Review on Large-Area Synthesis of Some Graphene Films, Characterizations and Applications

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Authors' contributions

This work was carried out in collaboration between all authors. Author VC designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author NAG effected the corrections on the revised manuscript. Author IJ managed the literature searches. All authors read and approved the final manuscript.

Article Information

Review Article

ABSTRACT

For two decades and beyond, remarkable progress has been made in the use of chemical vapour deposition methods for comprehending 2D materials growth. This review is aimed at providing an overview of several synthesis, characterizations and applications of large area graphene film on some substrates. First, the major growth methods are explained. Next, the mechanism of the graphene growth is discussed, focusing on reaction of precursors, diffusion of adatoms, energetics and kinetics of growth fronts, and effects of substrates. Then, the advantage of growing graphene film on some substrate over another is explained in some of the synthesis. Furthermore, the characterization of the various synthesized graphene films are explained, which suggests a suitable application to it.

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1. INTRODUCTION

Recently, much attention has turned to the structural and electronic properties of carbon-based materials. At present, graphene is the hottest topics in condensed-matter physics and materials science. This is because graphene has not only unusual properties regarding extreme mechanical strength, thermal conductivity and 2-diemensional films, but also peculiar electronic characteristics such as Dirac-particles with a linear dispersion, transport energy gap and simply absorption coefficient of lights [1]. These unique properties mean it could have a wide array of practical uses. In addition to monolayer graphene, few-layer graphene has been extensively studied. For example, bi-layer graphene creates a band gap when an external electric field is applied [2]. Graphene sheets have been produced mainly by exfoliating graphene flakes from bulk graphite and depositing them on the SiO_2/Si substrate. However, the size and crystalline quality are not easily controlled. Some groups have grown epitaxially graphene sheets on SiC(0001) [3], however the graphene layers have been widely distributed in thickness [4].

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice. It is a 2D material with outstanding physical properties. The successful isolation of graphene has drawn great interest for experimental investigations and has opened the route for a wide range of potential applications. Mechanically exfoliated graphene from bulk graphite has enabled fundamental investigations on the physical properties of graphene; however, this technique is not suitable for the integration in practical device fabrication processes nor for the synthesis of large surface area devices. For several applications, if one excludes active semiconducting devices exploiting the quantum properties of single carbon layers, a material composed of a few layers graphene (FLG) is also extremely promising. The overall characteristics of graphene films, both single and FLG, such as size, crystallinity, continuity, homogeneity and fabrication reproducibility are mandatory for successful practical application [5]. Here we reviewed some methods which some graphene films are synthesized in large area, its characterizations and some of its applications. The result obtained from the characterizations will also reveal a new application of graphene in the future, and will serve as bases for the study and discovery of future graphene synthesis and application.

2. SYNTHESIS METHODS

2.1 Synthesis of Graphene Films in a Flame

In this method, the temperature of 900–950°C and exposure time of 5 min are demonstrated to be suitable for the synthesis of graphene films on a nickel substrate, which is preferable to a copper substrate. It is indicated that the formation of graphene layers on the substrate occurs vertically along the flame height, with subsequent changeover to a soot structure. It is displayed that the minimum number of graphene layers (two or three) is observed at angles of inclination of the substrate relative to the vertical axis of the flame within 0°–30° [4].

The Ni surface is the excellent substrate for growth of single-layer-graphene sheet with macroscopic dimensions. Graphene sheets with a 1 x 1 atomic structure grew up epitaxially by Chemical vapour deposition (CVD) or surface segregation techniques. It was observed that the graphene growth of mono-, bi- and tri-layer step by step using carbon segregation phenomena on Ni by *Low-energy electron microscopy (*LEEM). The summaries are as follows:

1. One can grow the uniform monolayer graphene on Ni by adjusting the temperature. No domain boundaries and wrinkles were detected by LEEM.
2. The second- and the third-layer graphene grew at the interface under the first and the second layers. Bi-layer graphene domains grew at least 100μm scale. The third-layer started to grow before the completion of second-layer at 1050K in this experiment. More precise control of temperature seems to be required to complete the second-layer before starting the third-layer growth.
3. Shape of the islands differed depending on the thickness; the first- and third layer islands exhibit hexagonal edges, while the second-layer islands possess dendritic edges.
4. The different shapes of the first, second and third-layer islands presumably originate from the interfacial-bond strength depending on the graphene thickness.

5. The number of nucleation sites of graphene growth is extremely small on Ni surface, which is an important factor for growth of large single-domain graphene crystals.

6. Chemical etching of Ni substrate made it possible to separate macroscopic self standing graphene sheets.

2.2 Synthesis of Graphene Films on Copper Substrates by CVD of Different Precursors

Graphene films of the order of 1cm^2 were grown on copper foil substrates by CVD using hydrogen/methane or hydrogen/argon/ethanol mixtures as gas precursors. The growth processes were performed near 1,000°C both at atmospheric and low pressures. A system for the fast cooling of the sample, based on the fast extraction from the hot zone of the furnace, was implemented allowing for rapid decrease of the temperature below 600°C in few seconds. Samples grown under different conditions were analyzed by svcanning electron microscope (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) with the aim to assess their characteristics and to refine the growth process (R. Giorgi et al).

