

Large Area Graphene Derived Form Natural Graphite

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Abstract

Graphene is the ideal material for many dream applications, such as single electron transistors, field emission sources [1], light through electrodes, clothing solar cells, terra hertz surface acoustic wave (SAW) filters, wall paper displays, UV light emitting diodes, atomic gas sensors, DNA or antigen wafers...etc. However, a practical method to fabricate meter-sized graphene is still beyond imagination. We made use the mechanism of diamond synthesis in liquid phase and produced graphene of several hundreds microns. Such graphene revealed silk-like tenderness with transparent folding lines. This promising process appears scalable for making device-sized graphene in the near future. This paper also presented many intriguing aspects related to the growth of large graphene. We also proposed a new hypothesis of graphene formation by the catalytic exfoliation of graphite in molten iron group alloys.

Keywords: Graphene, Diamond Synthesis, Crystal Growth, Recrystallisation

1. Introduction

Graphene, the hexagonal network of a single graphite basal plane. It can carry electricity and heat two orders of magnitude higher than the best metal conductor, viz. silver. On a flat surface, graphene is much harder than even diamond, its allotrope, due to the shorter inter-atomic distance (1.45 Å versus diamond's 1.54 Å). However, unlike diamond that is brittle and may be shattered easily, graphene can be bent or even folded without breakage. These superlative properties make graphene an attractive material for the fabrication of future products, such as integrated circuits, semiconductor transistors, heat spreaders, transparent electrodes, solar cells, LED, humidity sensor, protein purifiers, and many more other gadgets. With a shorter bond distance (1.45 Å) than diamond (1.54 Å), graphene is actually harder diamond in two dimensions. As a surface, graphene can carry an electrical current density and phonon flux density one hundred times higher than copper. Moreover, the mobility of electrons or holes may also be two orders magnitude higher than even the fastest semiconductor.

Although graphene is the miracle material for many advanced gadgets, unfortunately, large area graphene are

not available for industrial applications. However, scientists have obtained small flakes of graphene by stripping them from graphite (e.g. pyrolytic graphite deposited by CVD [2-3]). Scientists also conceived exotic methods for making graphene. For example, graphene was formed during the thermal decomposition of acetylene with iron chloride as catalyst [4]. Graphene may be produced by evaporating silicon atoms out of SiC to force the re-arrangement of carbon atoms left behind. Graphene was also formed by exsoluting saturated carbon atoms in nickel foil [5]...etc. Most graphene samples were extracted by exfoliation of graphite in organic solvent [6]. Some graphene samples were made by reduction of colloidal dispersions of graphene oxide [7]. Even with such creative ideas, the practical way for massive production of graphene is not in sight. Moreover, as epitaxial graphene layers were deposited on a solid substrate, the lattice mismatch can distort the alignment of graphene atoms so high defectivity due to structural strain [8] is inevitable, particularly for large area deposition.

In this research, we reported a simple technology to harvest large quantities of graphene by using molten alloy as the catalyst (Chien-Min Sung, US patent pending). In the future, this method has the potential to produce meter-sized graphene by floating graphite on the molten metal like LCD glass is made today. Furthermore, a continual process (e.g. roll-to-roll) may be envisaged to produce graphene rolls as if plastic wrapper.

2. The Catalytic Conversion of Graphite to Diamond

Diamond has been synthesized for over half a century [9]. In 2007, about 1000 tons (five billion carats) of diamond grits were made as superabrasives (e.g. for sawing granite and concrete), mostly produced in China [10]. All such diamonds were formed by catalytic conversion of graphite by molten alloys. The most used today is iron-nickel alloy (e.g. Invar composition). Although there have been debate on the mechanism of diamond formation in the molten alloy, however, it is certain, the dissolution is the requirement for the molten alloy to be effective in converting graphite to diamond [11]. Iron group metals (Fe, Co, Ni) have the highest solubility of carbon of all materials; consequently, they became the prevalent catalyst for synthesizing industrial

diamond grits.

The mechanism of graphite to diamond transition has been proposed as follows. Graphite contains stacked hexagonal nets in two alternations. Each net is held tightly on the same plane with trivalent (sp^2) hybridization bonds. However, on each net, graphite atoms are not equivalent as every other atom are attracted by van der Waals force to the next net, while the others are relatively mobile. It so happens that the mobile atoms are separated by a distance (2.46 angstrom) that can be loosely matched with the size of transition metal atoms, especially when the latter is mobile in liquid form. Moreover, the electron energy of the extra carbon atom (the dangling pi bond) is close to the vacancy energy of some transition elements. The attraction of dangling electron by the vacant 3d orbital tends to pull the mobile atoms in perpendicular to the hexagonal network as to pucker the graphene layer. This puckering would displace the graphene toward making octahedral (111) face of diamond (Fig. 1). In essence, graphene is the stretched diamond surface; and diamond surface, the puckered graphene.

