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Research Article

Fabrication and Identification of Graphene Layers on Silicon Dioxide and Flexible PMMA Substrates

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Abstract: Graphene is a "wonder material" and rapidly rising star in all fields of physics. This strictly two-dimensional material exhibits exceptionally high crystal quality and band structure. Graphene, building block of all graphitic materials, has emerged as an interesting material of the 21st century. This two-dimensional, single-layer sheet of sp^2 hybridized carbon atoms has attracted tremendous attention and research interest, owing to its exceptional physical properties, such as high mobility, good thermal stability, excellent mechanical strength and high transparency. These properties make graphene a material of interest for many applications, for example in the fields of electronics, optoelectronics, photonics, composites as well as sensors. There are a number of methods for fabricating and characterizing graphene. Here in this work, graphene has been synthesized via micromechanical cleavage method and characterized via various techniques. Graphene is fabricated on oxidized silicon (Si/SiO_2) and polymethyl methacrylate (PMMA) substrates. Si/SiO_2 is a rigid substrate while PMMA is transparent, flexible and a versatile polymeric material having applications in flexible electronics. Micromechanical cleavage method is reproducible and large numbers of high quality graphene flakes were obtained by using this method on these two substrates. The graphene layers thus produced have been identified and characterized using optical microscopy, AFM and Raman spectroscopy showing single layer, bilayer, tri-layer and multi-layer graphene.

Keywords: Graphene, two-dimensional material, fabrication, micromechanical cleavage

1. INTRODUCTION

Graphene is made up of a single atom thick carbon layer arranged in a honeycomb-like lattice. Graphene is the thinnest, strongest and hardest material available so far. In recent times, graphene has attracted the huge attention of scientific fraternity in all areas of academic and industrial research due to its unique set of properties. Graphene is trying to replace the previously exiting modern material i.e. silicon which was set to change the face of research and technology. Due to its rapid popularity it can be said that Graphene is going to change the future of technology even making invisibility a reality [1-3].

Graphene is the first material in the new class of 2D materials. Although it was supposed that 2D materials cannot exist without 3D base until 2004. But this assumption has changed with the experimental discovery of graphene [4] by Geim and Novoselov [5]. Theoretically, graphene has been studied for sixty years [6-8] but there were some difficulties in isolating single layer. If we go back in the distant past, we are surprised to know that graphene also existed in ancient times. Because everyone while using an ordinary lead pencil probably produce graphene-like structures without knowing it (because graphite consists of stacked graphene sheets). So we can say that graphene was existed in past in the form of different carbon materials such as graphite, fullerenes and carbon nanotubes [9]. But in 2004, it was discovered as a single isolated layer [4]. After its discovery it became evident that graphene is the building block of all graphitic materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotube or stacked

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into 3D graphite [9].

Crystal structure of graphene consists of single layer of carbon atoms undergo hybridization with angle between each bond is 120° and the carbon distance is 0.142 nm. There are two carbon atoms per unit cell in a hexagonal honeycomb lattice of graphene [10]. The two dimensional linear network of carbons with no cross linking makes graphene flexible and stretchable. The electronic band structure of graphene considers only the electrons in the 2 orbitals. These electrons give rise to the π band and account for the transport properties of graphene. The conduction and valence band touches at the *K* and K^{-} points at the border of the first Brillouin zone which specifies that graphene has no band gap, and it is therefore called as a zero-gap semiconductor [5] or a semi metal [5].

Graphene has several useful electronic, optical, mechanical and thermal properties. Graphene has a charge carrier mobility ~200,000 cm^2/Vs [4] compared to the other semiconductor materials. Graphene is an optically transparent material. Single layer of graphene can absorb only 2.3% of light while 97.7% of light is transmitted [11]. Transparency of graphene reduces with increasing number of layers as 2.3% per layer [11]. In 2009, Le et al showed that graphene has breaking strength over 100 times greater than a hypothetical steel film of the same thickness, with a Young's modulus of 1 TPa [12]. Therefore, graphene; having the breaking strength of 42 Nm^{-1} and the Young's modulus of 1.0 TPa; is suggesting the strongest material ever measured [13]. Graphene is the superconductor of heat. It has highest thermal conductivity 3080–5300 W/mK [4] compared to the other carbon materials.

These properties of graphene make it an attractive choice for use in advanced applications. Graphene is a single atom thick flat sheet of carbon. Therefore, electrons and holes move much faster through it than through other materials. This property makes graphene a suitable candidate to replace silicon as an electronic material and can be used in high frequency transistor applications [14-16]. Graphene has also replaced semiconductors in photo detectors. Graphene with zero band gap has wide spectral range from ultraviolet to infrared [17]. While other semiconductor photo detectors have limited detecting spectral width. Graphene's high operating bandwidth makes it suitable for high-speed data communications [17]. Mechanical flexibility, electrical and optical properties (low sheet resistance and high transparency) make graphene an attractive choice for flexible electronic devices [3]. It is used as a transparent conductive coating in electronic products such as touch screen displays, organic light emitting diodes, etc. Due to its high strength properties, it is used in composite materials [13] such as body armour for military personnel, vehicles and aircrafts. Due to its good electrical conductivity, it is used to coat aircraft surface to prevent from lightning strikes. Due to its high demand in a number of applications, we have fabricated graphene over Si/SiO_2 and PMMA substrates using micromechanical cleavage method and characterized it using optical microscopy, AFM and Raman spectroscopy.

2. MATERIALS AND METHODS

There are different methods to fabricate graphene. However, micromechanical cleavage was the first method by which single layer of graphene was discovered. The same method was used in our experiment. The steps used are as follows:

Two types of substrates were used for graphene fabrication, one was Si/SiO_2 and the other was PMMA which is transparent and flexible. Si/SiO_2 was used with two thicknesses, 90 nm and 290 nm. While the thickness, length and width of PMMA rectangular bar was 3 mm, 43 mm and 15 mm respectively.

The substrates were cleaned using standard cleaning method discussed below.

2.1 Standard Cleaning

The steps involved shown in Fig. 1 are as follows:

Si/SiO_2 substrate was rinsed with Acetone and then IPA and dried with Nitrogen gas. Acetone removed the protective resist coating and IPA dissolved excess Acetone from the substrate. After baking at 120 °C the substrate was cleaned.

Fig. 2 shows the cleaning process of the PMMA substrate. PMMA being reactive with acetone

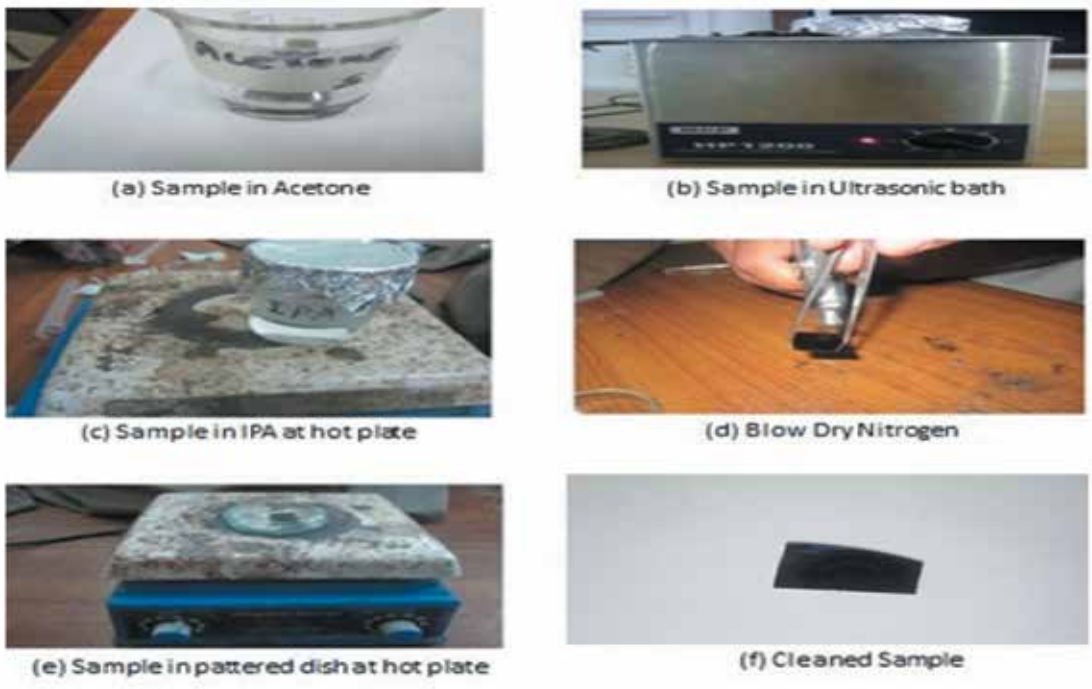

Fig. 1. Standard cleaning method used for Si/SiO_2 substrate.