Films consisting of less than 5 graphene layers have been grown by CVD both from methane and ethanol as precursors. The use of copper substrates has allowed the growth of large area continuous films of the order of 1cm^2; a wet procedure was followed for the transfer of the graphene films on to SiO$_2$/Si substrates more suitable for their characterization. Pressure and growth time have been found to be the main process parameters affecting the thickness and the quality of the graphene films. The grown films exhibited good crystallinity, but result composed of different overlapping regions with different
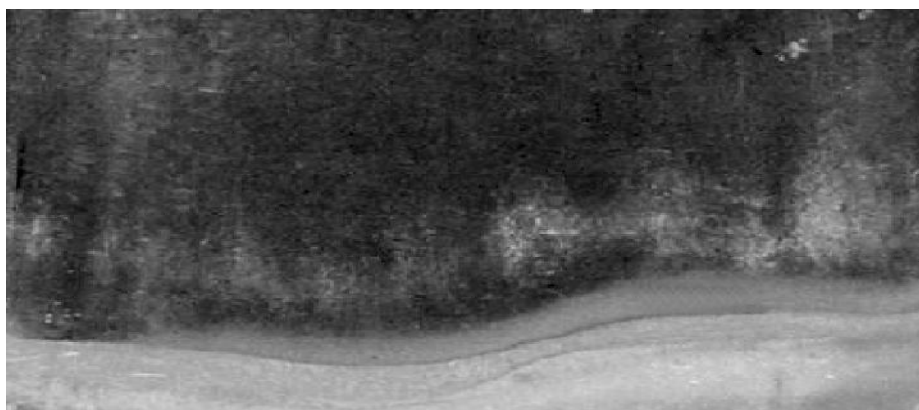

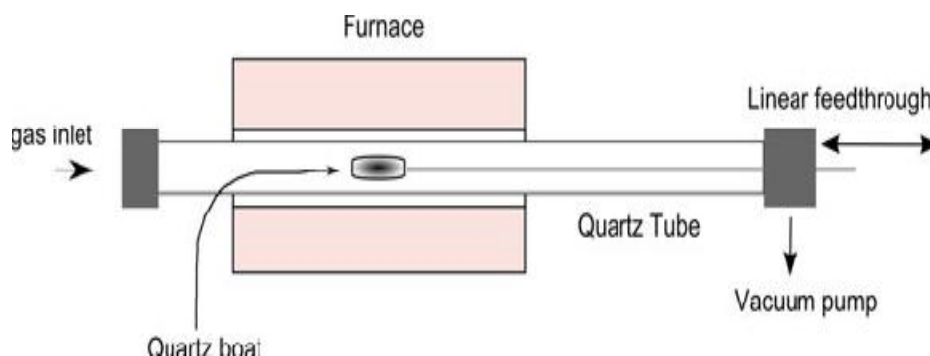**Fig. 1. Photograph of a nickel substrate with carbon structure.**
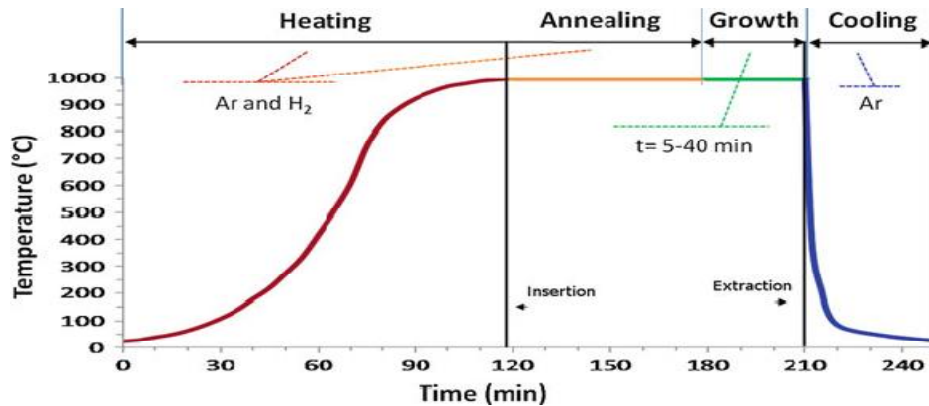