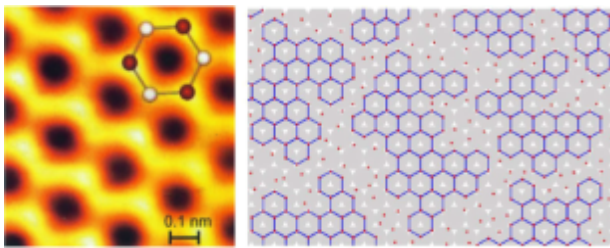


Fig. 1. The graphene as mapped by atomic force microscope with repulsive force between carbon electrons and AFM tips (left diagram). The matching of every other atom on graphene with atoms of an alloy made of iron group elements (right diagram) [12].

Due to the above described catalytic puckering of graphene by matching with molten iron group alloy, diamond is formed by converting graphite flakes of nanometer sized colloidal suspension into diamondoids that are attached to the growing diamond surface. Note that during the puckering process, while the mobile atoms are pulling toward metal atoms, the fixed atoms are bending in the opposite direction. These atoms are already loosely attached with the next layer atoms, so diamondoid bonds are formed. For growing cubic diamond, the third layer must be shuffled away from the position held by van der Waals bonds to form the rhombohedral sequence (e.g. ABCABC...). This would happen automatically as the adjacent graphene is puckered (Fig. 2).

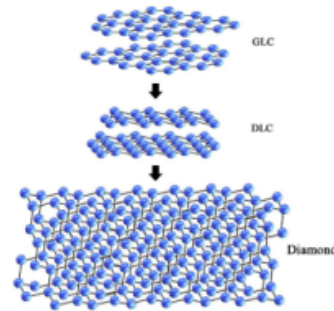


Fig. 2. The schematic illustration of puckering graphite to form diamond. Note that the graphene sequence in graphite must be shuffled to become rhombohedral before attaching to the growing diamond crystal.

Although the conversion of graphite to diamond may appear to be via the solution mechanism, there are solid evidence that the solution also act as catalyst. For example, amorphous carbon must first be graphitized before it could be converted to diamond in molten catalyst [13]. Moreover, most diamond crystals formed are euhedral with cubic (100) and octahedral (111) faces. These faces often carry oriented lamellae known as catalyst imprint. These lamellae marked the grain boundaries of solidifying catalyst (Fig. 3). It is important to note that the metal lattice tend to line up with diamond lattice.



Fig. 3. Catalyst imprint on diamond's cubic face reveal remarkable alignment of lattices between solidifying catalyst metal and growing diamond crystal.

Careful experiments performed by early GE scientists confirmed that graphite clung on the opposite side of the molten catalyst were fully in lined with diamond surface in crystal orientations [14]. All these observations confirmed that graphite may pucker to form diamond in molten catalyst, although each cluster of the puckered atoms can be nanometers in size.

3. The Experiment with Graphite and Molten Alloy

As discussed above, molten iron group alloy may act as a template to pucker graphite to form diamond under high pressure. Consequently, the same template can align graphite flakes to form polycrystalline graphene at ambient pressure. Under the influence of mobile metal atoms, the aligned graphite flakes may dissolve at the edges where the atoms are unstable, and dissolved carbon atoms may precipitate at grain boundaries as to mend the dislocated lattice. With this idea in mind, one of the authors (Sung) designed the following experiment.

4 grams of purified graphite designed for making diamond as made by Morgan Crucible (Fig. 4) were

covered on 30 grams of Invar powder (water misted) (Fig. 5). The sample was pre-pressed to form a disk of 30 mm in diameter by 20 mm in height. The charge was loaded in an alumina crucible and heated in vacuum (10^{-5} torr) at 1400 °C for four hours. The heating rate was 5 °C/min; and the cooling was made in furnace.

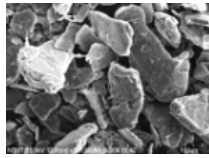


Fig. 4. The natural graphite grains up to 100 microns contain visible striations that indicated the presence of graphene layers.

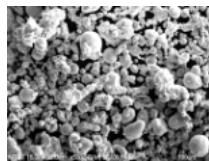


Fig. 5. The outer appearance of Invar (Fe_2Ni) alloy spheridized by spraying with steam quenched in water.