Fig. 2. Schematic of standard cleaning method for PMMA substrate.

only rinsed with IPA and dried with gas. Now the samples were ready for micromechanical cleavage

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2.2 Micromechanical Cleavage Method

Geim and Novoselov [4] used adhesive tape to fabricate single layer graphene by cleavage. Cleavage is also known as Mechanical exfoliation. Achieving single layers typically involves multiple exfoliation steps, each fabricating a slice with fewer layers, until only one remains. The graphene prepared by this method is of high quality with no defects and differ considerably in size and thickness, where the sizes range from few to hundreds of micron [4]. Our experiment was based on the same cleavage method.

The steps involved in this method were as follows:

A tape was taken and a piece of graphite was emplaced over it. By multiple folding and peeling the tape, the graphite piece was exfoliated into multiple thinner graphite flakes covering the entire tape surface.

Then the tape was put over the pre-cleaned Si/SiO_2 and PMMA substrates and pressed hard with thumb several times to ensure close contact between the flakes and the substrate and left for 1 hour. The sample, Si/SiO_2 with attached tape, was then immersed in Acetone solution for two to three minutes. Tape was left the surface and taken out with tweezer. Then the sample was transferred from Acetone to Fresh Acetone beaker and baked for three to five minutes at 58 to 60 °C. The PMMA rod with graphite tape was immersed into deionized (DI) water at 70 °C and was left for 10 minutes. The tape was removed mechanically. Both samples were then transferred to separate IPA solutions and baked again for five minutes at 50 °C. After that the samples were dried out with nitrogen gas. The sample with Si/SiO_2 substrate was then baked at hot plate at 120 °C for 15 minutes. While the sample with PMMA substrate was baked in microwaves oven at 50-60 °C for 15 minutes. This whole process removed the adhesions due to the tape. The samples were then picked up and left for some time until they maintained the room temperature. Finally, one last peeling with unused tape was performed to remove the thicker flakes and the substrates were left with graphene sheets and other thin graphitic layers. The steps involved for fabrication over $Si/SiO_2$and PMMA are shown in Fig. 3 and Fig. 4, respectively.

3. RESULTS AND DISCUSSION

The samples prepared by the experiment, discussed above, are then characterized by three techniques: optical microscopy, AFM and Raman spectroscopy. The results obtained are discussed below.

3.1 Optical Microscopy

The optical microscopy is the first immediate technique that is used for graphene flake identification. It is used to image various layers since it is the cheapest, non-destructive and readily available in laboratories. Optical microscope provides low resolution due to the light diffraction limit. Therefore, it could not provide conclusive evidence that a given flake was single, double or multilayer but by using the colour difference or reflection variations with image with back ground we can say that the layer is monolayer, bilayer or multilayer.

Fig. 5 to Fig. 12 illustrate main findings of this study. These figures show graphene viewed in an optical microscope (OLYMPUS, MM6C-AF-2) under normal, white-light illumination with different magnifications used in reflection mode on top of a Si/SiO_2 substrate.

Two samples were prepared having a number of graphene flakes over 90 nm and 290 nm Si/SiO_2 substrates. The graphene flakes fabricated over 90 nm Si/SiO_2 substrate are shown in Fig. 5 to Fig. 9 at three magnifications, i.e., (a) 20x, (b) 50x, and (c) 100x. Single layer, bilayer, tri-layer and multi-layer graphene can be identified by contrast analysis which shows that on 90 nm Si/SiO_2 substrate, single layer shows the grey color while multilayer goes towards the white. Single layer graphene are encircled.

The graphene flakes fabricated over 290 nm Si/SiO_2 substrate are shown in Fig. 10 to Fig. 12 at three magnifications: (a) 20x, (b) 50x, and (c) 100x. Single layer, bilayer, tri-layer and multi-layer graphene can be identified by contrast analysis which shows that on 290 nm Si/SiO_2 substrate, single layer shows the purple color and multilayer goes towards the blue. The encircled regions of optical micrograph indicate the single layer graphene of different flakes.

Graphene fabricated over PMMA substrate is shown in Fig. 13 to Fig. 16. The graphene flakes are easily identified on a PMMA substrate because the flakes add an additional optical path for the light reflected off the substrate surface (effective). Typically the colour of graphitic flakes is dark grey (thin flakes) to white grey (thick flakes) on PMMA substrate. In general, the optical contrast of single layer graphene depends on the substrate.

To obtain a better contrast we used the optical

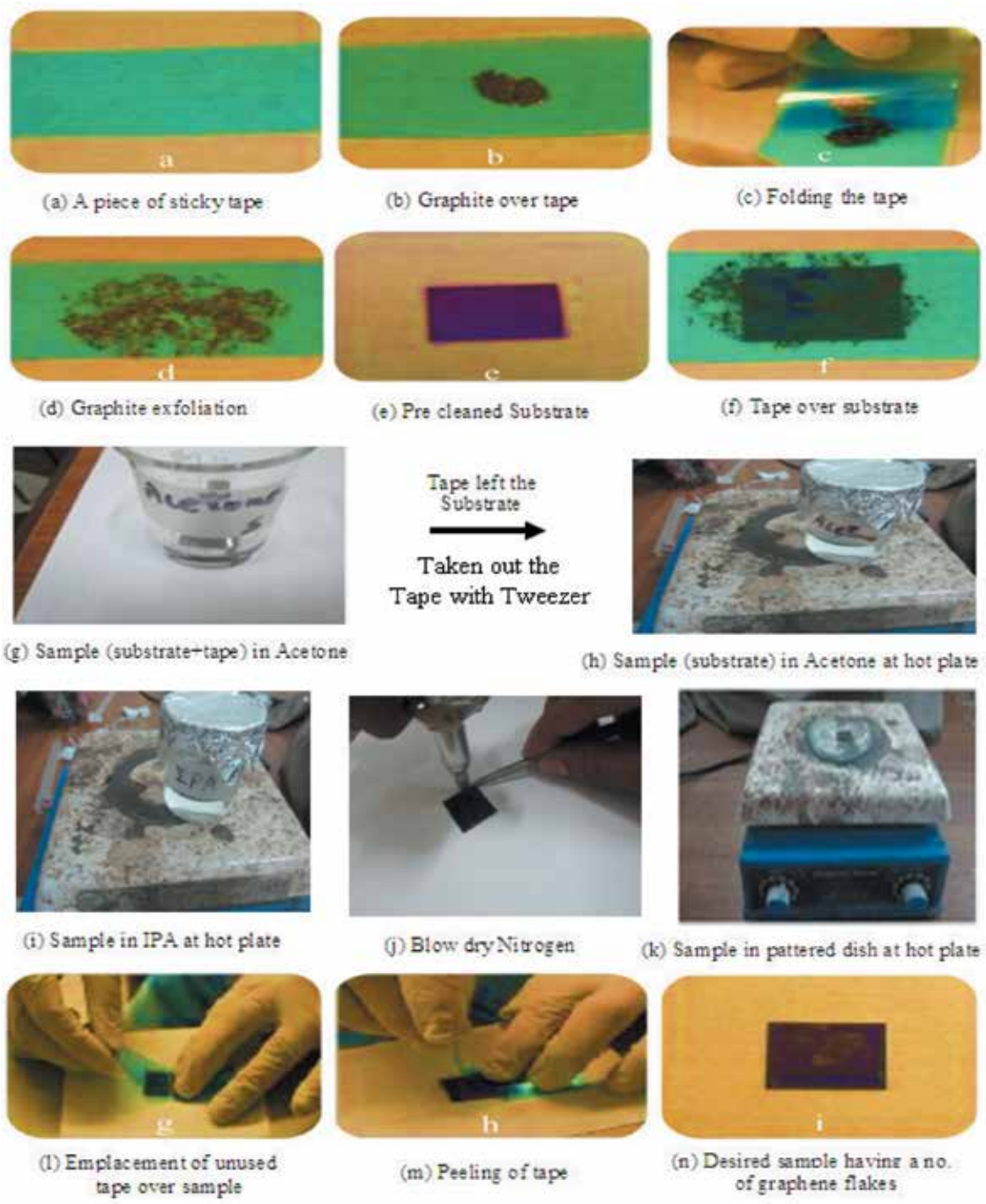

Fig. 3. Schematic of micromechanical cleavage method to fabricate graphene on Si/SiO_2 substrate.

filters. Fig. 14 illustrates the improvement in image quality using the optical filters with different wavelengths in optical microscopy. Different images of graphene flake at different magnification level using different filters are shown in Fig. 15 and Fig. 16.