Fig. 2. Scheme of the CVD reactor
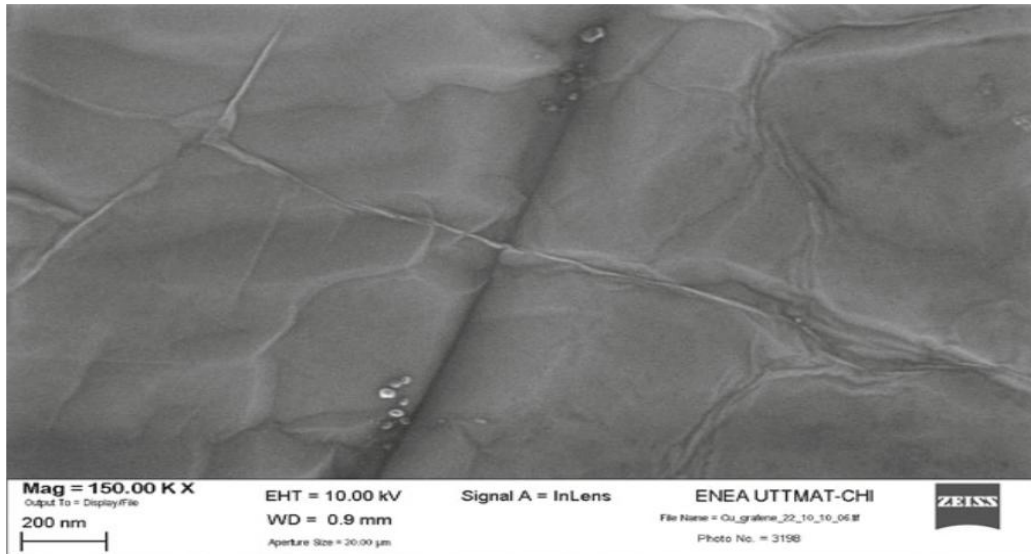
Fig. 3. Graphene growth process

Fig. 4. SEM image of Cu substrate after graphene growth

number of layer. Factors influencing the film homogeneity and uniformity have been identified in the substrate features. Future work will be focused on the optimization of substrate treatments, with the aim to achieve more uniform large area graphene films with controlled structure: number of layers and crystallinity. The matching of the large copper grain size (upto 1mm) with controlled growth of graphene (single and FLG) remains an interesting goal and a high challenge [5].

2.3 Large-Area of Graphene Films on Copper Foils Synthesis

The large-area graphene films of centimeters on copper substrates was grown by chemical vapor deposition by using methane. The films are predominantly single layer graphene with a small percentage (less than 5%) of the area having few layers, and are continuous across copper surface steps and grain boundaries. The low solubility of carbon in copper appears to help make this growth process self-limiting. Graphene film transfer processes were also developed to arbitrary substrates, and dual-gated field-effect transistors fabricated on Si/SiO_2 substrates showed electron mobilities as high as 4050 $cm^2V^{-1}s^{-1}$ at room temperature [6].

In recent work, thin Ni films and a fast-cooling process have been used to suppress the amount of precipitated C. However, this process still yields films with a wide range of graphene layer

thicknesses, from one to a few tens of layers and with defects associated with fast cooling [7]. Our results suggest that the graphene growth process is not one of C precipitation but rather a CVD process. The precise mechanism will require additional experiments to understand in full, but very low C solubility in Cu [8], and poor C saturation as a result of graphene surface coverage may be playing a role in limiting or preventing the precipitation process altogether at high temperature, similar to the case of impeding of carburization of Ni [9]. This provides a pathway for growing self-limited graphene films. To evaluate the electrical quality of the synthesized graphene, we fabricated dual-gated FET with Al_2O_3 as the gate dielectric and measured them at room temperature. Along with a device model that incorporates a finite density at the Dirac point, the dielectric, and the quantum capacitances [10], the data are shown in Fig. 3 The extracted carrier mobility for this device is ~4050 $cm^2V^{-1}s^{-1}$, with the residual carrier concentration at the Dirac point of no=3.2×10^{11} $cm^{-2.}$ These data suggest that the films are of reasonable quality, at least sufficient to continue

improving the growth process to achieve a material quality equivalent to the exfoliated natural graphite [6].

2.4 Synthesis of Multi-layer Graphene films on Copper Tape by Atmospheric Pressure Chemical Vapor Deposition Method

Graphene films were successfully synthesized by atmospheric pressure chemical vapor deposition (APCVD) method. Methane (CH_4) gas and copper (Cu) tapes were used as a carbon source and a catalyst, respectively. The CVD temperature and time were in the range of 800–1000°C and 10s to 45min, respectively. The role of the CVD temperature and time on the growth of graphene films was investigated in detail via scanning electron microscopy (SEM) and Raman spectroscopy techniques. The results of SEM images and Raman spectra show that the quality of the graphene films was improved with increasing of CVD temperature due to the increase of catalytic activity.
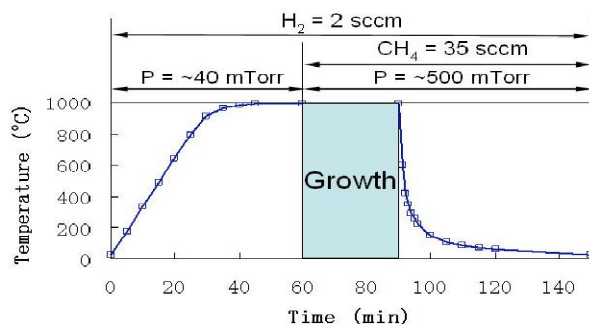

