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STUDY OF TRANSFER FREE GRAPHENE FORMATION

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ABSTRACT

The method of using CVD or Chemical Vapor Deposition [1-2] in the formation of graphene synthesis has recently progress quite a lot. The material shows exceptional electronic properties and also characterizes suspended graphene resonators. But the fabrication of this material involves the transfer of graphene from its copper catalyst to the required substrate using wet chemical etching method. This transfer procedure introduces metal residues, wrinkles and holes in the graphene. These issues are necessary to be dealt with and hence provide the need for a transfer-free fabrication method for suspended graphene, using CVD method. In this paper we fabricate suspended graphene without the use for any transfer technique. It can be grown both using a catalyst like thin copper films, and non-catalyst like directly on a dielectric substrate. Such a fabrication procedure includes the growth of graphene by CVD followed by the deposition of Au/Ti electrodes defined by e-beam lithography (ebl). Later on there will be graphene etching using oxygen plasma. The structures in the end are made suspended by chemically etching the substrate layer at the top and later on dried.

Key words: CVD, Graphene, Chemical etching, transfer process, Cu thin film.

I. INTRODUCTION

Graphene is a thin layer of carbon atoms which has a hexagonal lattice structure shown in Figure 1. Graphene does not exist in nature. In order to use the properties of graphene we need to fabricate it. It has shown very good electrical, optical and mechanical properties. Comparing with any other materials graphene has higher current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance and super hydrophobicity [3]. Graphene is very stable at room temperature. Researcher believes that silicon based technology will be replaced by graphene in future because of its outstanding properties. It was found from one experiment that graphene has electron mobility of 15,000 $cm^2 V^{-1} s^{-1}$ and which is higher than any other material exists. We are interested on Graphene because we want to make a new gas sensor and we want to increase its detection level by using graphene. Graphene has very high electron mobility which is very promising for such application.

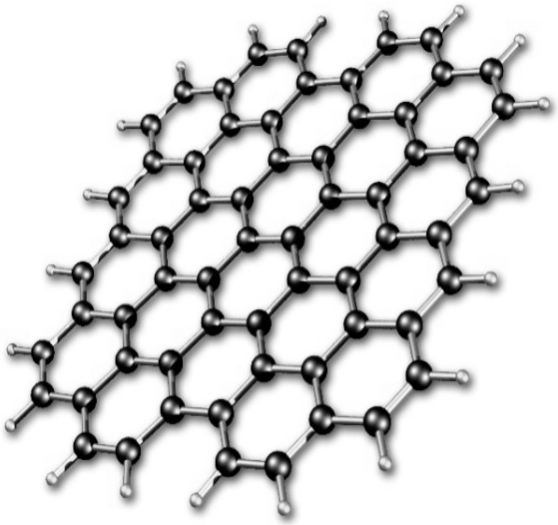

Fig. 1. Graphene, honeycomb-like lattice structure

II. PROCESS DIFFICULTIES

Graphene can be fabricated from carbon but fabricating graphene is difficult. Lot of problems encountered during research. Those problems like as selecting right catalyst, thickness of the catalyst and the accurate temperature for fabricating large scale good quality graphene will be discussed below.

Selecting a catalyst was a problem. Cu (copper) was chosen as a catalyst because Copper can accelerate the graphitization but only allows the carbon atoms to have a monolayer on the top of it. Carbon solubility in copper is very small. As a result when carbon atoms hit the copper surface they form a hexagonal shape which is graphene and when the surface area of copper is completely covered, the reaction stops. Also Cu is cheap and it is available.

Fabricating graphene on a large scale is a big problem. There are lots of techniques of fabricating graphene in a lager scale. One good technique for fabricating high-quality graphene in large scale is high temperature decomposition of SiC (silicon carbide) where Si (silicon) is evaporated, while leaving free carbon atoms behind that subsequently form graphene layers at the surface [4]. However, this technique is expensive and is not suitable for graphene transfer onto other substrates.

Chemical vapor deposition (CVD) was used to grow graphene on Cu substrate because it is very cheap and available technique. Large are and good quality of graphene can be achieved by CVD. CVD is a process which involves chemical reaction. In this process molecules are heated and transformed to gaseous form which is called precursor. At the initial phase of this process a substrate is placed into a chamber for coating. The gas molecules react with the heated substrate, as they come closer, and decompose to a solid material in the form of a thin film or powder on the surface of the substrate.

However, the main challenge is not only to grow high quality large area graphene layer but also a reliable and scalable transfer onto other substrates.

