, SU-8 photoresist was first spin-coated on cleaned silicon wafer (100) as shown in Fig. 1(a). In our typical process, the 20 μm thick SU-8 photoresist film on silicon wafer was obtained by spinning at 500 rpm for 50 s and at 2000 rpm for 100 s. The coated wafer was then soft baked at 40 °C for 30 min and 120 °C for 2 min. Exposure was performed by a Karl Suss MA6 mask aligner with the light intensity of 5 mW/cm<sup>2</sup> for 100 s. The exposed photoresist sample was then post baked for 30 min at 95 °C. After development, the patterned 3D photoresist microstructure was obtained as shown in Fig. 1 (b).

### B. Deposition of graphite particles

In this experiment, a thin layer (nanoscale order) of graphite particle was sputtered on the pattern surface by magnetron sputtering using graphite target in Ar discharge gas (10<sup>-3</sup> Pa) as shown in Fig. 1(c).

### C. Pyrolysis

After the deposition, the sample was then put into an alumina tube furnace to carbonize the photoresist during the pyrolysis process as shown in Fig. 1(d). In this process, the photoresist was baked in two steps. Fig. 1(e) shows the

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typical temperature control curve. Samples were baked in a  $N_2$  atmosphere in which  $N_2$  gas flow was introduced (2000 sccm) at 300 °C maintained for about 20 min after the furnace was heated up to 300 °C at the heating rate as about 15 °C/min. And then the temperature was heated up to 1100 °C at the same heating rate in a  $N_2$  atmosphere. At this point the  $N_2$  gas was shut off and forming gas (5%  $H_2$  in  $N_2$ ) was introduced (2000sccm). After maintained at 1100 °C in forming gas (5%  $H_2$  in  $N_2$ ) for 1 hour, the heater was turned off and the sample was naturally cooled down in  $N_2$  atmosphere to room temperature.

#### D. Testing methods

Scanning electron microscopy (SEM) analysis was performed with a FEI QUANTA microscope with an acceleration voltage of 15 kV. The transmission electron microscopy (TEM) was carried on a FEI TECHNAI T20 microscope operated at 200 kV to investigate the layered structure. Raman spectroscopy measurement was performed on HORIBA Jobin Yvon LabRAM Spectrometer with an Ar ion laser of wavelength of 514 nm, at a magnification of 100× and a CCD camera detector.

### III. RESULTS AND DISCUSSION

#### A. Morphologies and structures

Fig. 2 shows the typical SEM images of graphene-integrated carbon post obtained after pyrolysis at high temperature of 1100 °C, where a thin graphite layer was sputtered before pyrolysis. The microelectrode array with the height of around 7  $\mu m$  and the diameter of around 30  $\mu m$  is shown in Fig. 2(a). It is obvious that the Si substrate and carbon post are equipped with graphene flakes as shown in Fig. 2(a) and Fig. 2(b) with magnified view. The graphene sheets are observed as very thin and semitransparent and appeared to be curled. The graphene layer shows many irregularities and is not continuous. Because of the wrinkling and buckling of the sheets, only a small fraction of each sheet is in contact with the substrate.

#### B. Confirm information

To demonstrate that the majority of our material consists of single layers of functionalized graphene, we analyzed TEM images [21]. Fig. 3(a) shows the low resolution TEM image of the graphene layer. High resolution TEM image of graphene layers is shown in Fig. 3(b). It indicates that the layers of graphene are around six to nine layers. A measurement of graphene thickness shown by the length of a dark line is around 2.2 nm for the graphene layers of six to seven layers. It indicates that thickness of single layer is about 0.34 nm which is just the thickness of single graphene layer.

The existence of graphene exfoliated from graphite was also confirmed by the Raman spectra. Raman spectroscopy provides a quick and facile structural and quality characterization of the produced material [23]. Fig. 4 shows Raman spectra, collected from the graphene sample shown in Fig. 2(a) at room temperature. After transfer the graphene to a

silicon substrate with a 300 nm thick  $SiO_2$  layer, Raman measurements were applied to explore the chemical information. A 2.4 eV laser beam was focused to a spot of <1  $\mu m$  in diameter and the total laser exiting power was 10 mW. From the Raman spectrum in Fig. 3, G band at  $\sim 1580 cm^{-1}$  was observed, which denotes the symmetry-allowed graphite band (bond stretching between pairs of  $sp^2$  carbon atoms). The important feature appearing at approximately  $\sim 2700 cm^{-1}$  is usually called the 2D band in the graphite literature and is found in all  $sp^2$  carbon materials. 2D peak is used to confirm the presence of graphene and this second order Raman spectrum is due to a double resonance process involving two phonons of opposite wave vector. A symmetric 2D band centered at  $\sim 2680 cm^{-1}$  with a full width at half maximum of  $\sim 33 cm^{-1}$  shows typical features of graphene. There is a blue shift in the G band position when compared to bulk graphite ( $1581 cm^{-1}$ ) and this shift is attributed to the formation of bulk graphite crystal to graphene sheet. G and 2D band are both signals from graphene lattice and their intensity are correlated. In this sample, the high intensity of G and 2D bands could be resulted from the spatially non-uniform adhesion. The adhesion between graphene and a substrate can affect the intensity of Raman spectra. Disorder-induced D band (due to breathing modes of  $sp^2$  carbon atoms) is also observed around  $1350 cm^{-1}$ . D band is always correlated to the quality of the graphene and it intends to show a noisy feature. The relatively high D band in the spectra indicates low crystalline quality of the product.