3.2 Atomic Force Microscopy (AFM)

This technique of imaging can successfully determine the layer thickness at the nanometer scale. AFM images were observed under tapping mode in which cantilever tip touch the surface only for a short time, thus avoiding the issue of lateral forces [18] and drag across the surface. This enables tapping mode to image soft, fragile and adhesive surfaces without damaging them while work under contact mode allows the damage to occur.

Graphene flakes are analyzed by using AFM.

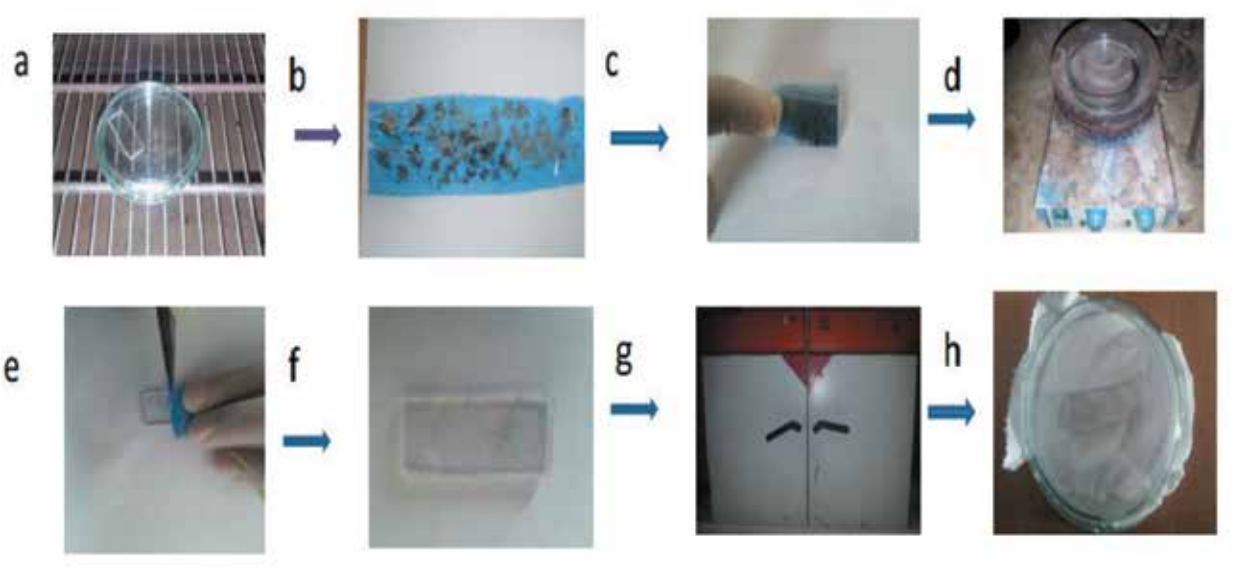

Fig. 4. Schematic for the fabrication of graphene on PMMA substrate.

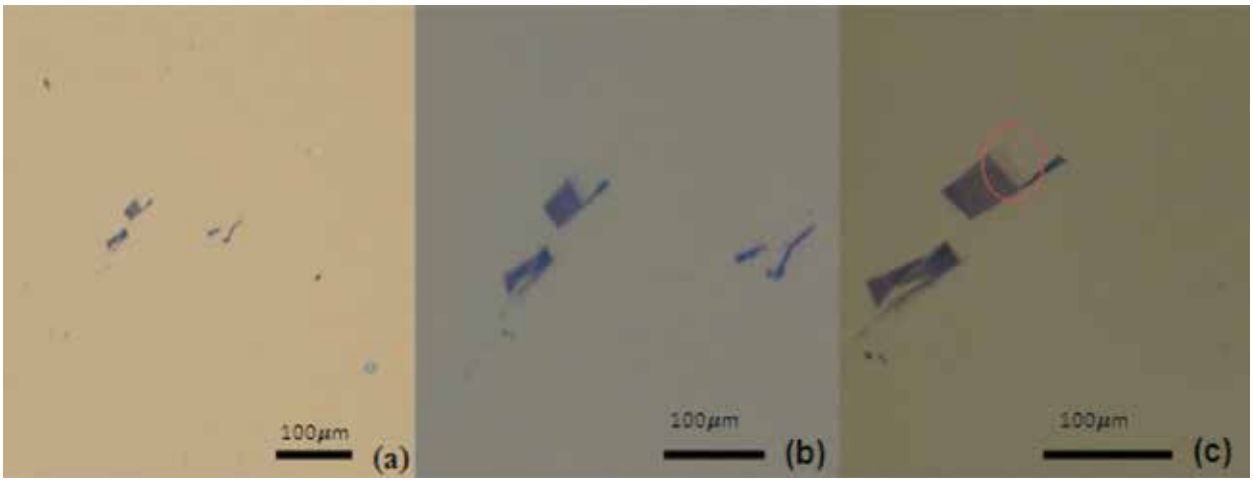

Fig. 5. Optical image of first flake over 90nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

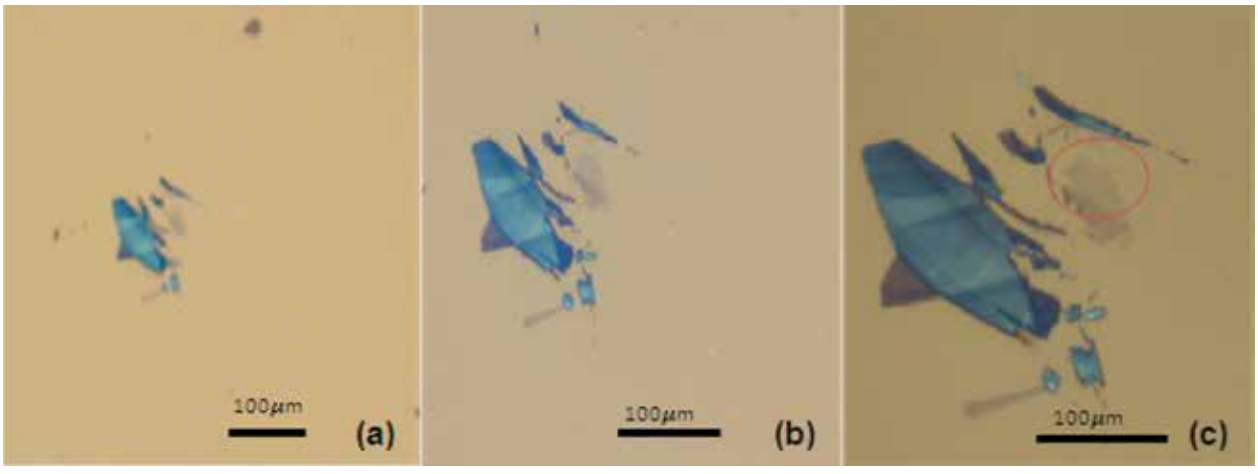

Fig. 6. Optical image of second flake over 90nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