Fig. 5. Time dependence of experimental parameters: Temperature, pressure, and gas composition/flow rate
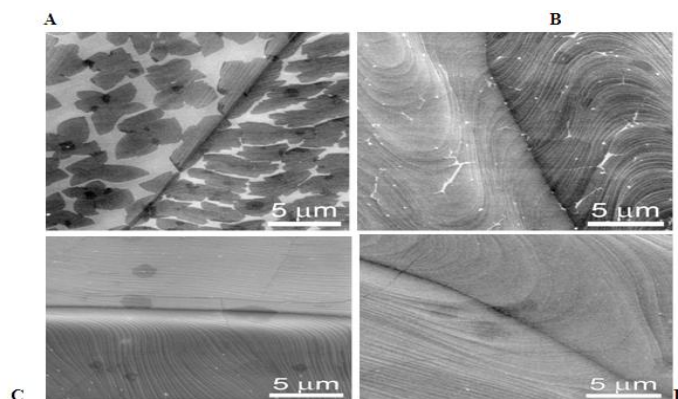

Fig. 6. SEM images of graphene on Cu with different growth times of (A) 1 min, (B) 2.5 min, (C) 10 min, and (D) 60 min, respectively

Multilayer graphene films were successfully synthesized on the Cu tapes by APCVD method. The quality of the graphene films was improved with increasing CVD temperature. The growth time does not much affect the number of layers of graphene films. CVD temperature of 1000°C and CVD time of 30min are the optimum temperature and time for growing high-quality graphene films on the Cu tape, respectively. The graphene films were successfully transferred from the Cu tape to other substrates by wet etching Cu with a solution of iron(III) nitrate [11].

2.5 Self-Standing Graphene heets Prepared with Chemical Vapor Deposition and Chemical Etching

The growth mechanism of graphene layers on Ni surface was studied. The in-situ observation of the graphene growth of mono-, bi- and tri-layers using carbon segregation phenomena on Ni by low energy electron microscopy (LEEM) were reported, which is a powerful technique to investigate thin films in mesoscopic scale. We also fabricated the self-standing graphene sheets by chemically etching the substrate [12]. The chemical process to remove the Ni substrate makes it possible to prepare a self-standing graphene sheets, which are characterized by scanning electron microscopy (SEM) or transmission electron microscopy (TEM).

The Ni surface is the excellent substrate for growth of single-layer-graphene sheet with macroscopic dimensions. Graphene sheets with a 1 x 1 atomic structure grew up epitaxially by

CVD or surface segregation techniques. We in-situ observed the graphene growth of mono-, bi- and tri-layer step by step using carbon segregation phenomena on Ni by LEEM. The summaries are as follows;

1. One can grow the uniform monolayer graphene on Ni by adjusting the temperature range. No domain boundaries and wrinkles were detected by LEEM.
2. The second- and third-layer graphene grew at the interface under the first and the second layers. Bi-layer graphene domains grew at least 100µm scale. The third-layer started to grow before the completion of second-layer at 1050K. More precise control of temperature seems to be required to complete the second-layer before initiating the third-layer growth.
3. Shape of the islands differed depending on the thickness; the first- and third- layer islands exhibit hexagonal edges, while the second-layer islands possess dendritic edges.
4. The different shapes of the first, second and third-layer islands presumably originate from the interfacial-bond strength depending on the graphene thickness.
5. The number of nucleation sites of graphene growth is extremely small on Ni surface, creating an important factor for growth of large single-domain graphene crystals.
6. Chemical etching the Ni substrate made it possible to separate macroscopic self standing graphene sheets [12].
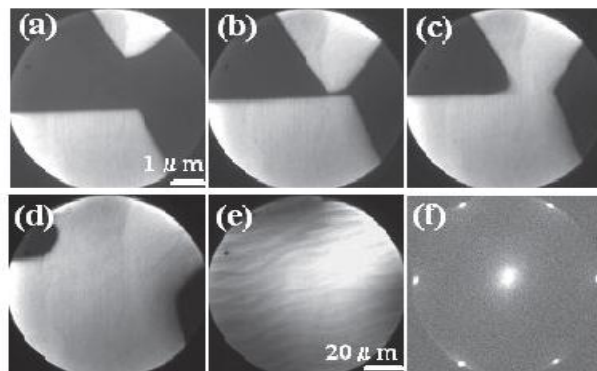

