Observation of diode-like characteristics in planar-type structures of graphite flakes

V Gunasekaran and S-J Kim
Nano Materials and System Lab, Department of Mechanical System Engineering, Cheju National University, Cheju 690-756 Korea
E-mail: kimsangj@cheju.ac.kr

Abstract. We have investigated transport behavior for several in-plane areas of planar-type structures of graphite flakes. Those areas of 10x10 μm², 6x5 μm² and 6x2 μm² are fabricated by focused ion beam (FIB). Electrical resistance has been measured from 300 K to 25 K for these planar-type structures with decreasing in-plane areas. This result indicates a reduced size of planar-type structure restricts the tunnelling of charge carriers by increasing resistance of planar-type structure area. All of these sizes of fabricated planar type structures show diode-like characteristics in current (I) - voltage (V) curves around 25 K and ohmic behaviour around 300 K. The size of the planar-type structure affects the shape of I-V curve. Due to weak interlayer interaction forces (Van der Waals forces) between neighbouring layers of graphite flake, the high electrical resistance may be generated by the adjacent domains.

1. Introduction
In recent days, the research on graphite materials such as two-dimensional graphene (single atomic layer of carbon), zero dimensional fullerenes (C60) and carbon nanotubes have been attracted much attention for their unique properties about micro and nano-electronic applications. Graphite is a three dimensional (3-D) material which has a sheet like layered structure where the carbon atoms all lie in a plane and are only weakly bonded to the graphite sheets above and below. Graphite is normally a basic material for all above structures. Particularly, graphene becomes an active replacement material for silicon which is being used heavily in semiconductor industries nowadays [1-3]. As per the relativistic Dirac theory, it is predicted that the charge carriers in graphene have mass less fermions which can travel thousands of lattice spacing without any scattering [4-5]. Graphite consists of stacked layers of many graphene sheets held together by weak interlayer interaction forces [6]. Each sheet have hexagonal lattice of carbon bonded by strong σ bonding (sp²) in the ab-plane. For ab-plane conductivity, the perpendicular π-orbital electrons along the c-axis are responsible [7]. To synthesize thin graphitic layers directly on top of a substrate [12] or to extract using chemical [13] or mechanical [14-15] has been experimentally performed to produce graphitic samples with thicknesses ranging from 1 to 100 nm. The studies on bulk graphite has been investigated for many years, however there has been no work done on thin graphite planar-type structures. The temperature dependent electrical transport measurements on these planar-type structures have not been measured due to the reason that the geometry and size for these structures are considered as too small for these experiments.

We present in this letter, a method used to extract thin graphite layers from bulk highly oriented pyrolytic graphite (HOPG). These graphite layers have thicknesses ranging from 400-500 nm. We
have used freshly cleaved HOPG material for this investigation. For temperature dependent transport measurement studies, we have fabricated the planar-type structure devices consisting graphite crystallites (thickness 400 nm to 500 nm). We were able to obtain micron scale thin graphite layers by simply peeling off the graphite layers using 3M scotch tapes. Alternative methods like epitaxial growth on SiC substrates [8] and exfoliation [9] can be also used to obtain quality graphite layers. However, these methods are not suitable for large-scale manufacturing. All of these methods are time-consuming and also not-simple.

2. Experiments
We used Si/SiO₂ substrates which were cleaned by acetone. Then the substrates were put in ultrasonic bath for 15 min. The thickness of SiO₂ layer on Si substrate is approximately 300 nm. In this peeling off method, we used HOPG as a source material. First, this graphite material is fixed on an adhesive tape. By using another adhesive tape, we have done repeated peeling off of graphite layers in order to obtain very thin graphite layers. Thin graphite layers were identified by an optical microscope. Next, these thin flakes of graphite layers are transferred to surface of Si/SiO₂ substrate by simply touching the adhesive tape where the thin graphite layers identified. This process allows us to prepare several samples in a matter of hours, which is the main advantage of this method. The rate of sample reproducibility is quite good in this method. The electrical contacts were prepared with silver paste for the electrical measurements. We annealed the contacts in 300 °C to decrease the contact resistance.

The planar-type structures on graphite layer were fabricated by focused-ion-beam (FIB) etching. The thickness 500 nm of graphite layer has chosen for fabricating planar-type structures. These micro-fabrication etching details were discussed in detail elsewhere [10,17]. We have fabricated 10x10 µm², 6x5 µm² and 6x2 µm² sizes of planar-type graphite structures using FIB. (SII Inc.Model SMI2050).

3. Results and Discussion
The temperature dependent transport measurements of the planar-type graphite structures were been carried out in Close-cycle refrigerator (SUMITOMO, Helium Compressor unit). In figure 1 we show a FIB image of the 10x10 µm² planar-type structure fabricated in thin graphite layer (scale 20 µm). We observed similar semi-conducting behavior for other planar-type structures 10x10 µm², and 6x2 µm². However the value of resistance at 300 K and 25 K varies which is depending on the fabrication size of the planar-type structures. It is observed that the sample generates high resistance when the fabrication size of the planar-type structure decreases.

![Figure 1](image1.png) **Figure 1** FIB image of planar-type structure fabricated in graphite flake by FIB.