As the Invar melted, graphite dissociated at the interface by the intercalation of catalyst atoms. The graphite flakes then formed a colloidal suspension that permeated downward. Carbon atoms were also dissolved in the melt from the corners and edges of graphite flakes. When carbon atoms are saturated, carbide (e.g. cementite) may be formed. The over-saturated carbon may also exsolve to precipitate out kish graphite at the deeper region of the molten catalyst.

The similar sizes of precursor graphite and exfoliated graphene indicated that the latter was derived from the former. This is further confirmed by the near identical Raman spectra of the two carbon materials.

It was intriguing to observe that the delicate graphene could be folded over and over without breaking. Such cloth like graphene layers were observed in profusion on the experimental sample (Fig. 6).

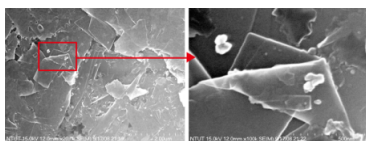


Fig. 6. The overlapping of many graphene layers with numerous folding lines. The striking feature was the cloth like bending pattern. The strength of graphene could tolerate angstroms radius bending without breaking. This figure demonstrated perhaps the sharpest folding point formed of all known materials (Fig. 7).

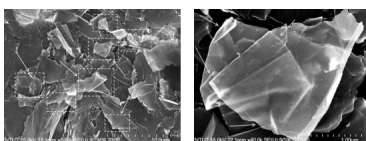


Fig. 7. The complicate overlapping of many graphene layers.

The transparency of graphene layers are demonstrated by the easy penetration of secondary electrons through hexagonal nets. This means that although graphene can carry the highest electrical density of all materials, these electrons would not block photon transmission due to their coherent energy (Fig. 8). Consequently, graphene can be the most transparent electrode possible. The application of such superb electrode can be numerous, such as the veneer of LCD screen or solar panel.

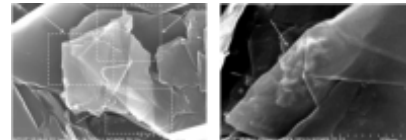


Fig. 8. The random folding of graphene cloth.

In order to enlarge the size of graphene, lower amount graphite was mixed with catalyst so the flakes were not as crowdy. This will provide rooms for expanding the graphene area (Fig. 9).

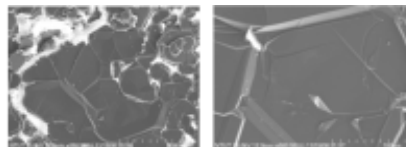


Fig. 9. Graphene stacks of larger than 200 microns were produced by growing with low congestion.

Although the low congested graphene samples were made, but the amount of graphite remained over abundant. Consequently, the folding of graphene layers on the borderlines were still commonplace.

The graphene stacks were scraped of the sample and they were separated in a liquid by ultrasonic agitation. The SEM micrographs showed many broken edges of the recovered graphene (Fig. 10).

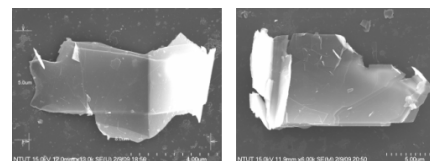


Fig. 10. The graphene flakes recovered from ultrasonic suspension revealed straight bending edges.

In order to estimate the number of layers of the recovered graphene, the books of graphene were revealed (Fig. 11).

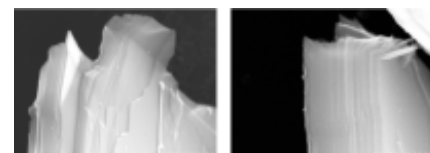


Fig. 11. SEM exposed the edges of the graphene books.

Further exposure of the graphene books demonstrated the formation of clusters of pages that may show remarkable straight edges extending in long distances (several microns) (Fig. 12).

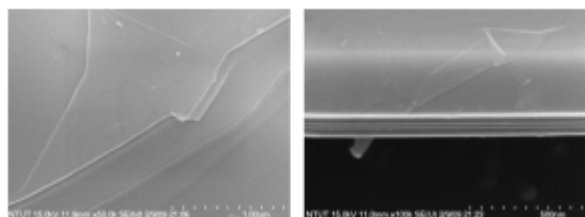


Fig. 12. The enlargement of graphene books exposed stuck pages that are about 20 layers of graphene.

This research demonstrated that catalytic exfoliation of graphite in molten catalyst can produce stacks of graphene that are scalable. The graphene books so produced can be used as the precursor for further exfoliation. The few layers of graphene can then be wafer bonded to a substrate. The graphene wafer so formed can be etched (e.g. by hydrogen or fluorine plasma) to remove extra materials. It should be noted that at the interior of a perfect graphene, the carbon atoms are last etched away, so the layers of graphene can be peeled one by one. For many devices, more than one layer of graphene is needed. For example, as the CMOS design, the transistors on the surface layer may be insulated from the bottom layers. Since graphene layers are held by van der Waals force, the large spacing prevent current leakage better than semiconductor on insulators (SOI) that are used for the fabrication of transistors loaded ICs (e.g. game chips).