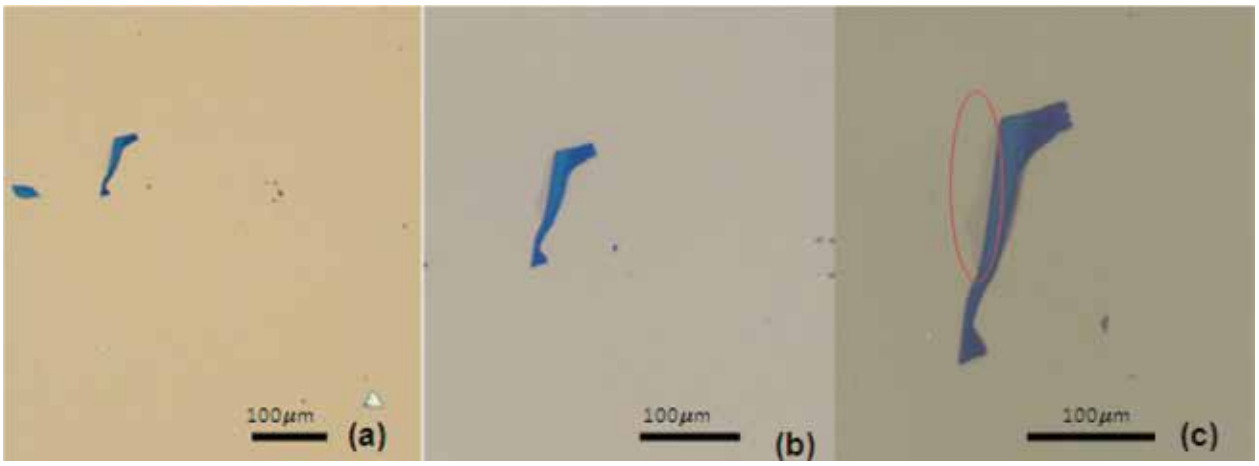

Fig. 7. Optical image of third flake over 90nm Si/SiO_2 substrate at (a) 20x (b) 50x (c) 100x.

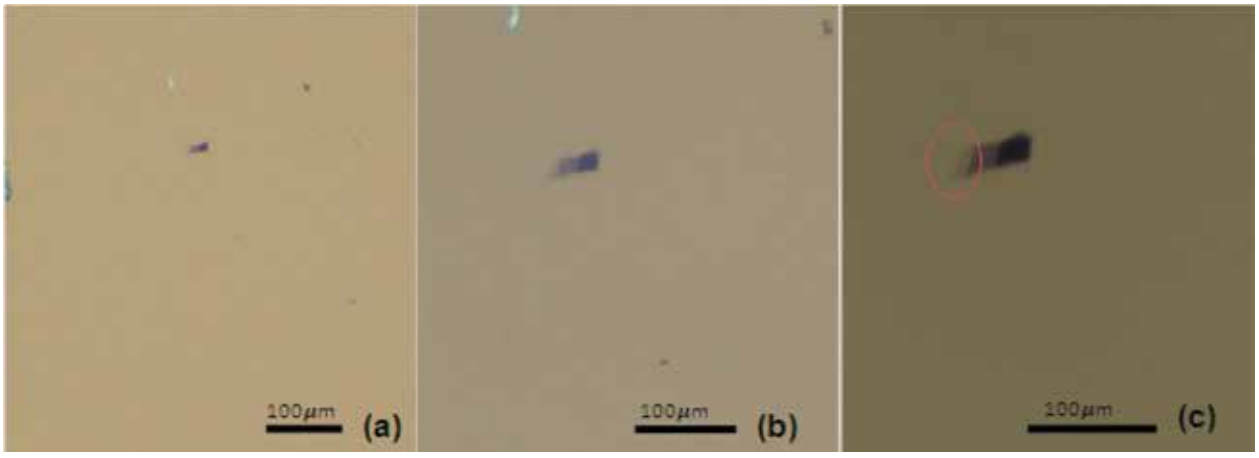

Fig. 8. Optical image of fourth flake over 90nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

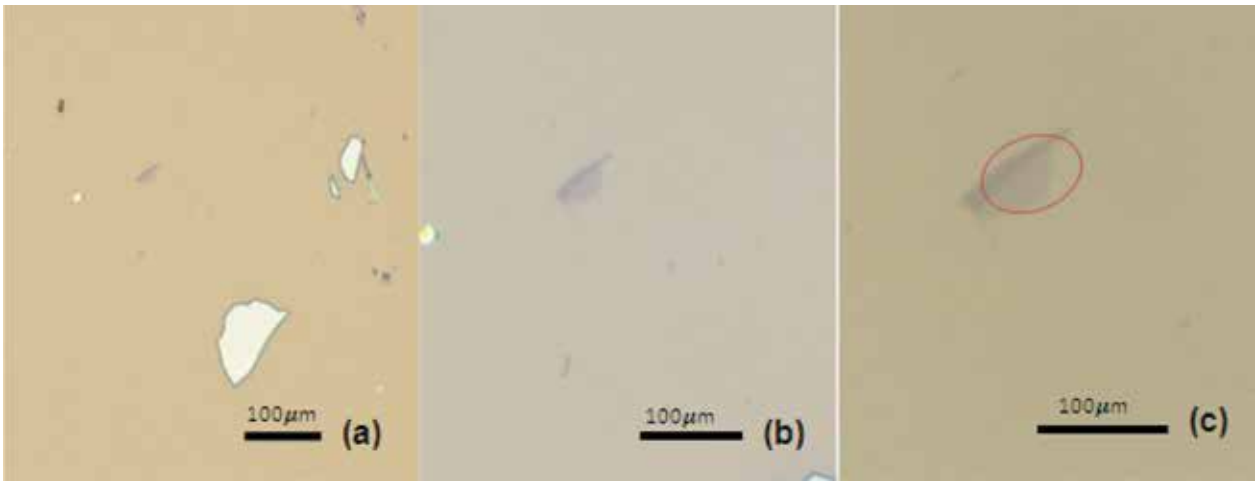

Fig. 9. Optical image of fifth flake over 90nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

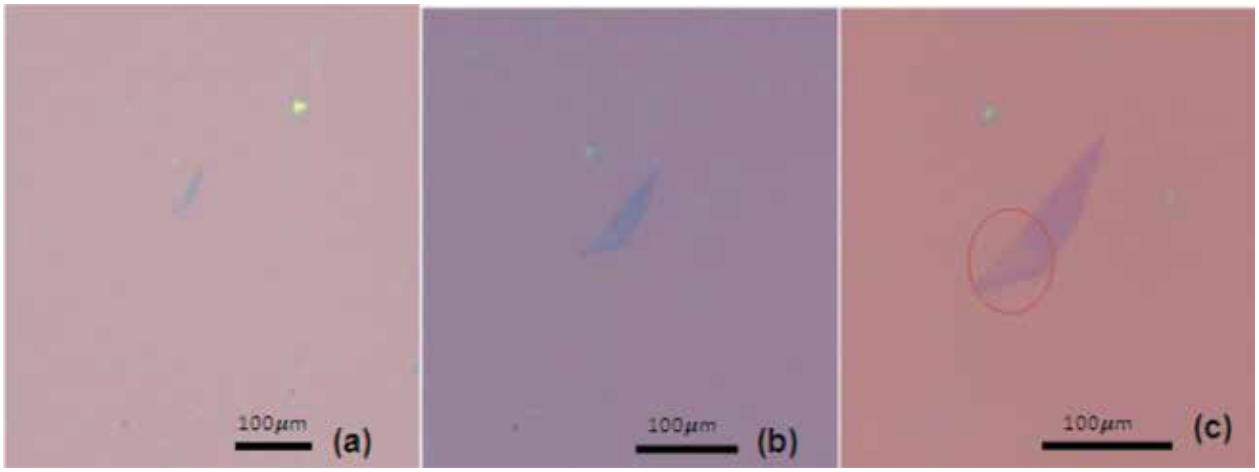

Fig. 10. Optical image of first flake over 300nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

