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Wet Transfer Process for MEMS Freestanding PMMA/Graphene Membrane Development

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ABSTRACT

Process of transferring poly (methyl methacrylate) (PMMA)/Graphene layer to form a freestanding membrane requires a proper method to ensure that the membrane is well suspended with high graphene coverage. This paper demonstrates a method for transferring PMMA/Graphene onto an etched silicon cavity, which forms freely suspended graphene using ferric chloride ($FeCl_3$) solution. The characterisation was performed with an optical microscope and Raman spectroscopy to examine the quality of the transferred PMMA/Graphene membrane. Wet transfer process by $FeCl_3$ etchant was successfully applied to develop a freestanding PMMA/Graphene membrane on a silicon etch cavity. From the study, 0.5M concentration of $FeCl_3$ etchant is more suitable to be applied compared to 1.0 M in order to form a freestanding PMMA / Graphene membrane.

Keywords: Freestanding PMMA/Graphene, Ferric Chloride Etchant, PMMA/Graphene Transfer, PMMA/Graphene Membrane.

1. INTRODUCTION

As graphene is one of the thinnest elastic membrane [1], it is gaining more attention to be used as a membrane. Monolayer graphene becomes one of the strongest materials with a 42 N/m of intrinsic strength [2]. Fabricating a freestanding membrane of the graphene layer is not an easy task, since it is fragile to handle due to a very thin structure [1]. A wet transfer process is one of the commonly used to transfer chemical vapour deposition (CVD) graphene [3]. However, the transfer of the CVD graphene to form a freestanding PMMA/graphene membrane is extremely sensitive and can influence ultimate performance. Inaccurate physicality of this technique and inappropriate etchant's concentration may lead to significant damage such as tears, wrinkles and ruptured [4][5].

Chemical solvents such as ferric chloride ($FeCl_3$), ammonium persulfate ($(NH_4)_2S_2O_8$), and ferric nitrate ($Fe(NO_3)_3$) are the most commonly used etchant to etch the copper foils of CVD graphene [3]. Basically, most wet chemistry transfer methods are conceptually the same. They involve etching the metal substrate to free graphene and then scooping the graphene using the target substrate. Improvements might include providing a support layer for the graphene before etching to prevent tearing of the graphene sheet which is a crucial challenge in transferring graphene film.

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Polymer poly(methyl methacrylate) (PMMA) is the most commonly used supporting layer which is coated on the CVD graphene's surface before the wet transfer process [6]. The PMMA's function is to hold the graphene and prevent it from sinking in the etchant. Some researchers conducted studies on suspended graphene membrane [7]–[12] using various types of the transfer method.

In this paper, the suspended single graphene membrane on silicon nitride/silicon cavity (Si_3N_4/Si) was fabricated using a $FeCl_3$ etching transfer method. Raman spectroscope was used to investigate the characteristics of graphene transferred. The square cavity of 1.0 mm^2 area was fabricated by wet potassium hydroxide (KOH) etching. Figure 1 shows a MEMS freestanding of PMMA/Graphene. This suspended PMMA/graphene membrane is useful for a high sensitivity pressure sensor as the graphene is an elastic 2D material with highly conductive, high elastic, and high tensile strength [13][14] which makes it a suitable choice for the application.

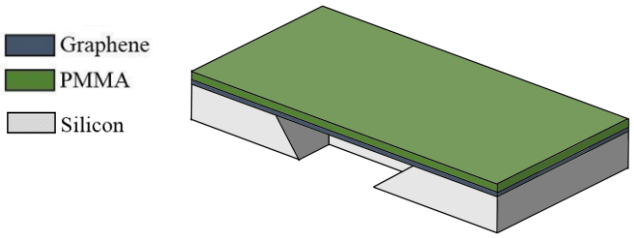

Figure 1. MEMS freestanding of PMMA/Graphene membrane.

2. MATERIALS AND METHODS

The silicon cavity was fabricated by potassium hydroxide (KOH) wet etching as described in the previous research [15][16][17]. Chemical vapour deposition (CVD) monolayer graphene films were purchased from Universitywafer, Inc. Before the graphene film was transferred to the silicon cavity, the top graphene was coated with PMMA at 3000 rpm for 60 s. The PMMA function is to hold the graphene film and to avoid the graphene from sinking in the $FeCl_3$ solution. Next, the sample was placed on the hot plate at 110˚C for 5 min. Then, the sample was floated on $FeCl_3$ solution with two different concentrations of 0.5 M and 1.0 M. A 0.5M $FeCl_3$ solution was prepared by adding 2.4 g $FeCl_3$ powder to 30 ml distilled (DI) water, while a 1.0 M was prepared by adding 3.2 g $FeCl_3$ powder to 20 ml DI water. Sample was floated on a 0.5 M and 1M $FeCl_3$ solution for 3 hours and 1.5 hours, respectively. After all copper is fully etched, the graphene film was transferred to the clean DI water in order to remove $FeCl_3$ residues. Finally, the floating PMMA/Graphene layer was scooped from the DI water container with silicon cavity substrate. As soon as the PMMA/Graphene landed on the substrate, the samples were baked at 100°C for 20 min. Figure 2 shows the monolayer graphene transferring process and Figure 3 shows the etching process of CVD graphene using $FeCl_3$ etchant.