4. Conclusion

A simple process of making large quantities of graphene was invented. The process employs the molten iron group elements as catalyst. The catalyst can dissociate graphite to form graphene layers. In this research foldable graphene layers were first photographed with intricate folding lines. The appearance of cloth softness for graphene implies large area (e.g. 1 m by 1 m) may be made by floating graphene on molten alloys. The temperature of the bath can be cycled to “cook out” all the wrinkles of the gigantic graphene. The graphene can be extracted by a roll-to-roll process so the future use is as convenient as plastic wraps. Moreover, graphene layers can be stretched to stick on silicon wafer and lithographic etched to make single electron transistors. The large area graphene may also be made in mural displays thinner than wallpapers. It can also be fabricated into transparent window covering with shades that are controllable. The applications of this dream material can be endless.

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References

[1] Alexander Malesevic, Raymond Kempes, Annick Vanhulsel, Manish Pal Chowdhury, Alexander

Volodin and Chris Van Haesendonck, Field emission from vertically aligned few-layer graphene, *Journal of applied physics* 104 (2008) 084301.

- [2] Anton N Sidorov, Mehdi M Yazdanpanah, Romaneh Jalilian, P Jouseph, R W Cohnl and G U Sumanasekera, Electrostatic deposition of graphene, *IOP PUBLISHING* (2007) 135301.
- [3] A Banerjee and H Grebel, Depositing graphene films on solid and perforated substrates, *Nanotechnology* 19 (2008) 365303.
- [4] Thomas Laude, Hiroaki Kuwahara and Kazuhiko Sato, FeCl₂-CVD production of carbon fibres with graphene layers nearly perpendicular to axis, *Chemical Physics Letters* 434 (2007) p.78-81.
- [5] Qingkai Yu, Jie Lian, Sujitra Siriponglert, Hao Li, Yong P. Chen and Shin-Shem Pei, Graphene segregated on Ni surfaces and transferred to insulators, *APPLIED PHYSICS LETTERS* 93 (2008) 113103.
- [6] Yenny Hernandex, Valeria Nicolosi, Mustafa Lotya, Fiona M. Blighe, Zhenyu Sun, Sukanta De, I. T. Mc Govern, Brendan Holland, Michele Byrne, Yurii K. Gun'Ko, John J. Bliand, Peter Niraj, Georg Duesberg, Satheesh Krishnamurthy, Robbie Goodhue, John Hutchison, Vittorio Scardaci, Andrea C. Ferrari, and Jonathan N. Coleman, High-yield production of graphene by liquid-phase exfoliation of graphite, *ARTICLES* (2008) p.583-588.
- [7] C. Nethravathi and Michael Rajamathi, Chemically modified graphene sheets produced by the solvothermal reduction of colloidal dispersions of graphite oxide, *carbon* 46 (2008) p.1994-1998.
- [8] Nicola Ferralis, Roya Maboudian and carlo Carraro, Evidence of Structural Strain in Epitaxial Graphene Layers on 6H-SiC(0001), *Physical review letters* (2008) 156801.
- [9] Chien-Min Sung, A Century of Progress in the Development of Very High Pressure Apparatus for Scientific Research and Diamond Synthesis, *High Temperatures-High Pressures*, 29 (1997) p.253-293.
- [10] James Chien-Min Sung, The Eastern Wind of Diamond Synthesis, *New Diamond and Frontier Carbon Technology*, 13, 1 (2003) p.47-61
- [11] Chien-Min Sung, Min Fong Tai, Reactivities of Transition Metals with Carbon: Implications to the Mechanism of Diamond Synthesis under High Pressure, *International Journal of Refractory Metals and Hard Materials*, 15 (1997) p.237-256.
- [12] Keynote Speech, 5th Zhenzhou International Conference of Superabrasives, September 5 (2008).
- [13] James Chien-Min Sung, Graphite to Diamond Transition under High Pressure: A Kinetics Approach, *Journal of Materials Science*, 35 (2000) p.6041-6054.
- [14] R. H. Wentorf, Jr., Solutions of Carbon at High Pressure, *Sonderdruck aus der Zeitschrift: Berichte der Bunsengesellschaft für physicalische Chemie*, Band 70, eft 9/10, Seite (1966) p.975-982.