#### C. Mechanism discussion

In pyrolysis process, the graphite deposited sample is charged into a quartz tube and purged with nitrogen. During the pyrolysis process, the SU-8 photoresist pillars were slowly converted to desired glassy-like carbon posts and various gases were released such as carbon oxides, water vapor, methane and hydrogen. Rapid heating to 1100 °C and maintaining for 1 hour splits the graphite into graphene sheets through evolution of all kinds of gases such as carbon oxides, water vapor, methane and hydrogen from carbonization of SU-8 photoresist involving epoxy and hydroxy sites. The rapid expansion of intercalated gases were thought to be responsible for the exfoliation process. In addition, the gases such as methane and hydrogen may play a deoxidizer in the exfoliation process.

### IV. CONCLUSION

In summary, graphene with less than 10 layers was produced through thermal exfoliation of graphite by a high-temperature pyrolysis process during the fabrication of glassy-like carbon microelectrode array. SEM and TEM images reveal morphologies and structures of graphene we produced and Raman spectra confirms the existence of graphene. The obtained graphene was integrated simultaneously onto the carbon microelectrodes, which provides a new structure platform for the development of various high performance electrochemical devices such as super-capacitors and sensors.

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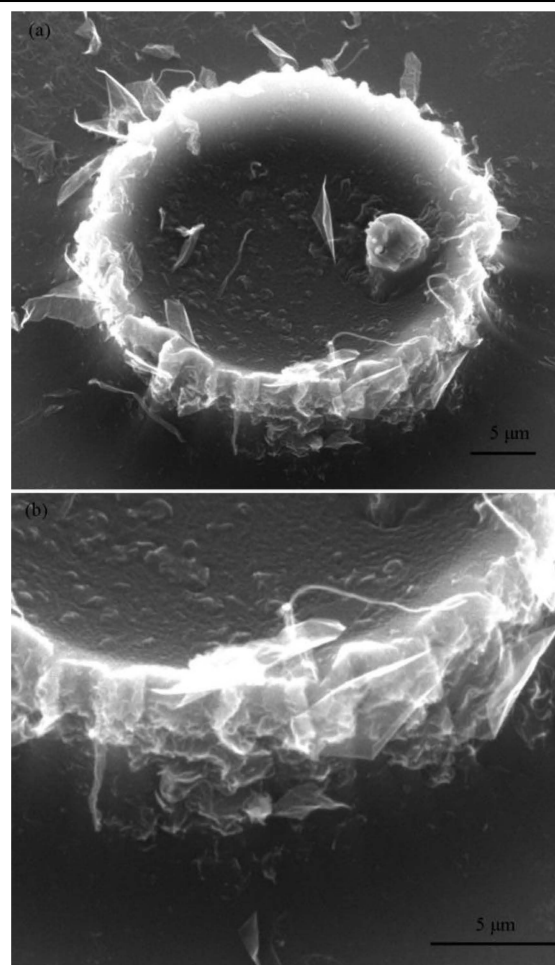
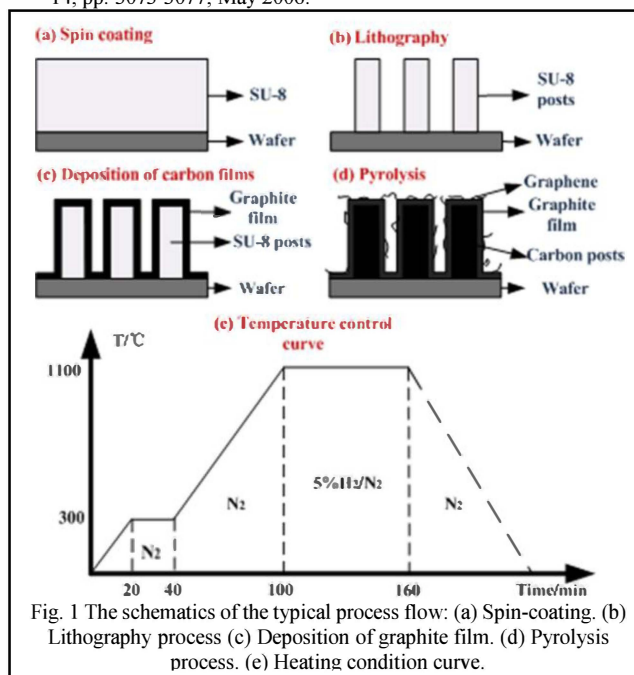


Fig. 2 (a) SEM image of graphene produced through thermal exfoliation of graphite by a high-temperature pyrolysis process on the photoresist-derived carbon post. (b) Magnified SEM image of (a).