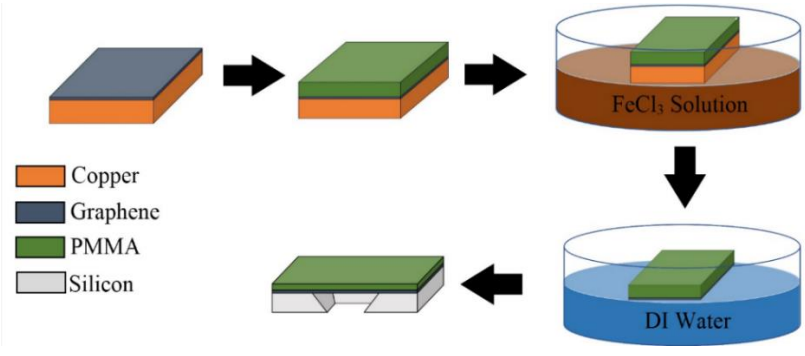

Figure 2. PMMA/Graphene film wet transferring process.

Figure 3. Etching process of CVD graphene using $Fecl_3$ solution.

3. RESULTS AND DISCUSSION

3.1 Raman Spectrum of PMMA/Graphene

Raman spectroscopy is a commonly applied technique for graphene films characterisation. Conceptually, Raman spectroscopy detects the inelastic Raman scattering of monochromatic light. The laser wavelength used for this sample was 532 nm with power 10 mW. For a perfect, detect-free graphene, Raman exhibits signal at peaks D, G and 2D at Raman shift of (1350/cm), (1580/cm) and (2690/cm), respectively [4]. Figure 4 shows the Raman spectrum of CVD graphene on copper (before the transfer process) and suspended PMMA/Graphene membrane (after the transfer process). From Figure 4, the peak at 2D band was much greater than the peak at G band for the suspended PMMA/Graphene membrane. This indicates that the graphene was prominent in the composition of PMMA/Graphene layer. Meanwhile, for the graphene on copper (before the transfer process), there is not much difference between the 2D and G bands. This might be due to the copper substrate which also affects the Raman reading. Also, from Figure 4, the peak intensity of the D band was very low, testifying its high-quality graphene. Table 1 shows the Raman peak values of G and 2D bands for the graphene on copper and the suspended PMMA/Graphene membrane. The intensity ratio of peak 2D and G identifies the number of graphene layer. If the peak ratio of I_{2D}/I_G is in between 2–3, it is indicated that the graphene is monolayer graphene. While, if the peak ratio in the range $2 > I_{2D}/I_G > 1$, is for bilayer graphene and for $I_{2D}/I_G < 1$ indicates the multilayer graphene [18]. From Table 1, the ratio of I_{2D}/I_G for the suspended PMMA/Graphene was 2.05 indicating that this sample consists of monolayer graphene.

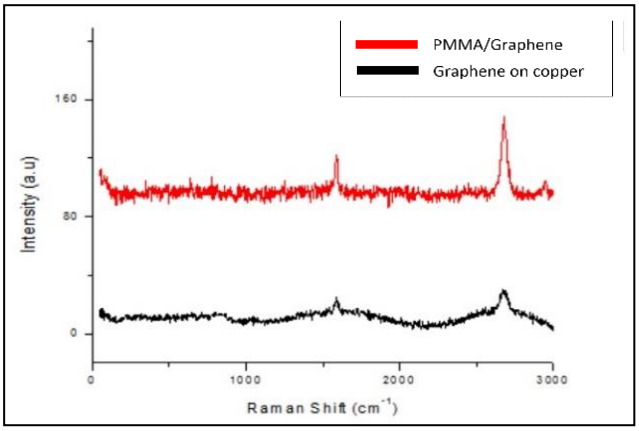

Figure 4. Raman shift of PMMA/Graphene membrane and CVD graphene on copper

Table 1 Raman Peak at G and 2D band for CVD Graphene

Test sample	Intensity at Peak G	Intensity at Peak 2D	I_{2D}/I_G
Graphene on Copper	20.57 (at 1592 cm^{-1})	27.97 (at 2677 cm^{-1})	1.36
Suspended PMMA/Graphene	23.28 (at 1583 cm^{-1})	47.68 (at 2680 cm^{-1})	2.05

3.2 Microscopy Image of Suspended PMMA/Graphene

Figure 5 shows the optical microscope's image of the suspended PMMA/Graphene on the etched silicon cavity by using 0.5 M $FeCl_3$ concentration. From Figure 5, the images of the microscope show a transferred PMMA/Graphene was well suspended without defects (tears and cracks). Figure 6 shows the close-up picture of the PMMA/Graphene membrane. From Figure 6, it shows that the strong van der walls force holds the PMMA/Graphene perfectly on the Si_3N_4 layer. Figure 7 shows the image optical microscope of the suspended graphene on the etched silicon cavity using 1.0 M $FeCl_3$ concentration. From Figure 7, the microscope image shows some defects of the PMMA/graphene membrane. The PMMA/Graphene membrane was torn and cracked might be due to the high $FeCl_3$ concentration (1.0M) and rough handling in the transferring process.

