



Synthesis and transfer of large area graphene without support layer

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Graphene is a 2-dimensional flat sheet of carbon species confined into a honeycomb structure exhibits unique optical, electrical, thermal and mechanical properties. Graphene due to its fascinating properties finds application in the area of flexible electronics, nano-devices, health care, defence, photovoltaics and many others. In this work, graphene is grown on a copper foil using thermal chemical vapor deposition (CVD) at 1000 °C. Methane is used as a carbon source and hydrogen is supplied for the reduction of copper catalyst. Raman spectroscopy along with surface morphology and surface topology confirms the formation of graphene layer. Further, the fabricated graphene is directly transferred to glass substrate without any support layer. SEM and Raman confirms the defect-free transfer of graphene. Moreover, transferred graphene sheet shows high transparency along with hydrophobic nature with a contact angle of 93°.

Keywords: 2D, Graphene, CVD, Transfer, Copper

1 Introduction

If the 20th century is of plastics then 21st century can be of graphene¹. Due to its unique mechanical, optical, thermal and electrical properties it has a huge potential to be used in almost every nanoscale application and nanodevices². In 2004 graphene is first fabricated using mechanical exfoliation (scotch-tape method)¹. However, this method to produce graphene is highly time consuming. Moreover the yield and quality of graphene produced using this method is inadequate to be used for optical or electronic devices.

Recently, to overcome these issues chemical vapor deposition (CVD) technique is reported to grow large area and high-quality mono and multi-layer graphene^{3,4}. Moreover, among various transition metals used as a catalyst to grow graphene; copper (Cu) is the most popular due to its ease in availability⁵. However, in CVD graphene is fabricated only on metals but in real applications a direct growth of graphene on most of the electronic devices is highly required but still not possible to perform⁶. Therefore, for all the electronic devices graphene is grown in CVD on metals such as Cu and is then transferred to the substrate of interest⁷. There are several methods used to transfer graphene from metal to other substrates using a support layer of polymer such as polydimethylsiloxane, polycarbonate or Poly (methyl methacrylate) etc.⁷⁻⁹. These polymers are coated on graphene and after etching metal the graphene is transferred to substrate of interest while

polymer is removed using organic solvents. However, it is observed that despite proper removal of polymer from graphene surface some polymer residues stick to the graphene surface. These residue polymers drastically reduce the optical, mechanical, thermal and electrical properties of graphene^{10,11}. Consequently, alternative route to transfer graphene from metal to substrate of interest is required. In this study, a method to transfer graphene from Cu metal to glass without use of support layer is described. It is observed that the transferred transparent graphene layer is of high quality.

2 Material and characterization tools

For the growth of graphene a polished copper foil (2 X 2 cm) having a thickness of 0.5 mm was used. Gases used for the growth of graphene (argon, hydrogen and methane) were procured from Sigma-Aldrich with 99.999% purity. For copper etching, 98% crystalline FeCl₃ was purchased from Alfa Aesar.

Scanning electron microscopy (SEM) [Jeol, model 6610LV] was used to study the surface morphology of graphene sheet synthesis using thermal CVD and after transfer. Whereas the surface topology of fabricated graphene sheets and after transfer was studied using Atomic force microscopy (AFM) in tapping mode with an AFM tip radius of 5-8 nm [Bruker, USA]. Moreover energy-dispersive X-ray spectroscopy (EDS) [Bruker, X-Flash 6-30, USA] and Raman spectroscopy was performed using LabRAM HR Evolution (Horiba, Japan) on graphene samples.

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Transmission spectra was recorded using UV/Vis/NIR spectrophotometer (PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer, USA) from 300 to 2,000 nm wavelength range. Moreover contact angle study of transferred graphene was studied using contact angle analyzer [First Ten Angstroms, UK].

3 Results and Discussion

3.1 Synthesis of graphene

Before graphene growth, copper foil was cleaned by washing in acetone followed by ethanol to remove any dust and oil layer present on the copper foil. Copper foil was further placed in a mixture of 1 ml hydrofluoric and 30 ml deionised water to remove native oxide layer present. To stop growth of native oxide layer the copper foil was directly loaded in the quartz tube of thermal CVD chamber with a 350 sccm argon flow for 22 minutes at 300 °C. Further hydrogen was supplied for the reduction of copper¹²⁻¹⁴. Moreover, hydrogen plays a dual role in the graphene synthesis process. (1) The essential required surface bound carbon species (CyHx)s is formed by hydrogen acting as a cocatalyst¹². (2) Grain dimension and shape was controlled by hydrogen pressure and flowrate¹². These two roles of hydrogen are critical deciding factors regarding the nucleation and growth rate of graphene. Therefore, for better nucleation and higher growth rate of high-quality

graphene 30 sccm hydrogen is continuously supplied for 30 minutes while raising the temperature of CVD furnace to 1000 °C. For growth of grapheme, 30 sccm methane (carbon source) was supplied along with hydrogen (15 sccm) for 5 minutes. After graphene growth furnace was cool down to room temperature under inert atmosphere as shown in Fig. 1a.