![Figure 2](image2.png) **Figure 2** R-T characteristics of 6x5 µm² planar-type structure. Inset shows metallic behavior of graphite flake which have no planar-type structure.
Resistance (R) – Temperature (T) measurements were carried out for these planar-type structures. In figure 2 we show R-T results on a 6x5 μm² planar-type structure. The measurement was carried out from 300 K to 25 K. The in-plane resistance shows a gradual increase into high resistance value of Mega ohm at 25 K. This exhibits semi-conducting behavior and also found a small drop in resistance at 49 K. The generation of high resistance is contributed by stronger boundary scattering in thinner samples [11]. As well as it has been previously reported that the energy gap in thinner layers becomes large which provides high resistance to charge carriers [16]. The enough π-orbital electrons are not available in case of thinner layers, cause less mobility of charge carriers. However the thicker flakes which don’t have planar-type structures show metallic behavior as well (The inset in figure 2). The reason for temperature value where the resistance drops (∼ at 49 K) is believed due to the offset of weak localization behavior of charge carriers in graphite layer at this temperature range. Since graphite is considered as a low carrier density, high purity semi-metal [6], we observed both metallic nature for thicker samples and semi-conducting behavior for thinner samples.

The I-V characteristics of 6x5 μm² planar-type structure measured at various temperatures from 300 K to 25 K is shown in figure 3. The I-V characteristics show ohmic behavior at 300 K and diode-like characteristics observed at 25 K. The asymmetric I-V curves were obtained. As the temperature goes down, the ohmic characteristics turn into diode-like behavior. The comparison of I-V characteristics for 10x10 μm², 6x5 μm² and 6x2 μm² planar-type structures, measured at 25 K presented in figure 4. It is observed that while the fabrication size reduces, the value of respective forward and reverse bias voltages in I-V curve get increases. Due to weak interlayer interaction forces (Van der waals forces) between neighboring layers of graphite flake, the high electric resistances generated by adjacent domains. Because of this resistance, the bias voltage is shifting to higher value gradually when the temperature goes down to 25 K. This result indicates a reduced size of planar-type structure restricts the tunnelling of the charge carriers.

**Figure 3**  I-V characteristics for the 6x5 μm² planar-type of structure in various temperatures. Asymmetric I-V curve observed.

**Figure 4** Comparison of I-V characteristics of all planar-type structures at 25 K, show diode-like characteristics.
4. Conclusion
In conclusion, our studies have shown a new pathway for fabrication of planar-type structures in thin graphite flakes using FIB. Our results have the implication that by using FIB 3-D etching technique, micrometer size planar-type structures can be fabricated in any desired shape. Particularly, we observed diode-like characteristics at 25 K and ohmic behavior at 300 K from our $I-V$ measurements done for planar-type structures fabricated in graphite flake. A clear asymmetric $I-V$ curves were observed for these planar-type structures. These planar-type structures are suitable to be used as building elements for fabricating new microelectronic devices and nano structured materials.

5. References
[1] Javey A, Jing G, Qian W, Lundstrom M and Dai H 2003 *Nature (London)* **424** 654
[2] Wind S J, Appenzeller J, Martel R, Derycke V and Avouris P 2002 *Appl. Phys. Lett.* **80** 3817
[3] Tans S J, Verschueren R M and Dekker C 1998 *Nature (London)* **393** 49
[4] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 *Proc. Natl Acad. Sci. USA* **102** 10451
[5] Zhang Y, Tan Y W, Störmer H L and Kim P 2005 *Nature* **438** 201
[6] Kelly B T 1981 *Physics of graphite; Applied Science: London, Englewood, N.J* pp 267-361
[7] Banerjee S, Sardar M, Gayathri N, Tyagi A K and Baldev Raj 2006 *Appl. Phys. Lett.* **88** 062111
[8] Claire Berger, Zhimin Song, Xuebin Li, Xiaosong Wu, Nate Brown, Cécile Naud, Didier Mayou, Tianbo Li, Joanna Hass, Alexei N M, Edward H C, Phillip N F and Walt A. de Heer 2004 *J. Phys. Chem. Lett.* **B 108** 19912
[9] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666
[10] Kim S J and Yamashita T 2002 *J. Appl. Phys.* **91** 8495
[11] Yuanbo Z, Joshua P S, William V P and Philip K 2005 *Appl. Phys. Lett.* **86** 073104
[12] Itoh H, Ichinose T, Oshima C and Ichinokawa T 1991 *Surf. Sci. Lett.* **254** L437
[13] Viculis L M, Jack J J and Kaner R B 2003 *Science* **299** 1361
[14] Ebbesen T W and Hiura H 1995 *Adv. Mater. (Weinheim, Ger.)* **7** 582
[15] Lu X, Huang H, Nemchuk N and Ruoff R 1999 *Appl. Phys. Lett.* **75**, 193
[16] Zhou S Y, Gweon G H, Fedorov A V, First P N, Deheer W A, Lee D H, Guinea F, Castro Neto A H and Lanzara A 2007 *Nature*, **6** 770 - 775
[17] Kim S J, Latyshev I Yu and Yamashita T 1999 *Appl. Phys. Lett.* **74** 1156

Acknowledgments
We gratefully thank Prof. H.– J. Lee, POSTEC, Korea for supply of graphite material for our research.