From out of ten PMMA/Graphene membrane samples, seven of them were tears and were not successful to suspend on the silicon cavity when using 1.0M $FeCl_3$ solution. Meanwhile, all ten samples of PMMA/Graphene membrane were successfully transferred and well suspended on silicon cavity without tears when 0.5M $FeCl_3$ solution was used. Hence, a low etchant concentration of etchant (0.5M) of the ferric chloride is more appropriate to apply for the development of freestanding PMMA/Graphene membrane. This is in agreement with research conducted by T. Ondarçuhu et al. [19]. In their research, they stated that a low etchant concentration (0.5M) was used to promote a slow, steady etch rate (<500 nm/h) necessary to prevent the fragmentation of the copper foil into sub-millimeter grains, which may tear and sink the floating graphene layer [19]. Apart from the etchant concentration factor, proper handling technique is also one of the factors that influence the efficiency of PMMA/Graphene layer to be transferred as a freestanding membrane on silicon cavity.

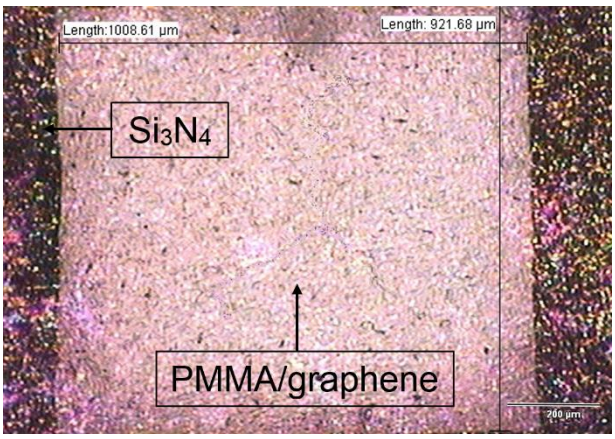

Figure 5. PMMA/Graphene membrane transferred by using 0.5 M FeCl3.

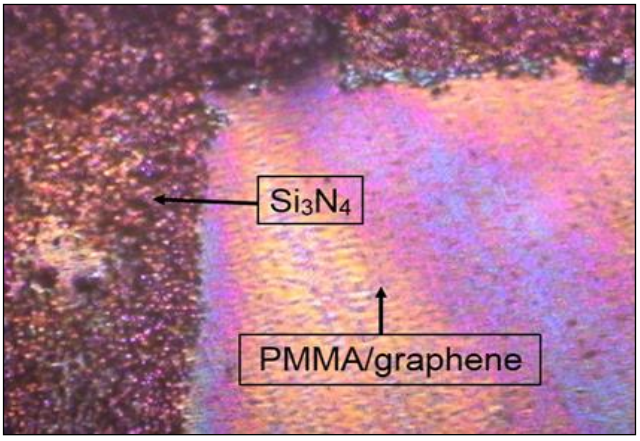

Figure 6. Close up image of PMMA/Graphene membrane transferred by using 0.5 M $FeCl_3$.

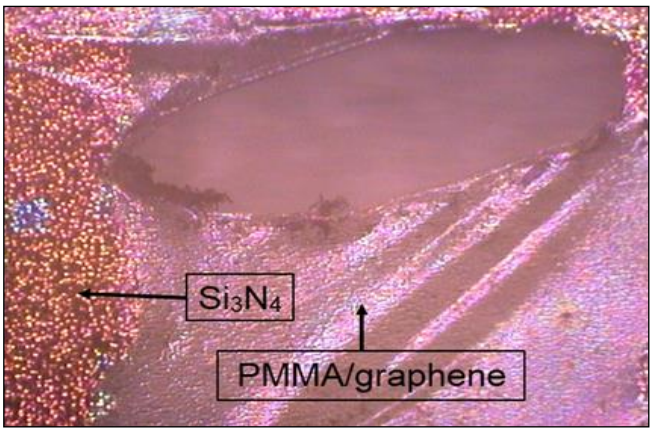

Figure 7. The tears of PMMA/Graphene membrane transferred by using 1.0M $FeCl_3$.

4. CONCLUSION

In this paper, a simple method to transfer PMMA/Graphene layer onto an etched silicon cavity using $FeCl_3$ etchant was discussed. The Raman spectroscopy and microscope analysis indicate that the transferred process was successfully demonstrated to realise a suspended PMMA/Graphene membrane. A low etchant concentration (0.5M) of the ferric chloride is suitable to be applied compared to high concentration (1.0M) due to the more stable rate of etching in order to deliberately stimulate a stable rate of etching. A proper handling technique also important to be applied in transferring PMMA/Graphene layer to be transferred as a freestanding membrane on silicon cavity. The PMMA layer was coated on the graphene surface before the transfer process to prevent the floating graphene layer from sinking. The successful freestanding PMMA/Graphene membrane opens up the possibility of applications for membrane based MEMS application.

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