Fig. 7. Typical snapshots of LEEM images obtained as the temperature was decreased from 1200 K to 1125 K (images (a) to (d)) The observed area was 6µm field-of-view
Letter in each image indicates the time-lapse order. Two graphene domains were united to form one graphene sheet. Image (e) is a typical LEEM image of 100µm field-of-view. The surface was entirely covered with monolayer graphene. LEEM images were obtained at the primary electron energy of 3.5 eV. Image (f) is a typical LEED pattern observed in the graphene covered surface. The orientation of the graphene was slightly altered because the sheet is curved.
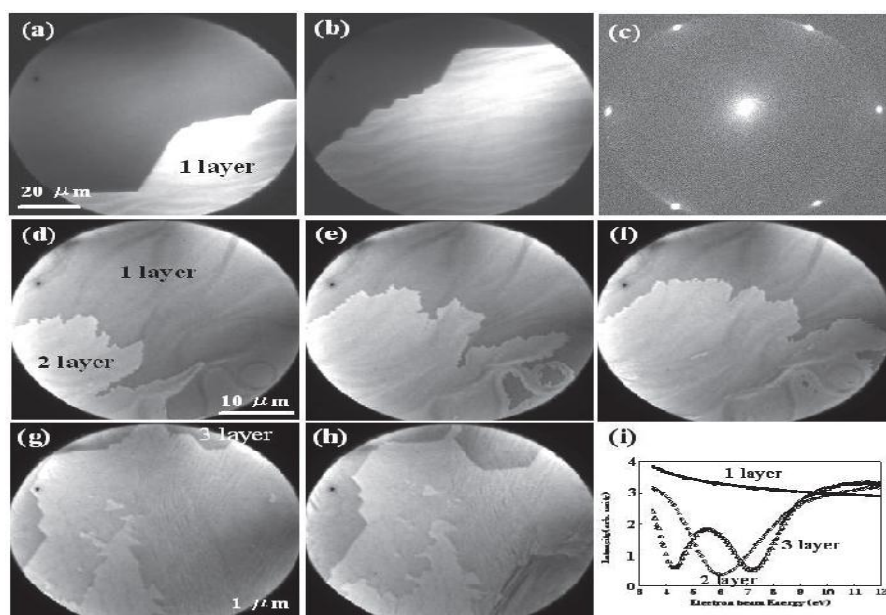
Fig. 8. Typical LEEM images of the graphene growth at different stages: (a)-(b) the first layer growth observed at 1125K, (d)-(f) the second layer at 1050K and (g)-(h) the third layer at 1050K. Image (c) is a typical μLEED pattern of a 1 x 1 atomic structure obtained from the single-layer graphene-covered surface. Image (i) is the electron reflectivity-energy curves obtained from each area. Image (e) is a growth stage that followed after stage (d) before stage (f)
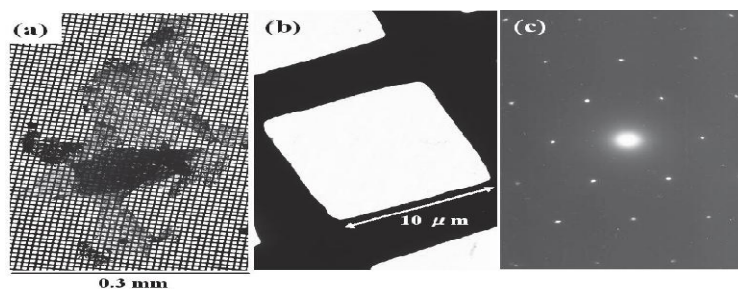
Fig. 9. A TEM image of a carbon aggregate on the Au mesh with squares 10 μm × 10 μm in area, (b) A magnified TEM image of the thinnest area of the carbon aggregate, and (c) its electron diffraction pattern
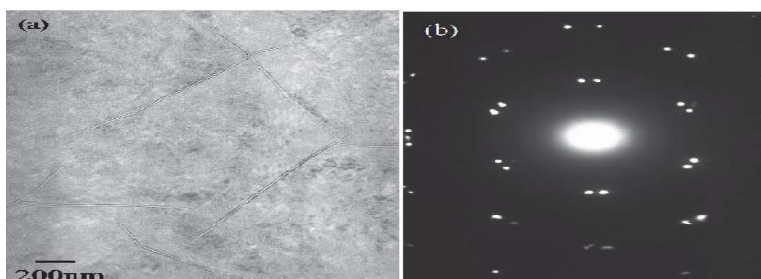
Fig .10. A TEM image of the other area in the carbon aggregate (a) and its diffraction pattern (b). One can see clearly doublets of diffraction spots in (b), and new cabon-nano-tube like structures in (a). The hole was covered with double-layer graphene
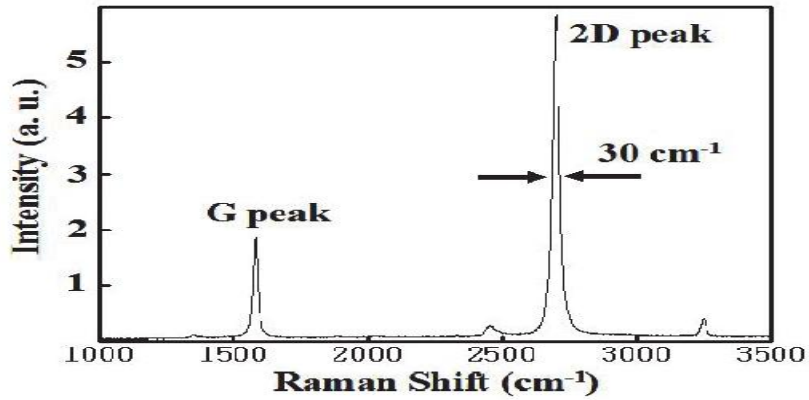
Fig. 11. Typical Raman spectrum of the monolayer self-standing graphene sheets
Small defect-origin D peak was detected at ～1350 cm-1
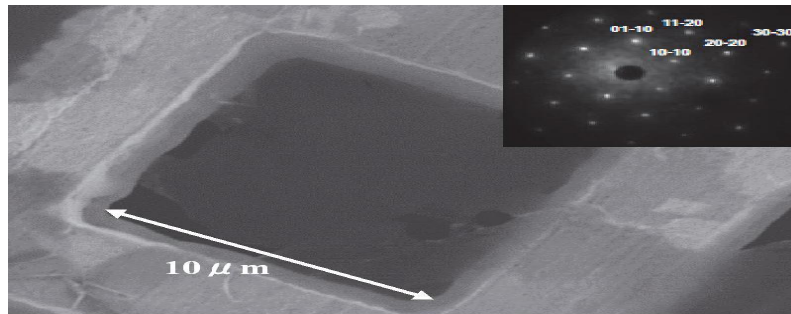
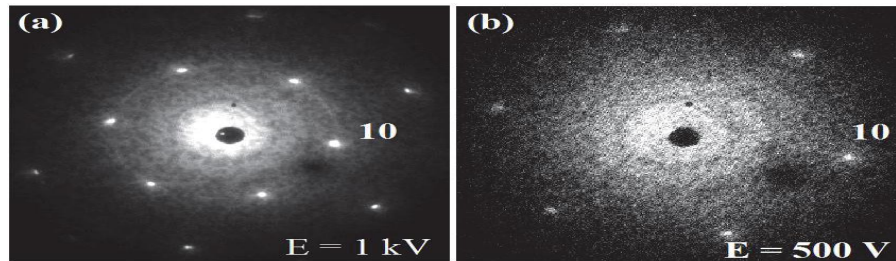**Fig. 12. The SEM image of single graphene sheet at 5 kV and its LETED pattern (upper right)**