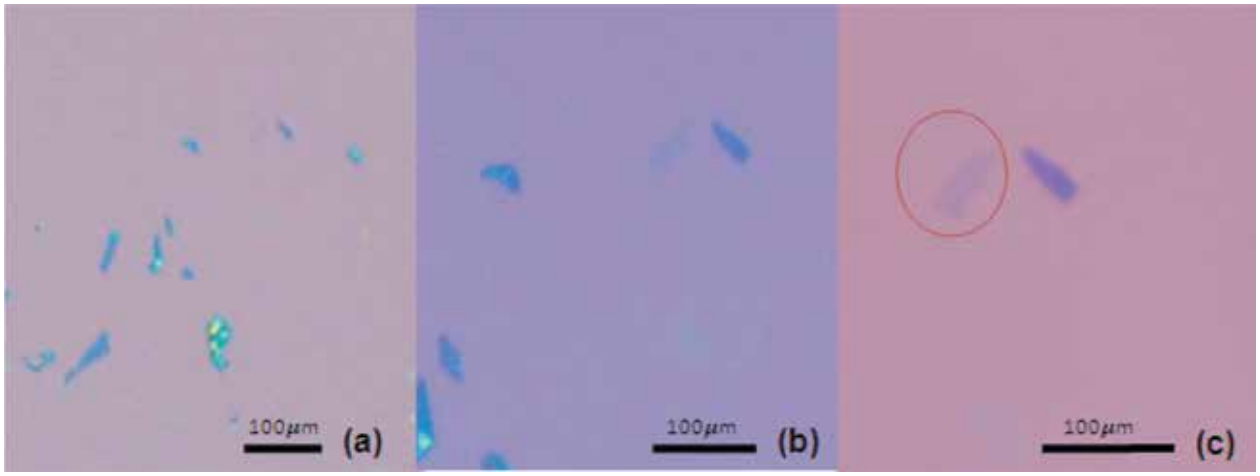

Fig. 11. Optical image of second flake over 300nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

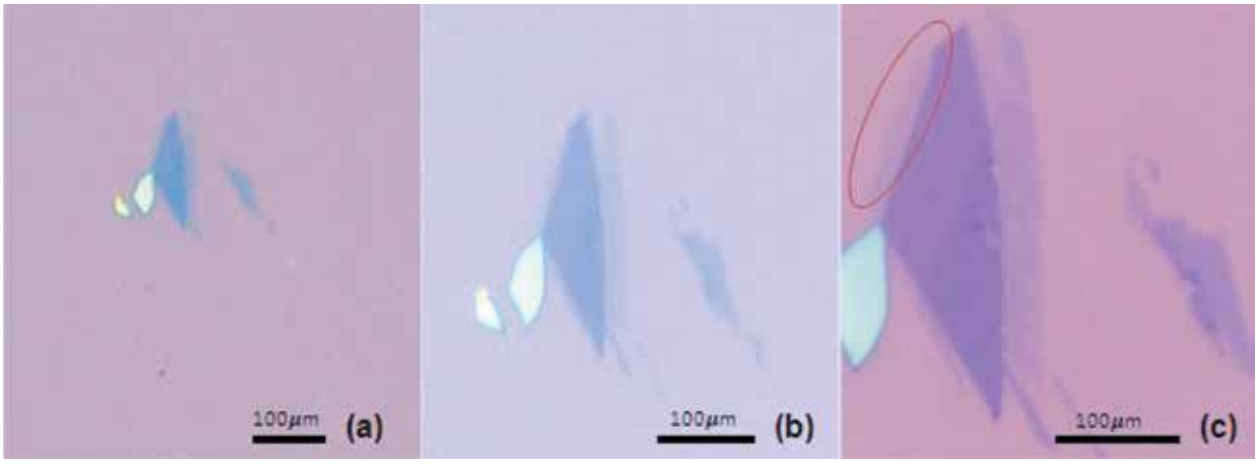

Fig. 12. Optical image of third flake over 300nm Si/SiO_2 substrate at: (a) 20x; (b) 50x; (c) 100x.

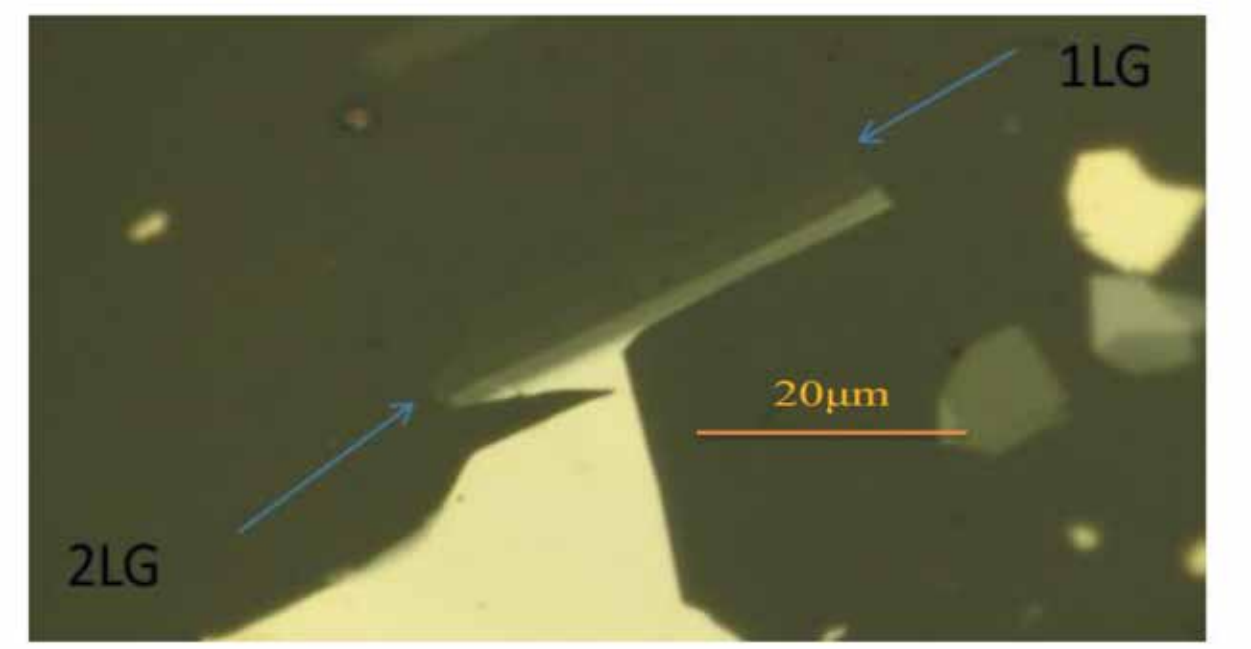

Fig. 13. Optical image for single (1LG), bi-layer (2LG) and few-layer graphene on PMMA substrate at 100x.

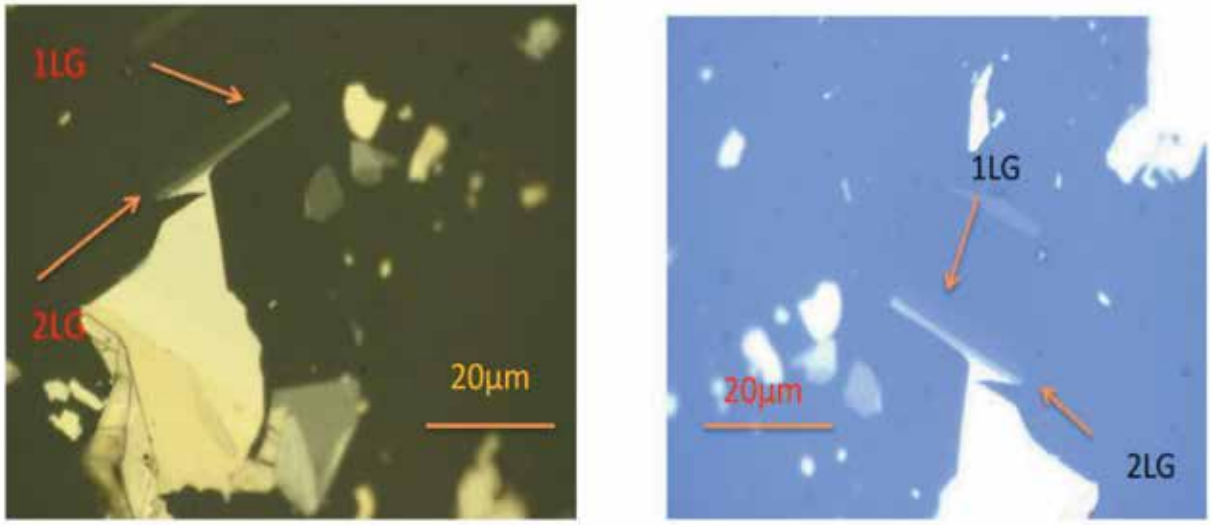

Fig. 14. Improvement in the optical contrast of graphene flakes using optical filter.

Fig. 17 shows the AFM analysis of graphene flake prepared on Si/SiO_2 substrate. When cantilever passes over the desired portion represented by the square box in Fig. 17(a), image contrast as Fig. 17(b) was obtained. By analyzing the folded region, step height of graphene layer over the substrate was obtained. The graph of Fig. 18 represents the height profile which can be used to find the number of layers. The average of these peaks is about 0.3 nm which clearly indicates that it is a single layer.

