ESSAY ON TWO DIFFERENT NANOSTRUCTURED ALLOTOPES OF CARBON

ENEE416 GROUP ACTIVITY 7
Jeremy Feldman, Daniel Gerzhoy

Keywords: Chemical Vapor Deposition (CVD), Cathodic Arc Physical Vapor Deposition (Arc-PVD)

INTRODUCTION

Carbon nanostructures come in at least three to four allotropic forms: fullerenes, graphene and graphite, carbon nanotubes, and diamond. Diamond has been researched mostly for its use in tribological and thermal coatings, while graphene, a mono-layer of graphite, has gained popularity for use in functionalized coatings and electronics. The key to understanding the various structural, thermal, and electric properties of carbon nanostructures is the carbon bond, which can be single, double, or triple bond order. Graphene is held together by sp2 bonds, and diamond is held together by the stronger sp3 bonds.

Diamond is one of the most well-known allotropes of carbon, and is both one of the hardest known natural minerals; it has the highest heat conductivity. [1] Diamond also has a wide bandgap and high optical dispersion. [1] Diamonds are one of the most popular gemstones for jewelry due to their high optical dispersion, luster, and mechanical properties. Diamond is created naturally in high temperature, high pressure environments such as the earth's mantle: taking billions of years to form from carbon deposits hundreds of kilometers below the earth's surface. Synthetic Diamond Manufacture: CVD is most often used in research and the electronics industry, while Arc-PVD is mostly used for tool coatings. [3] Diamond is a good insulator, though some natural blue diamonds and doped diamond act as a semiconductor. [4] Diamond has remarkable material properties; and has been highly valued in both mechanical and the electronics industry, as much if not more so than the jewelry industry.

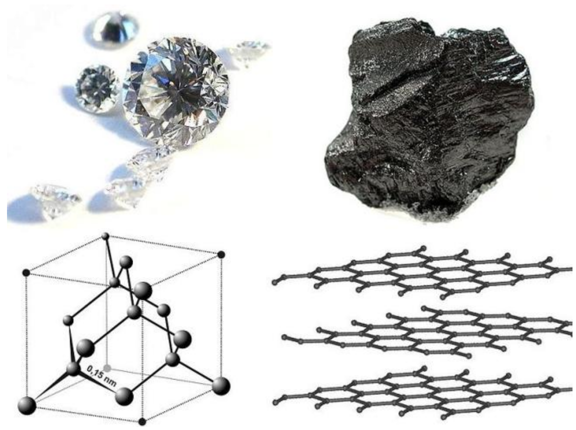

Figure 1: Diamond on the left and graphene on the right are two allotropes of carbon.

Graphene carbon is rapidly becoming a major field of study in the field of microelectronics. It is a single layer of hexagonal carbon crystal. It has some amazing properties such as its high electrical and thermal conductivity, lack of band-gap, ambipolarity, low light absorption (see through) and high tensile strength. These unique properties are crucial to the application of Graphene in high quality electronics such as transistors and sensors. However, one of the biggest problems with Graphene is the difficulty with which it is manufactured, and the characterization of the manufactured product. Many of the properties of Graphene come from the perfection of the crystalline lattice; Graphene with flaws often has different properties than perfect Graphene. [5]

DIAMOND STRUCTURE & PROPERTIES

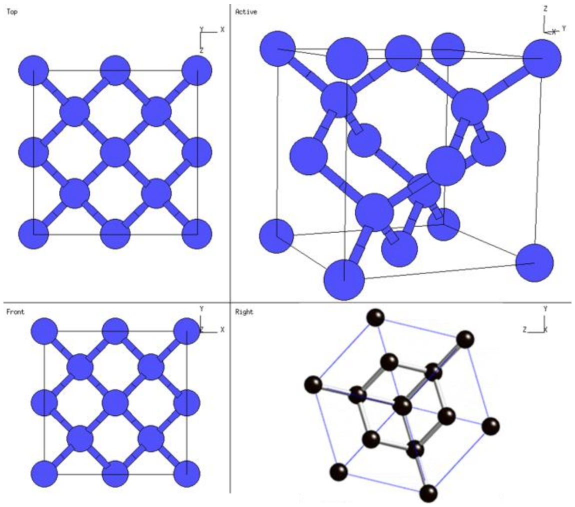

Figure 2: Different view angles of a diamond face centered cubic lattice unit cell.