Fig .13. The LETED pattern of single-layer graphene at (a) 1 kV and (b) 500 V.
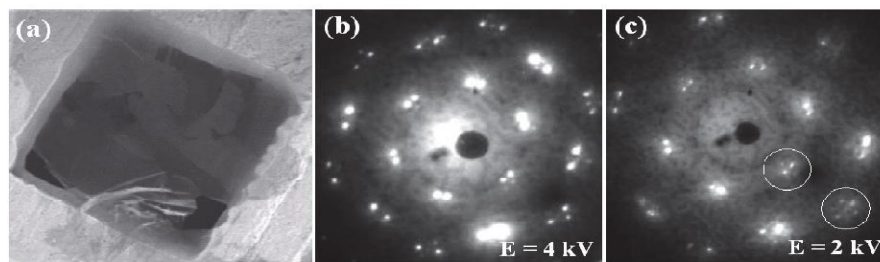*LETED stands for (Low Energy Transmission Electron Diffraction)*

Fig. 14. The SEM image of folding double graphene sheet (a) and its LETED pattern at (b) 4 kV and (c) 2kV

3. APPLICATIONS OF LARGE SCALE GRAPHENE

3.1 Graphene for Nanoelectronics

Graphene shows a glaring ambipolar electric field effect whereby charge carriers can be tuned continuously between electrons to holes. Single layer graphene atop a thermally grown SiO_2 layer on a highly doped Si substrate may serve as a prototype of a field effect transistor. Under this arrangement, SiO_2 play the role of an insulating layer, so a back-gate voltage can be applied to vary carrier concentration. Early graphene FET devices demonstrated by Novoselov exhibited dopant concentrations as high as 1013 cm^{-2} and achieved a mobility that could exceed 10,000 cm^2 /Vs [13]. This translates into ballistic transport on submicron scales. The room-temperature mobility is limited by impurities or corrugations of the graphene surface, which means that it can still be improved significantly up to the order of 105 cm^2 /Vs [14,15].