Fig. 19 shows the AFM analysis of another graphene flake prepared on Si/SiO_2 substrate. In this case, step height of about 1.0 nm was obtained which clearly shows ~ 3 layers over the substrate.

The atomic force microscopy (AFM) measurement is the most direct way to identify the number of layers of graphene. However, this is cumbersome for imaging large area graphene

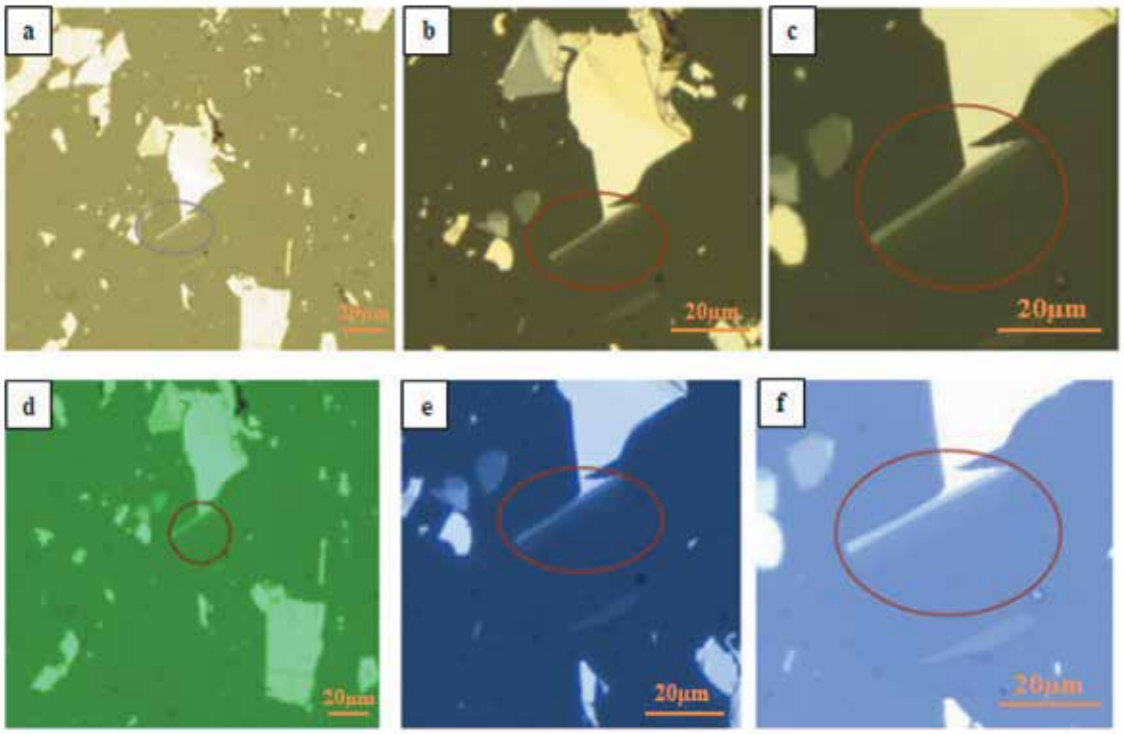

Fig. 15. Optical images of graphene flake on PMMA substrate: (a) at 20x using white light; (b) at 50x using white light; (c) at 100x using white light; (d) at 20x with green filter; (e) at 50x with blue filter; (f) at 100x with blue filter.

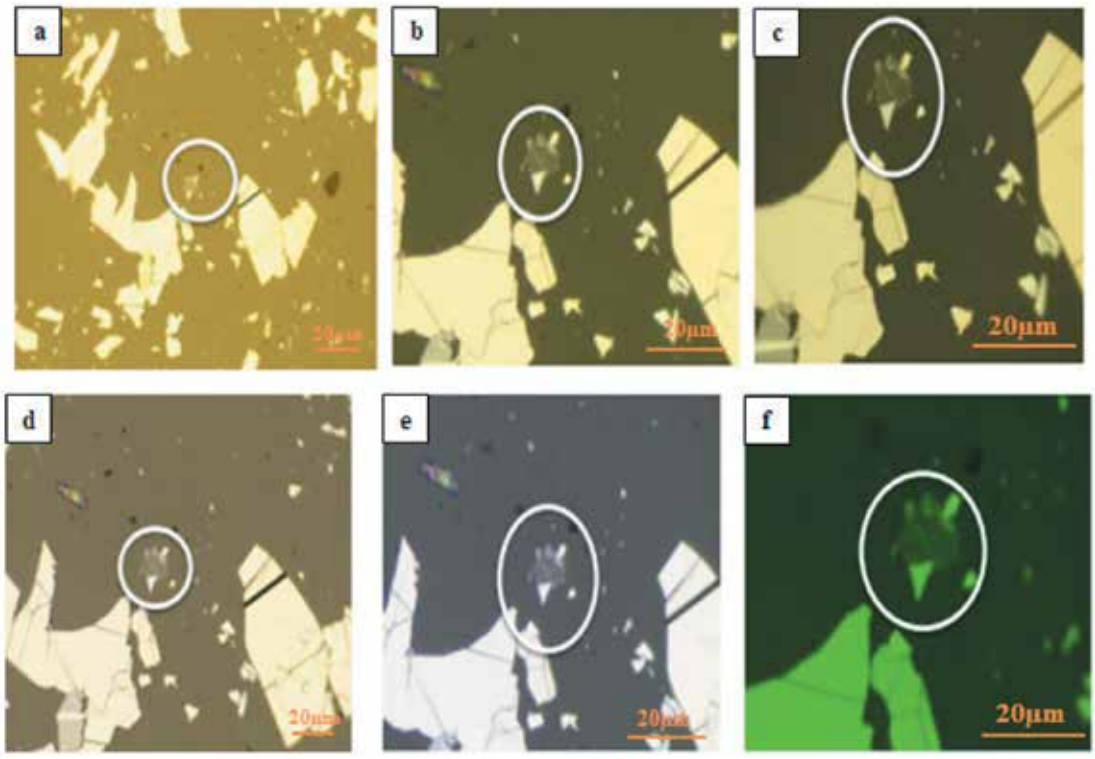

Fig. 16. Optical images of graphene flake on PMMA substrate: (a) at 20x using white light; (b) at 50x using white light; (c) at 100x using white light; (d) at 20x with LB145 filter; (e) at 50x with LB145 filter; (f) at 100x with GB530 filter.

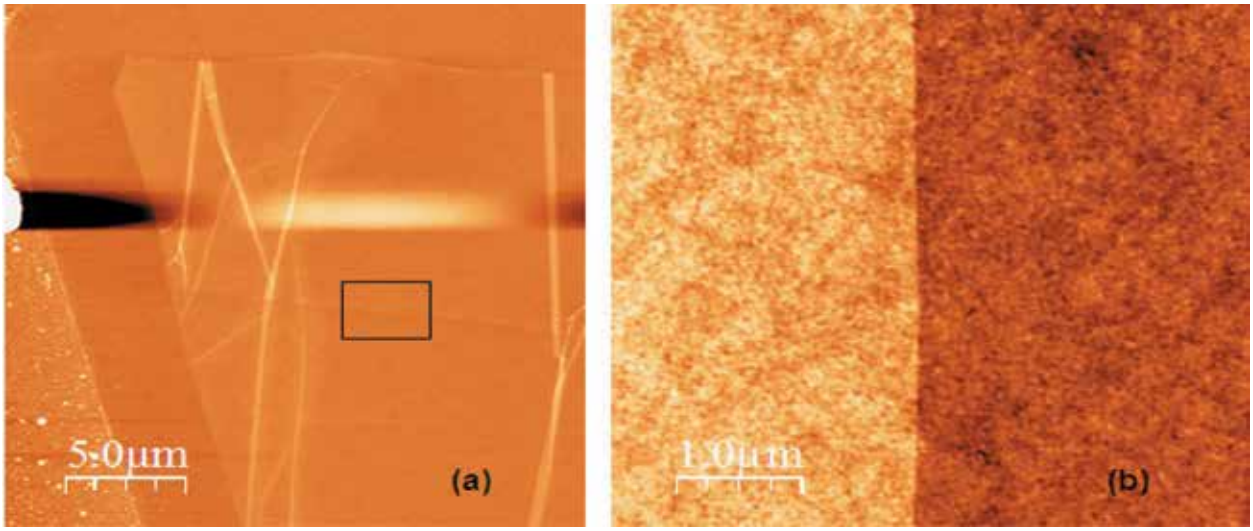

Fig. 17. AFM analysis of graphene flake.