Surface topology and morphology of graphene layer grown on copper foil at 1000 °C was analysed using AFM and SEM as shown in Figs. 1b and 1c. Wrinkles and flakes of grapheme ripples were observed in SEM and AFM after CVD run on the copper substrate^{15,16}. It was also found that the graphene formed on copper substrate has a flake of 2 μm as shown in Fig. 1c. Moreover, the quality and number of layers formed by the hexagonal graphene structure was analysed using Raman spectra shown in Fig. 1d. It was observed that, the graphene grown on copper substrate was having very small D band compared to the G band. This depicts that the fabricated graphene layer is of high quality with minimum defects. The ID/IG ratio of graphene formed was 0.35 with an $I2D/IG$ of more than 1 showed that the graphene formed is multilayer.

3.2 Transfer of graphene

Graphene grown on copper substrate was transferred to glass slide using process described in Fig. 2. For transferring of graphene, first graphene was etched from

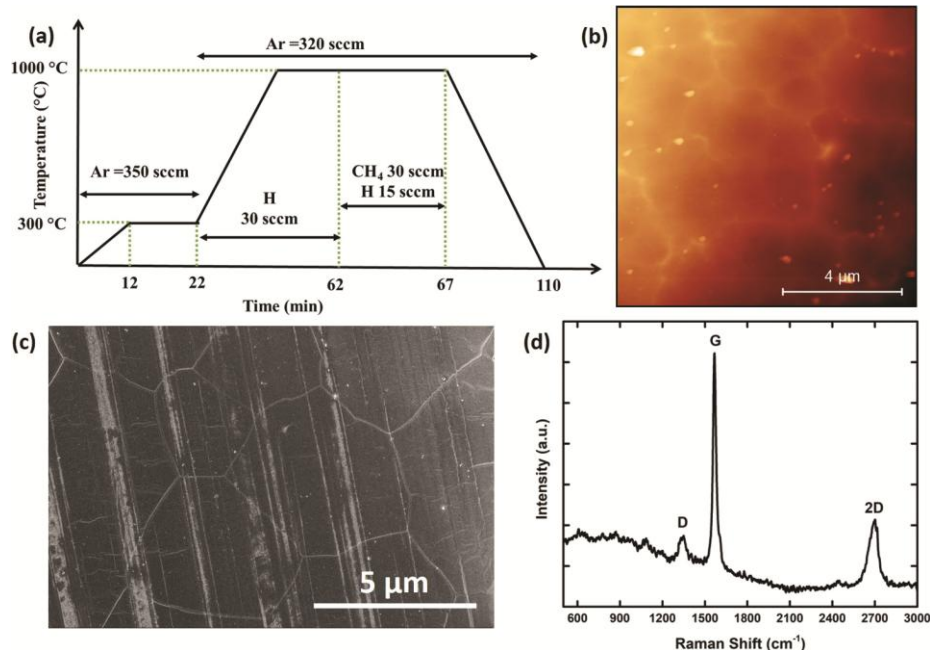


Fig. 1 — Graphene layer grown on copper foil using thermal CVD (a) Growth protocol, (b) AFM study, (c) surface morphology showing wrinkles and flakes of grapheme and (d) Raman spectra of graphene synthesis at 1000 °C.

backside of copper foil (as graphene is grown on both side of copper foil during growth process). For etching the graphene, copper foil containing graphene was placed gently on a solution having a mixture of 2 ml nitric acid (69% concentrated) and 6 ml deionised water. After graphene etching from backside, the copper foil was placed in FeCl_3 etching solution (graphene side upward) and which keeps floating as shown in Fig. 2. At this point, continues drop wise addition of chloroform in the solution is performed. Chloroform covers the graphene, while FeCl_3 starts etching the copper foil. After 10 hours copper foil gets completely etched and only graphene sheets is observed floating on the FeCl_3 + chloroform solution. Further, to minimize and contamination from copper etching solution the graphene was transferred to chloroform solution. It should be noted that the chloroform addition reduced the surface tension of graphene water interface drastically, due to that graphene remained intact and did not pulled apart. After copper etching substrate of interest was scooped and graphene was collected on the substrate. Substrate is further annealed in furnace at 100°C to remove water or any other impurities present.

Further the graphene transfer on glass substrate was verified by Raman spectra and surface morphology as shown in Fig. 3. It is observed that graphene transfer

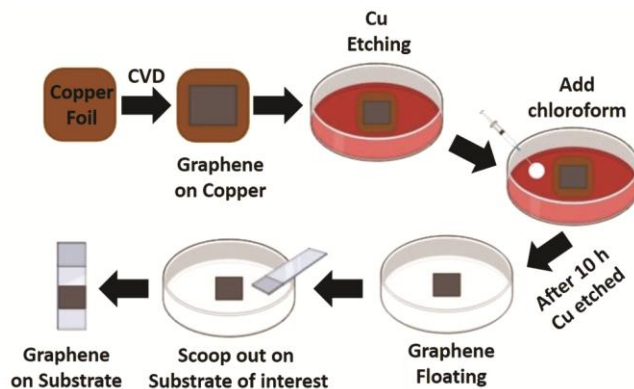


Fig. 2 — Schematic of graphene transfer process on substrate of interest.