Electrons present in graphene act like mass-less comparable particles controlling a majority of its electronic properties. Among the most important results of such uncommon diffusion relation can be seen in the case of half-integer "Quantum Hall Effect" and the unavailability of localization, which can be very essential for graphene-based field effect transistors, (FET), [1]. Mechanical exfoliation of highly ordered pyrolitic graphite (HOPG) or high purity graphite flakes can lead to the generation of graphene crystals with very few flaws, which in turn show high movability of the charge carriers. Fig. 12 shows scanning electron microscopy (SEM) and atomic force microscopy (AFM) of the graphene based device reported in the literature as having the highest electron mobility to date [14]. The graphene film was obtained by mechanical exfoliation of graphite on Si/SiO_2 substrate in which the oxide layer below the graphene was etched in order to obtain a free-standing graphene flake connecting the metal electrodes.

Electrical measurements of resistivity vs. gate voltage show the intrinsic ambipolar characteristics of graphene. It was also established that the transfer characteristics of the device is greatly improved after undergoing a high-current annealing procedure to remove contaminants from the graphene surface. Mobility μ for this device reaches an exceptional value of 230,000 cm^2/Vs measured at the highest carrier density n = 2x1011cm^{-2}. Such high

mobility would in principle favor high frequency performance. Furthermore, graphene devices pursuing high frequency have demonstrated encouraging characteristics, exhibiting a cutoff frequency fT of 26 GHz, which is the frequency at which the current gain becomes unity and signifies the highest frequency at which signals are propagated [10]. Only recently, P. Avouris and collaborators reported the fabrication of graphene FETs on SiC substrates with cutoff frequency of 100 GHz for adevice of gate length of 240 nm and using a source-drain voltage of 2.5 V [12]. This fT exceeds those previously reported for graphene FETs as well as those for Si metal-oxide semiconductor FETs for the same gate length (~40 GHz at 240 nm) [11].

3.2 CVD Graphene for Macroelectronics: Transparent Conductive Films

Another intrinsic property of graphene is its transparency. A single sheet of graphene absorbs only 2.3 % of the incident light. Such combination of high conductivity and lowlight absorption makes this material an ideal candidate as a transparent conductive film. It is very tempting to use the unique properties of graphene for technology applications even beyond graphene FET applications. Composite materials, photo-detectors, support for biological samples in TEM, mode-lockers for ultrafast lasers and many more areas would gain strongly from using graphene for non-FET purposes [14].

3.3 Graphene Applications in Photovoltaics

3.3.1 Photovoltaic cells: Graphene vs ITO

Solar energy harvesting using organic photovoltaic (OPV) cells has been proposed as a means to achieve low-cost energy due to their ease of manufacture, light weight and compatibility with flexible substrates. A critical aspect of this type of optoelectronic device is the transparent conductive electrode through which light couples into the device. Conventional OPVs typically use transparent indium tin oxide (ITO) or fluorine doped tin oxide (FTO) as such electrodes [15]. However, the scarcity of indium reserves, intensive processing requirements, and highly brittle nature of metal oxides impose serious limitations on the use of these materials for applications where cost, physical conformation, and mechanical flexibility are important.
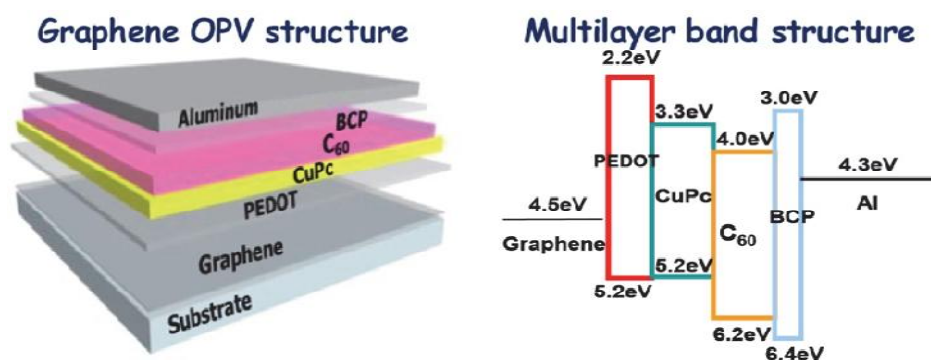
Fig .15. Schematic representation of the energy level alignment (right) and construction of the heterojunction organic solar cell fabricated with graphene as anodic electrode: CVD graphene / PEDOT / CuPc / C60 / BCP / Al.

Graphene monolayer has a transparency of 97-98 percent and the sheet resistance of undoped graphene is of the order of ~6kΩ; for which graphene films are suitable for applications as transparent conductive electrodes where low sheet resistance and high optical transparency are essential [13]. Conventional methods to obtain graphene thin films such as epitaxial growth, micromechanical exfoliation of graphite and exfoliation of chemically oxidized graphite are either expensive, unscalable or yield graphene with limited conductivity due to a high defect density. However, chemical vapor deposition has surged as an important method to obtain high quality graphene films. In particular, films with sheet resistance of 280 Ω/sq (80% transparent) and 770 Ω/sq (90%transparent) have been reported in the literature for graphene synthesized on Ni films,while sheet resistance of 350 Ω/sq (90% transparent) has been reported for CVD graphene on Cu films, which represents a good advance in the use of graphene as transparent conductive films. Another advantage of CVD is its scalability; we have reported wafer-scalesynthesis and transfer of single- and few-layer graphene for transistor and photovoltaic device fabrication [13].