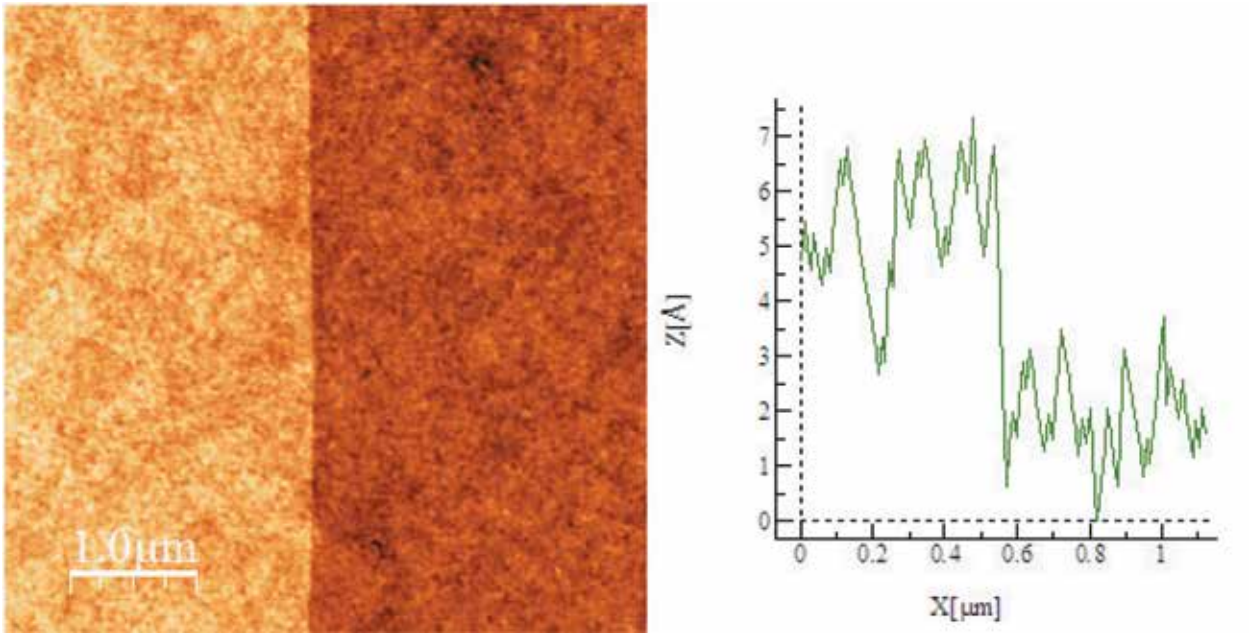

Fig. 18. Step height ~ 0.3 nm (1 layer).

and also this method has a very slow throughput. Therefore, Raman spectroscopy was used because it not only determines the number of layers but also the structure of graphene.

3.3 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Raman study of single layer, bi-layer and multilayer graphene has been reported for the first time in 2006 [19]. This is quick and unambiguous technique to provide the information about the number of layers of graphene.

In our experiment, high quality monolayer graphene was prepared on Si/SiO_2 by Micromechanical cleavage. Fig. 20 shows the Raman spectra of single layer graphene on Si/SiO_2. Two bands (G band and 2D band) were observed on Raman spectra of graphene flake. G band is used to determine the number of graphene layers. When the layer thickness increases, the band position

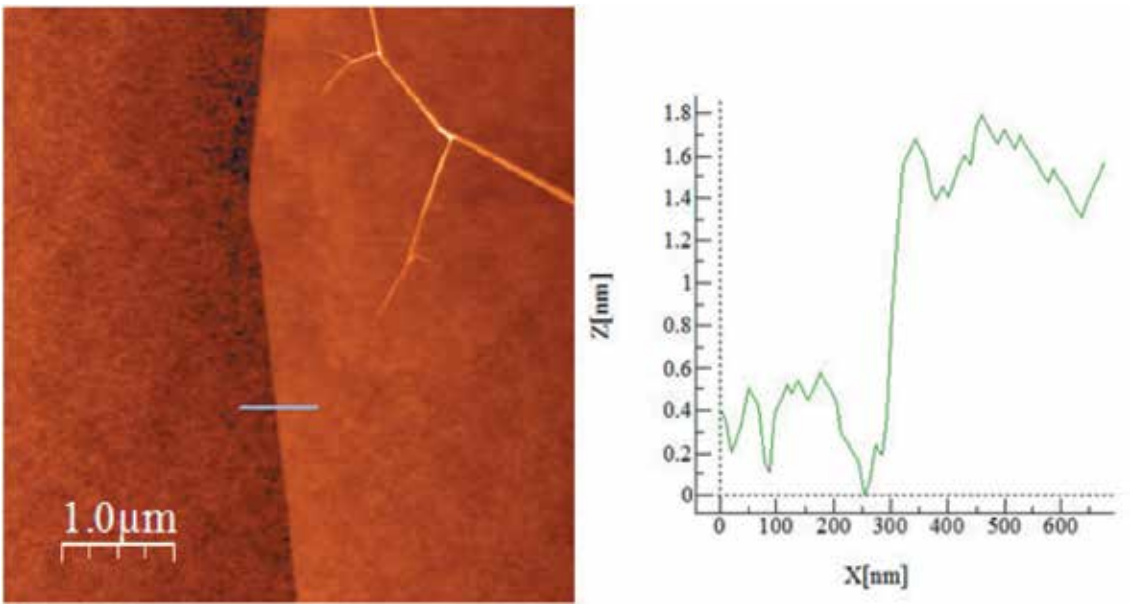

Fig. 19. Step height ~1.0nm (3 layers).

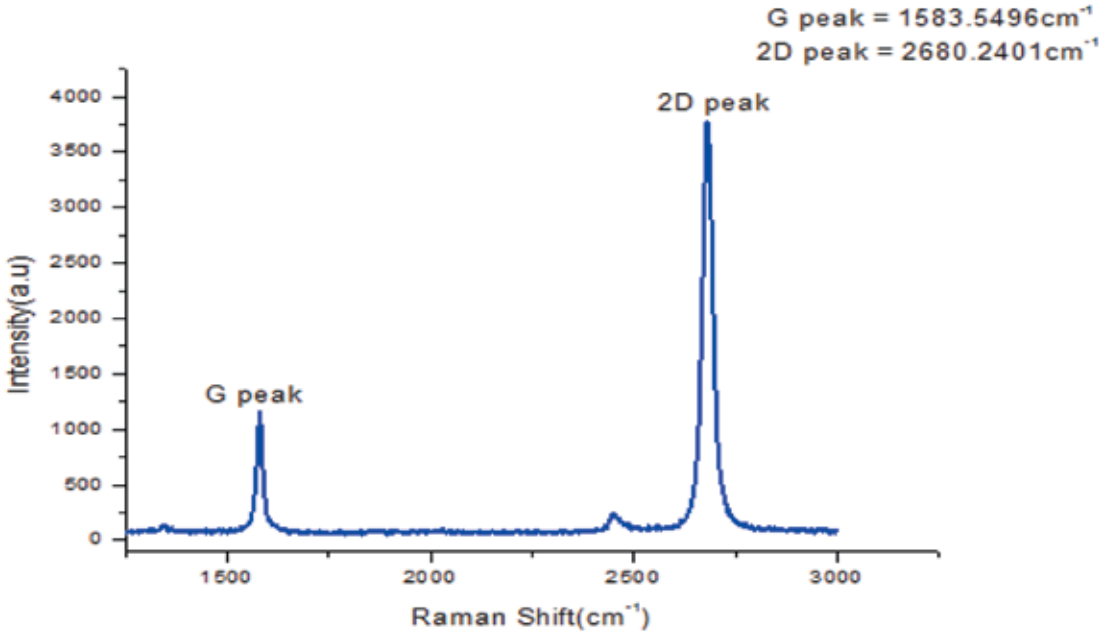

Fig. 20. Raman spectra of single layer graphene on Si/SiO_2 substrate.