In this paper, we chose to use Cu thin film for graphene deposition because this will allow us to get rid of transfer-process by locally removing the substrate, causing us to have suspended graphene based devices [5]. But before making suspended graphene, it is very important to know the proper thickness of Cu substrate and the temperature. Traditional transfer-process is very useful to investigate the thickness and the correct temperature which could be used for future suspended graphene fabrication. The transfer-process is more elaborately discussed in next section.

III. TRANSFER METHOD

A. Step 1

Copolymer MMA/MAA (Methyl methacrylate**)** was spin coated on top of graphene to mechanically support the graphene after the Cu was etched away.

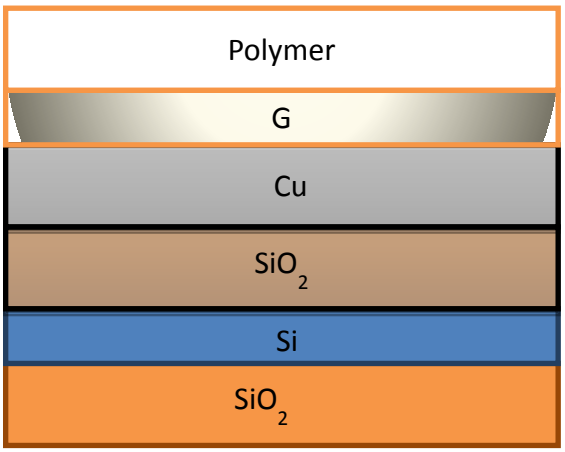

Fig. 2. Polymer coating

B. Step 2

Edges were scratched carefully to allow etchant to interact with the Cu and hence etch it away. Diluted HCL (hydrochloric acid) in water, with compound ratio of 1:7, and 3 drops of H_2O_2 (hydrogen per oxide) were added later to accelerate the reaction. This total volume was used as etchant.

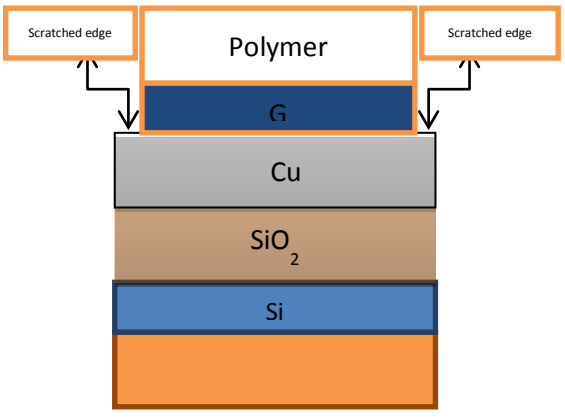

Fig. 3. Scratched edges

C. Step 3

The sample was kept in the etchant for a night until Cu was fully etched away. An adhesive tape was also attached to the polymer beforehand graphene would be suspended after Cu was etched away as shown in Figure 4.

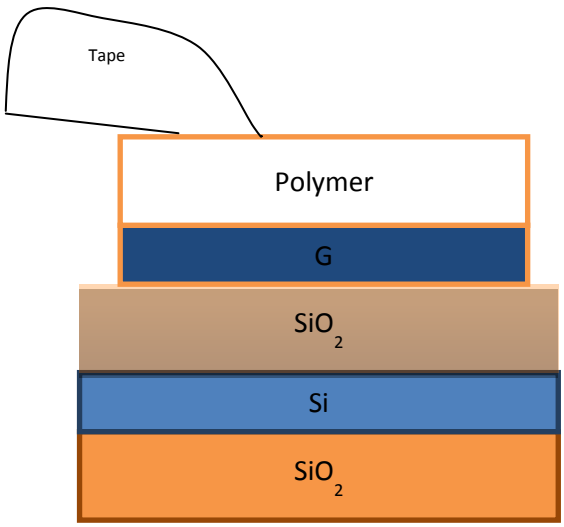

Fig. 4. Cu is etched and an adhesive tape is attached

D. Step 4

Once the Cu was completely removed, graphene would become transferred resist by aligning a substrate beneath them, and then slowly removing the water. The substrate used was oxidized silicon with 300 nm of oxide; thickness was chosen to give optimum optical contrast.

Graphene with polymer was placed carefully on the top of another substrate. Acetone, IPA (isopropyl alcohol) was used sequentially to remove polymer layer and blow dry in N_2 (nitrogen).