4. SUMMARY AND CONCLUSION

The report reveals some detailed synthesis methods of large area graphene from different precursors, starting from the growth processes, the precise mechanisms with given optimized parameters, to yield some maximum graphene films with good properties. Results obtained from the characterization of the various synthesized graphen films confirmed that the properties of the films are of good quality, which makes them useful and can be employed for different applications.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Nitinchopra, Junchiwu, Paarasagrawal. Synthesis of nanoscale heterostructures comprised of metal nanowires, carbon nanotubes, and metal nanoparticles: Investigation of their structure and electrochemical properties. Journal of Nanomaterials. 2015, Article Id 125970, 13 Pages
2. Gunho Jo, Minhyeok Choe, Sangchul Lee, Woojin Park, Yung Ho Kahng, Takhee Lee. The application of graphene as electrodes in electrical and optical devices. Nanotechnology. 2012;23:112001.
3. Yu V, Davydova C, Yu D, Usachovb SP, et al. Study of the crystal and electronic structure of graphene films grown on 6h-Sic (0001) Semiconductors. 2017;51(8): 1072–1080.
4. Prikhod'ko NG, Lesbaev BT, Auelkhankyzy M, Mansurov ZA. Synthesis of graphene films in a flame. Russian Journal of Physical Chemistry B. 2014;8(1):61-64.

5. Keun Soo Kim, Yue Zhao, Houk Jang, et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature. 2009;457(5).

6. Xuesong Lia, Weiwei Caia, Jinho Ana, Seyoung Kimb, Junghyo Nahb, Dongxing Yanga, Richard Pinera, Aruna Velamakannia, Inhwa Junga, Emanuel Tutucb, Sanjay K. Banerjeeb, Luigi Colomboc, Rodney S. Ruoffa. Large-area synthesis of high-quality and uniform graphene films on copper foils. Science. May 7, 2009 (Science Express Article).

7. Giorgi R, Dikonimos Th., Falconieri M, Gagliardi S, Lisi N, Morales P, Pilloni L, Salernitano E. Synthesis of graphene films on copper substrates by Cvd of different precursors. Nicola Lisi, 15 January 2014.

8. Lei Liu, Jewook Park, David A. Siegel, Kevin F. Mccarty, Kendal W. Clark, Wan Deng, Leonardo Basile, Juan Carlos Idrobo, An-Ping Li. Gong Gu1†. Heteroepitaxial growth of two-dimensional hexagonal boron nitride templated by graphene edges. Science. 2014;343(10).

9. Whi Dong Kim, Jung Min Park, Ji Young Ahn, Soo Hyung Kim. Journal of Nanomaterials Volume 2011, Article Id 736219, 7 Pages R. Giorgi, Th. Dikonimos, M. Falconieri, S. Gagliardi, N. Lisi, P. Morales, L. Pilloni, E. Salernitano. Synthesis of graphene films on copper substrates by Cvd of different precursors. Nicola Lisi, 15 January 2014.

10. Perkins FK, Friedman AL, Cobas E, Campbell PM, Jernigan GG, Jonker BT. Chemical vapor sensing with monolayer Mos2. Nano Lett. 2013;13:668−67.

11. Van Tu Nguyen, Huu Doan Le, Van Chuc Nguyen, Thi Thanh Tam Ngo, Dinh Quang Le, Xuan Nghia Nguyen, Ngoc Minh Phan. Synthesis of Multi-Layer Graphene films On Copper Tape by Atmospheric Pressure Chemical Vapor Deposition Method. Adv. Nat. Sci. Nanosci. Nanotechnol. 2013;4: 035012.

12. Genki Odahara, et al. Edited By Jian Ru Gong. Graphene – Synthesis, Characterization, Properties and Applications, ISBN 978-953-307-292-0

13. Helin Cao, Qingkai Yu, Deepak Pandey, Dmitry Zemlianov, Robert Colby, Isaac Childres, Vladimir Drachev, Eric Stach, Jie Lian, Hao Li, Steven S. Pei, Yong P. Chen. Large scale graphene films synthesized on metals and transferred to insulators for electronic applications.

14. Goniszewski S, Gallop J, Adabi M, Gajewski K, Shaforost E, Klein N, Sierakowski A, et al. Self-supporting graphene films and their applications.

15. Fei Chen, Lei Wang, Ting Wang, Xiaohong Ji. Enhanced local photoluminescence of a multilayer Mos$_2$ nanodot stacked on monolayer Mos$_2$ flakes. Optical Materials Express. 2017;7(4):1366.