shifts to lower intensity [19]. The G peak position is another important parameter which is sensitive to doping and strain. Doping causes the higher shift while strain causes the lower shift. 2D band which is also used to determine the number of graphene layers; however the differences between single and bilayer graphene in this band are more complex than that observed with the G-band. There is a general shifting to higher wave numbers as the layer thickness increases, but the more noticeable change in the band shape as 2D band splits and becomes more complex for two or more layers. With single layer graphene, there is only one component to the 2D-band, but with bilayer graphene, there are three components to the 2D-band [20]. The 2D peak conventionally called G′ peak in the Raman spectra of graphene layers. The intensity of the 2D peak is greater than G peak in single layer of graphene,

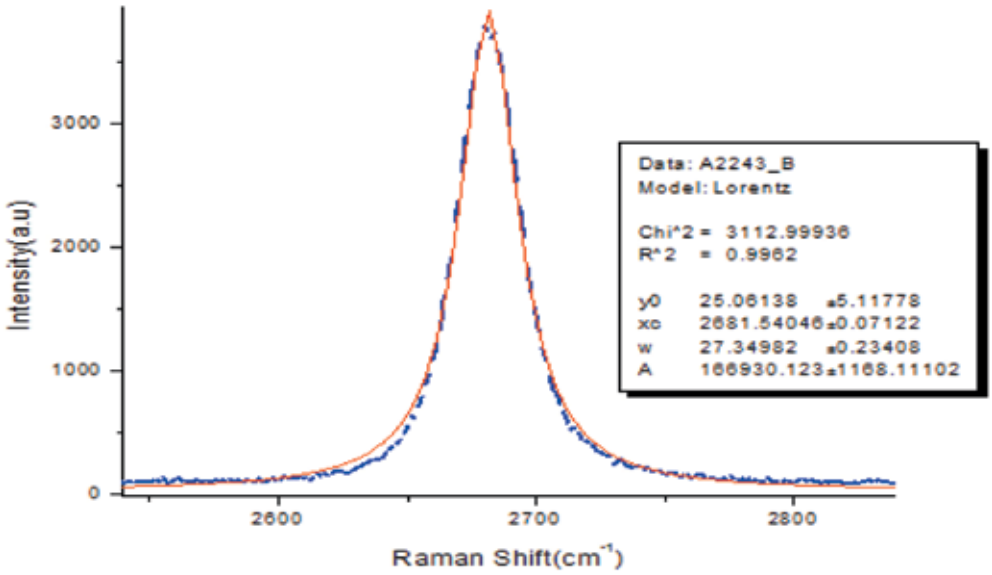

Fig. 21. Determination of width of 2D band by Lorentz fitting.

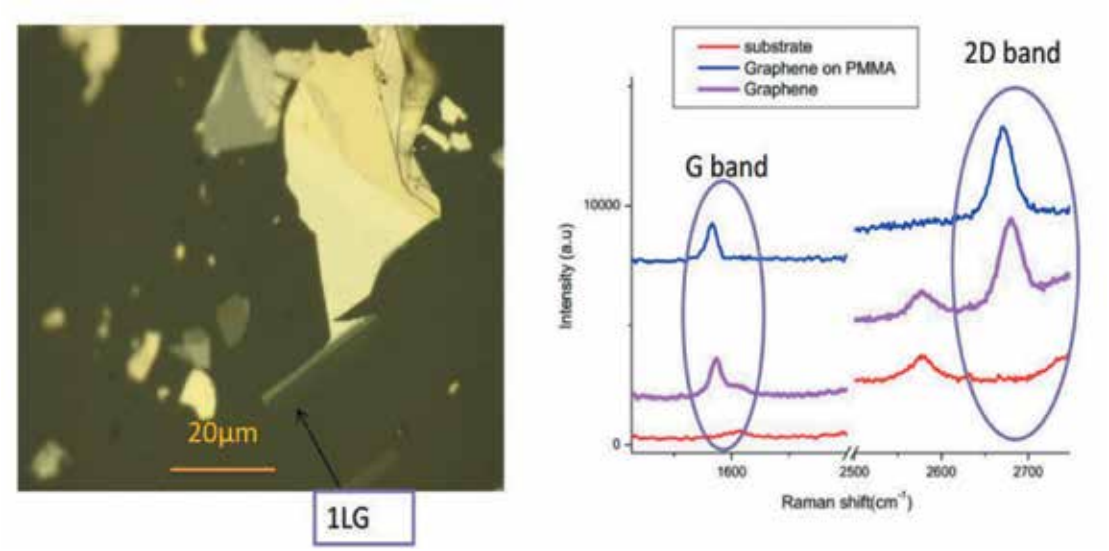

Fig. 22. Raman spectra of monolayer graphene (1LG) over PMMA substrate.

but as the number of graphene layers increased, its intensity decreased. Number of layers can be better examined by using the width of 2D peak. As the number of graphene layer increases, its width (FWHM) increases [20].

In our experiment, the peak position of G and 2D band for graphene fabricated over Si/SiO_2 were respectively located at 1583.54 cm^{-1} (very close to the actual value for single layer ~ 1580 cm^{-1} [21] and is doped) and 2680.24 cm^{-1} (very close to the actual value for single layer ~ 2700 cm^{-1} [21]).

We used lorentzian curves to fit the spectra and obtained the FWHM of 2D band as shown in Fig. 21. The FWHM of 2D band was 27.34 cm^{-1} indicates that it is single layer [20, 22-23].

The Raman spectra of the graphene fabricated over PMMA using laser of 514 nm wavelength is shown in the Fig. 22. The prominent G peak appears at 1580 cm^{-1} and 2D peak (Ǵ peak) at 2680 cm^{-1} in the monolayer of graphene. The same peak was obtained on Si/SiO_2 substrate, which means

that these peaks are independent of the substrates. The intensity of the G line changes with the number of graphene layers. After applying the Lorentzian in origin we have found that 30 cm^{-1} is FWHM in monolayer and 50 cm^{-1} in bilayer graphene over PMMA substrate.

4. CONCLUSIONS

Samples of graphene have been fabricated on oxidized silicon (with 90 nm and 290 nm oxide thickness) and PMMA substrate by using micromechanical cleavage method. Micromechanical cleavage method is reproducible and yield large number of high quality graphene flakes successfully.

The graphene layers thus produced have been successfully identified and characterized using optical microscopy showing single layer, bilayer, tri-layer and multi-layer graphene by contrast analysis which shows that on 90 nm Si/SiO_2 substrate single layer shows the grey color and multilayer goes towards the white, on 300 nm Si/SiO_2 substrate single layer shows the purple color and multilayer goes towards the blue. But on PMMA substrate thin flakes show the dark grey color and thick flakes go towards the white grey. By using optical filters image quality is improved and better contrast can be obtained.

Two graphene flakes identified by optical microscopy were selected for AFM analysis. The graphene flake fabricated on 90 nm Si/SiO_2 substrate shows the step height ~ 0.3 nm (very close to the actual value of single layer ~ 0.335 nm) indicates that it is single layer. The other fabricated on 300 nm Si/SiO_2 substrate shows the step height ~ 1.0 nm (very close to the actual value of three layers ~ 1.005 nm) indicates that it is tri layer over the substrate.

Raman spectroscopy was performed for graphene fabricated on 90nm Si/SiO_2 substrate and PMMA substrate. Raman spectrum for Si/SiO_2 substrate shows two peaks named as G peak and 2D peak at the positions 1583.54 cm^{-1} (very close to the actual value that is ~ 1580 cm^{-1}) and 2680.24 cm^{-1} (very close to the actual value that is ~ 2700 cm^{-1}), respectively. The same peaks were obtained for PMMA substrate named as G peak and 2D peak at the positions of 1580 cm^{-1} and 2680 cm^{-1} respectively. It suggests that underlying substrate does not change the graphene peaks that are G and 2D. Lorentz curve fit was applied to 2D peak to determine the width of peak as 2D width is helpful in counting the number of graphene layers. Our results give the FWHM of about 27.34 cm^{-1} for graphene sampled on Si/SiO_2 showing mono layer. For graphene sampled on PMMA, FWHM of about 30 cm^{-1} and 50 cm^{-1} were obtained showing mono layer and bilayer.

5. ACKNOWLEDGEMENTS

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