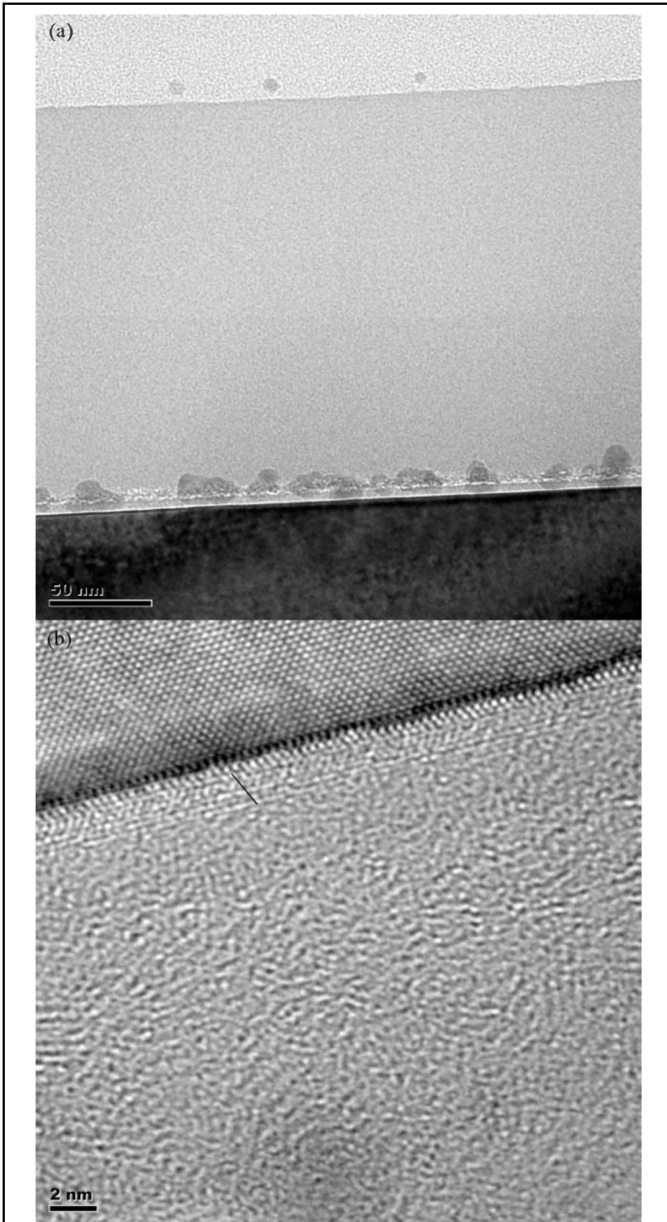


Fig. 3 TEM images showing individual thermally exfoliated graphene: (a) Low resolution TEM image of graphene layers. (b) High resolution TEM image of graphene layers. The length of the dark line is around 2.2 nm for the graphene layers of six to seven layers which indicates the thickness of single layer is about 0.34 nm.

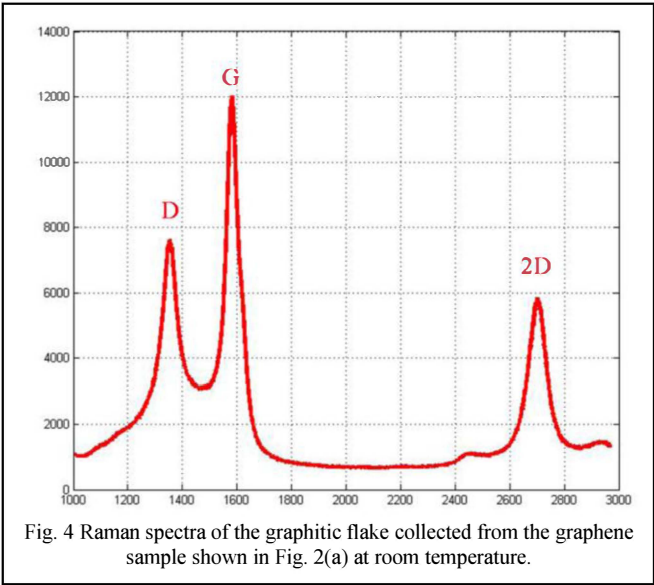


Fig. 4 Raman spectra of the graphitic flake collected from the graphene sample shown in Fig. 2(a) at room temperature.