# ENLARGING THE SURFACE AREA OF MONOLAYER GRAPHENE SYNTHESIZED BY MECHANICAL EXFOLIATION

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**Abstract**–A method of enlarging the surface area of monolayer graphene produced by mechanical exfoliation of graphite and increasing the possibility of obtaining monolayer graphene is suggested. The enlargement of the surface area of monolayer graphene is due to additionally cleaving few layer grapheme adjacent to the monolayer. Raman spectroscopy and atomic force microscopy (AFM) are used to characterize as-prepared and enlarged areas of monolayer graphene and graphite.

Keywords: monolayer graphene, graphite, mechanical exfoliation, Raman spectroscopy, AFM

#### **1. Introduction**

Graphite is a highly anisotropic material made of weakly coupled layers of carbon atoms bonded in a hexagonal lattice. Its building-block, an isolated single atomic layer (monolayer) called graphene, is only recently accessed experimentally [1-6]. Although the stacking of graphene layers is only supported by a weak interlayer coupling, the electronic properties change dramatically for the monolayer graphene as compared to the bulk graphite. As graphene is a new nano-material with unusual electronic properties, its electronic, optical, thermal and other properties have not been studied completely yet [7-11]. Knowledge of how these properties evolve from monolayer graphene to graphite will facilitate the development of graphene devices. In particular, optical detection relying on light scattering is especially attractive, because it is fast, sensitive, and non-destructive. Raman scattering has recently emerged as a viable, non-destructive technique for the identification of mono- and few layer graphene [12-15].

Currently, graphene is prepared by different methods such as mechanical exfoliation of graphite using scotch tape [2], chemical exfoliation of graphite [3], epitaxial growth of graphene by thermal graphitization of SiC [12], chemical vapor deposition of hydrocarbon gases on transition metals [13], exfoliation of graphite by sonication [14], etc. However, at present there is no ideal method for synthesizing defect free graphene sheets. Detailed understanding of growth kinetics and production control is highly desired to prepare large-scale high quality graphene. Disadvantages of the mechanical exfoliation (cleavage) or Scotch tape method, which is the first method of obtaining two-dimensional crystals, are small surface area of monolayer graphene obtained [15].

The aim of the paper is to enlarge the surface area of monolayer graphene produced by mechanical exfoliation of graphite and increase the possibility of the obtaining monolayer. To reach these goals an additional cleaving method is suggested.

### 2. Experiment

Graphene samples are synthesized by Scotch tape method, identified by optical microscopy, and characterized then by Raman spectroscopy and AFM. For synthesizing graphene samples, oxidized Si wafers (with areas of ~1×1 cm<sup>2</sup>, thickness of 525  $\mu$ m and resistivity of 0.001–0.005  $\Omega$  cm) are used. The thickness of SiO<sub>2</sub> on the top of Si substrate was 300 nm.

The Raman spectra are measured by WITec Alpha300 Raman system (spectral resolution of spectrometer is 1 cm<sup>-1</sup>) using a laser excitation of 632.6 nm, 514.5 nm and 487.9 nm (with a triple frequency He-Ne and Ar lasers as excitation source) delivered through a single-mode optical fiber, whose spot size is limited by the diffraction. Using a long working distance focusing objective lenses ( $10 \times$  and  $100 \times$ ) with numerical apertures NA = 0.90 and 0.80, the spot size of about 500 nm is obtained. With an incident light power of 0.2mW, heating effects can be neglected. The Raman spectra are measured using a grating with 1800 g/mm and a solid state cooled CCD detector. The Raman spectra of as-prepared and elaborated monolayer graphene samples with different areas were recorded under the same experimental conditions. The topography and height profiles of graphene samples are obtained by non-contact AFM.

#### 3. Results and Discussion

Graphene samples are prepared by Scotch tape method, which is the following [1]. Graphene is produced by micromechanical cleavage or exfoliation (repeated peeling) of highly oriented pyrolytic graphite by the scotch tape, i.e. slicing this layered material by gently rubbing it against another surface on the scotch tape. After that, it is transferred to an oxidized silicon wafer covered with SiO<sub>2</sub> layer with thickness of 300 nm. Under an optical microscope with a  $50 \times$  or  $100 \times$ objective lens, it is possible to see plenty of thick and tiny flakes of graphite on Si/SiO<sub>2</sub> wafer: large, shiny pieces of all kinds of shapes and colors (Fig.1a). The optical images of as-prepared graphene samples with different magnification obtained after micromechanical cleavage of bulk graphite are shown in Fig.1. It is possible to observe monolayer graphene: highly transparent, crystalline shapes having little color compared with the rest of the substrate (Fig.1b). The ability to create graphene with such a simple procedure ensures that graphene was produced an uncountable number of times since graphite was first mined and the pencil invented in 1565.

After preparation of the graphene samples the identification of graphene layers is still a serious obstacle. It is extremely difficult to find small graphene pieces in the haystack of millions of thicker graphitic flakes, which appear during the cleavage (Fig.1a). For that reason at the beginning the surface of graphene carefully scanned in an optical microscope, which allows distinguishing mono- or few-layer graphene from bulk graphite. With the thickness of 300 nm of SiO<sub>2</sub> cap layer, the ultrathin graphitic flakes get visible with an optical microscope. Few layer graphene flakes are

sufficiently transparent to add to an optical path, which changes their interference color with respect to an empty substrate. For a certain thickness (300 nm) of  $SiO_2$  layer, even a monolayer was found to give sufficient contrast to differentiate graphene layers among thicker flakes scattered over a substrate. These layers have a slightly different color in the optical microscope (Fig.1b). It appears that darker color corresponds to thicker sample. The color of much thicker layers (more than 10 layers) does not follow this trend and can change from blue to yellow and then to gray (Fig.1a).