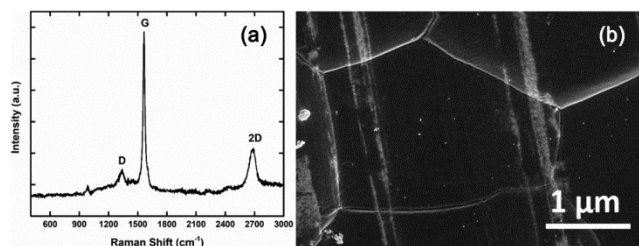


Fig. 3 — Graphene layer after transfer on glass substrate (a) Raman Spectra and (b) surface morphology.

on glass substrate from copper had ID/IG of 0.35 and I2D/IG of 1. Raman spectra shown in Fig. 3a and 1d was found similar which depicts that the graphene has no defects or contamination during the transfer process. It should be noted that during the transfer process no support layer was used in the current process. Due to this no contamination from any kind of support layer is added in the graphene which is one of the biggest problem in the majority of transfer processes. Moreover, the surface morphology also verified the successful high quality transfer of graphene, as shown in Fig. 3b.

3.3 Transmission study

Transmission capability of transferred graphene was analysed in UV-Vis-NIR wavelength range. Transmission spectra of bare glass and graphene transferred glass was recorded, as shown in Fig. 4a. It is observed that, the fabricated and transferred graphene transmit more than 70 % of incident light in UV-Vis region and $\sim 80\%$ in NIR region. Moreover, Fig. 4b shows the transmission capacity of fabricated graphene showing high transparency. Due to this high transparency, the fabricated graphene finds application in photovoltaics and electronic devices and wearable gadgets¹⁷⁻¹⁹.

3.4 Contact angle study

A large number of graphene-based devices are operating in ambient conditions at coastal areas where high amount of humidity is present in the air²⁰. Moreover, variation of humidity throughout the year drastically affect the optical, mechanical and electrical properties of graphene nano devices^{20,21}. Therefore the knowledge of graphene water affinity is highly required. To study the wettability behaviour, contact angle analysis is performed on both graphene grown on copper substrate and transferred graphene. Contact angle study revealed that the graphene grown on copper

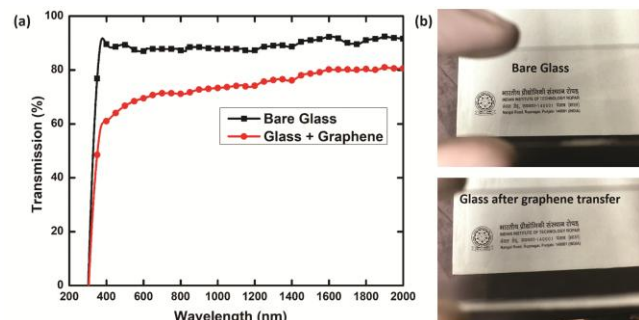


Fig. 4 — (a) Transmission spectra of bare glass and graphene transferred glass in UV-Vis-NIR wavelength region and (b) photograph showing transmission capacity of fabricated graphene.

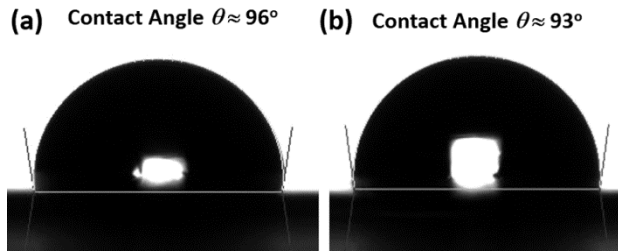


Fig. 5 — Contact angle of graphene with water droplet before and after transfer (a) copper substrate after CVD and (b) glass substrate after transfer.

substrate after CVD is hydrophobic with a contact angle of $96 \pm 3^\circ$ as shown in Fig. 5a²². However, the contact angle of graphene after transfer to glass substrate slightly reduces to $93 \pm 3^\circ$ as shown in Fig. 5b.

4 Conclusions

High-quality graphene is grown on copper foil using thermal CVD. Surface morphology and topology of graphene is analysed along with Raman spectra which confirms that the fabricated graphene is of high quality. Further the developed process shows potential to transfer graphene layer to any substrate of interest using chemical route. In this process graphene is transferred without any support layer which reduces contaminations drastically. The chloroform is supplied to reduce the surface tension which did not allow graphene to be pulled apart. Moreover, it is observed that the fabricated graphene has transmission of more than 70 % in UV-Vis and ~ 80 % in NIR wavelength range. In addition to this, the fabricated graphene is hydrophobic in nature with a contact angle of 96° . It is envisaged that the present graphene synthesis and transfer process is a significant step ahead in developing better electronic devices.

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