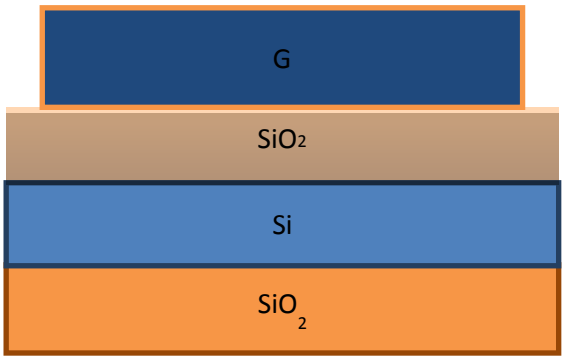

Fig. 5. Transferred Graphene

IV. EVALUATION

We have done several trials to find out the best procedure for growing graphene on Cu films. We found out that the most important parameters included in achieving that recipe are temperature, Cu film thickness and transfer condition. From our trials the best achieved composition to grow graphene involves - 100 nm Cu annealed in 70°C for five minutes, followed by 1 minute growth in 2 sccm H_2, 5 sccm diluted methane in argon, and 1 sccm argon. It is then transferred using MMA as resists, HF and HCL as the etchant, and acetone as treatment. Post annealing included heating at 50°C for 1 minute in H_2 and argon atmosphere.

During investigating samples produced in this work, scanning electron microscopy (SEM) was used to study the surface morphology. SEM is a machine where focused high energy electrons are used to form an image. Image is attained by detecting the backscattered or secondary electrons from the surface of the sample. Generally SEM can be compared with microscope because both techniques are used to observe the sample but the working principle is different.

In this experiment the SEM characterization technique is used because it is a quick and convenient technique. An image taken by SEM has been given below along with the discussion.

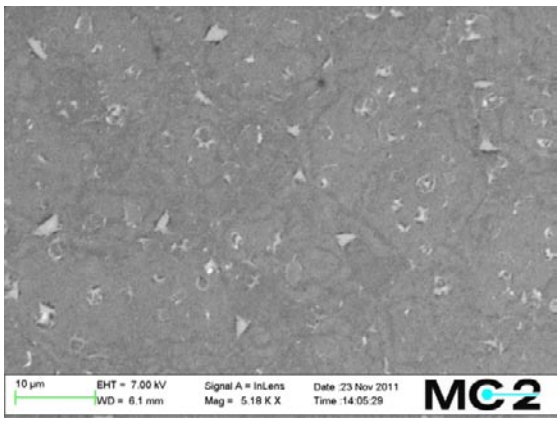

Fig. 6. Graphene, etching solution as HF and then HCl later, PMMA as resist used and treated with acetone

Figure 6 shows the graphene grown using this recipe. It exhibits good quality of the graphene covering quite large area. Figure 7 shows bad quality graphene which was grown by using different method.

In Figure 7, a lot of cracks and small grain boundaries are clearly visible and also it is not uniform at all. Our goal was to have larger grain boundaries, less cracks and it was achieved for the recipe used to grow graphene for Figure 6. By using multimeter, resistance of graphene was measured though it was very rough measurement but it offers a quick estimate of the true sheet resistance and also it does not require fabricating devices. We got several kilo ohms for the best recipe (Figure 6) and got several mega ohoms for the worst (Figure 7) case which also proves that the quality has been improved a lot. Now we are working with suspended graphene using the method discussed above.

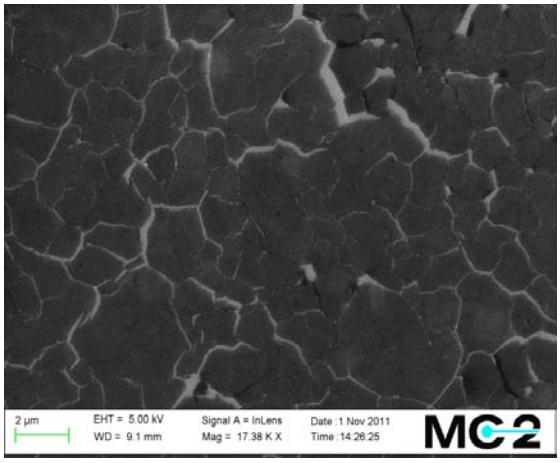

Fig.7. Graphene grown on 300 nm Cu thin film.

IV. CONCLUSION

We have optimized the growth of Graphene on Cu thin films and the thickness of Cu thin film is 100 nm which requires annealing in 50°C for five minutes, which increases the grain domain of Cu and subsequently the domain of graphene too, and have to be continued by 1 minutes growth in 2sccm H_2, 5sccm diluted methane in argon, and 1sccm argon. We have also optimized the transfer process and the condition is to transfer using PMMA as resists and HF and HCl as the etchant and acetone treatment. After that, post annealing at 50^oC for 1 minute in H_2 and argon atmosphere is also important.

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