Fig.1. Optical images of monolayer graphene with  $10 \times$  and  $100 \times$  magnification.

After rough identification of monolayer graphene by optical microscope (Fig.1b), it is characterized by the Raman spectroscopy (Fig.2). Raman spectra of monolayer graphene at excitation wavelength of 514 nm are shown in Figs.2 and 3. For reference Raman spectra of graphite on a SiO<sub>2</sub>/Si substrate is presented. There are four pronounced peaks in the Raman spectra of graphene and graphite on the SiO<sub>2</sub>/Si substrate (Fig.2). The first two peaks at 520 cm<sup>-1</sup> and 960 cm<sup>-1</sup> are due to first- and second-order Raman scattering by optical phonons of the Si substrate. The third peak at 1580 cm<sup>-1</sup> (the G peak) is due to the  $E_{2g}$  phonon at the Brillouin zone center of graphene; while the last peak – the second order of the D peak (the 2D peak) at around 2700 cm<sup>-1</sup> is due to second-order Raman scattering by in-plane transverse optical phonons near the boundary of the Brillouin zone of graphene. There is also another peak – D peak, which lies at around 1360 cm<sup>-1</sup> (Fig.2). The D peak is due to the breathing modes of sp<sup>2</sup> atoms and requires a defect in graphene for its activation.

The Raman signal of monolayer graphene is strong and even comparable to that of bulk graphite. The major Raman features of graphene and graphite are the G and 2D bands. The obvious difference between the Raman features of monolayer graphene and graphite is the 2D band. It is always seen, even when no D peak is present, since no defects are required for the activation of second order phonons. The shape of 2D peak distinguishes mono- and multilayer graphene. Monolayer graphene has a sharp and symmetric, single 2D peak, in contrast with few-layers graphene and graphite it can be fitted with four peaks.



Fig.2. Raman spectra of monolayer graphene and graphite on SiO<sub>2</sub>/Si at excitation wavelength of 514 nm.



Fig.3. Raman spectra of monolayer graphene and graphite at excitation wavelength of 514 nm.

Our samples showed that the G band is at 1580 cm<sup>-1</sup> and 2D band at 2700 cm<sup>-1</sup> (Figs.2 and 3). As our samples have good quality, there is no the D band at 1340 cm<sup>-1</sup>, which shows the absence of defects of graphene. The FWHM of the 2D peak of monolayer graphene is 30 cm<sup>-1</sup>. Thus, Raman spectra confirm that there is a monolayer graphene on silicon substrate [1-4]. The analysis of Raman spectra shows that the most obvious differences of Raman features in graphene layers and graphite are as follows (Fig.3): a) 2D peak is single and sharp for monolayer graphene, b) FWHM of 2D peak is ~ 30 cm<sup>-1</sup> for monolayer graphene, c) ratio of intensity of 2D peak over intensity of G peak ( $I_{2D}/I_G \ge 1$ ) is more than one, d) G peak position of graphene with lower wave number than graphite. The topography imaging of mono- and few-layer graphene is performed by the AFM measurement (Fig.4). The AFM gives a height of 0.66 nm of monolayer graphene (Fig.5).



**Fig.4.** Optical images of a) as-prepared (by Scotch tape method) and b) enlarged (by suggested method) monolayer graphene areas with  $100 \times$  magnification.



Fig.5. Height profile of monolayer graphene taken by AFM.

Thus, the Scotch tape method was found to be highly reliable and allows preparing graphene samples – mono- and few-layer (less than 10) graphene flakes with different areas on  $Si/SiO_2$  substrates. However, the surface areas of monolayer graphene prepared by this method are too small. To enlarge them the following method is suggested. Usually after preparation of graphene sample by Scotch tape method monolayer graphene areas are mostly formed in few layer graphene areas adjacent to monolayer. According to the suggested method an additional cleaving of the sample by scotch tape is realized. For that purpose, the scotch tape is stuck to the surface of the sample, removed from it and then the procedure is repeated for several times. As a result of this common procedure, few layer (double, triple, etc) areas adjacent to the monolayer graphene area will be additionally cleaved and new monolayer areas will be formed on the expense of the cleavage of the few layer graphene areas. Consequently, the initial surface area of monolayer graphene prepared by Scotch tape method (Fig.4a) can be enlarged several times (Fig.4b). Besides, additional

cleavage of graphene sample will increase the possibility of obtaining monolayer graphene. The enlarged areas of monolayer graphene (Fig.4) are characterized by the Raman spectroscopy (Fig.3) and AFM (Fig.5) to make sure that the obtained enlarged areas are monolayer graphene too.

## 4. Conclusion

The suggested method allows enlarging the surface area of monolayer graphene produced by mechanical exfoliation of graphite and increasing the possibility of obtaining it. The enlarging of the surface area of monolayer graphene is due to the additional cleaving of few layer graphene adjacent to the monolayer. The Raman spectroscopy, which is non-destructive, fast and sensitive to the structure and chemistry of the material, and AFM are used to characterize as-prepared and enlarged areas of monolayer graphene and distinguish it from few-layer graphene and graphite.

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