Diamond is a transparent crystal made up of a repeating pattern of 8 carbon atoms. The pattern makes up one unit cell of the diamonds face centered cubic bravis lattice, seen in figure 2. There are two tetrahedrally bonded atoms in each primitive cell. [6] The atomic packing factor of the diamond cubic structure is about 0.34, which is the fraction of volume in a crystal structure that is occupied by atoms. An important characteristic of materials with diamond blende structures used in fabrication is that they present open hexagonal ion channels which enable more efficient ion implantation if done from any of the <110> directions, seen in figure 3. These Diamond structures display octahedral cleavage, with fewer bonds and exposing points of structural weakness. This characteristic can guide chemical etching to produce pyramidal structures as mesas, points, or etch pits, and can be useful in MEMS fabrication. [7,8] In addition to the aforementioned properties, diamond is also valued for:

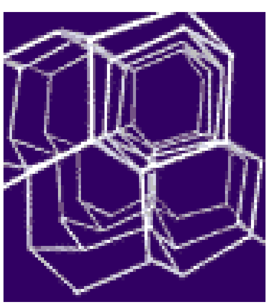

Figure 3: Diamond cubic crystal viewed from a <110> direction.

- Scratch resistance
- Low coefficient of friction for nano-structured diamond like carbon films (especially for polished NCD films) [9]
- Resists abrasive and adhesive wear [9]
- Provides lubricity (both in and out of vacuum) [9]
- Has good chemical resistance to corrosion [12]
- Is a good insulator (if no impurities) [10]
- Can be doped and used as a semiconductor (P and N) [10]
- High thermal conductivity
- Bio-compatible
- Chemically very stable [11]
- Superconductive at 11.4 K (heavily boron doped) [12,13]
- Highest thermal conductivity of any known solid at room temperature [14,15]

DEPOSITION OF DIAMOND

Two deposition methods for depositing and growing crystalline diamond discussed in this paper are CVD, and Arc-PVD. Arc-PVD is a physical vapor deposition done with a high temperature electrical arc and is used mostly for coating cutting or grinding tools for industry. CVD is currently the only way to grow good quality single crystal electronics grade diamond. The process for diamond growth using CVD consists of applying a seed layer to the substrate (the new diamond needs something to grow on), then, under low vacuum of around 20 torr and heated to around 800°C. Running a carbon based gas such as CH_4 and H_2 (about 1:100, CH_4:H_2), and creating a plasma to break apart the molecules into chemically active radicals in plasma. A simplified visualization of the concept can be seen in figure 4. [3]

GRAPHENE STRUCTURE & PROPERTIES

Many people use a material related to Graphene each day: Graphite. Graphite has the same hexagonal structure as Graphene but consists of layers of these hexagonal sheets. “Bulk Graphene” is sometimes referred to when speaking about a thin (but not single) layer of graphite. A perfect, single, “sheet” of Graphene has some amazing properties. It has very high thermal and electrical conductivity which- especially when coupled with its transparency- makes it an attractive option for electrodes on solar cells, panels, and other electrical devices. This conductivity can alter the properties of other materials when made into a composite with Graphene as well. Another important property of Graphene is its lack of a band gap. [5] When semiconductor materials are voltage biased in one direction or another, electrons enter the conduction band (positive bias), or holes enter the valence band (negative bias). The holes and electrons in these two situations then become the dominant mobile carriers [18]; essentially Graphene can be switched from p-type to n-type simply by changing the bias voltage. Graphene is thus deemed “ambipolar,” giving rise to flexible circuits that can create junctions on demand for various logic purposes. For example, it is possible to take a sheet of Graphene, place a layer of silicon oxide between it and an electrode, and place electrodes on either side of the Graphene creating a MOSFET-like device that can act as “PMOS” or “NMOS” [5]

GRAPHENE DEPOSITION

Creating a quality Graphene product is one of the most difficult topics studied in microelectronics, and materials science today. Because true Graphene is only an atom thick (one layer of carbon atoms), it requires very precise development. One of the most successful ways, and the first, to create a single layer of Graphene is mechanical exfoliation. This technique involves ripping layers of Graphene off from each other using various methods. One method is intercalation and exfoliation, which inserts (for example) Potassium between the layers of carbon. The potassium then reacts violently with alcohol to rip apart the layers. Another method, one which has seen very good results: the “peeling” method involves using common cellophane tape to successively remove layers from a flake of graphite. Once a thin enough (not one layer) the tape is pressed onto a substrate and removed. Van der Waals attraction can de-laminate a single sheet and leave it on the substrate. The problem with mechanical exfoliation is that it is neither scalable nor high throughput, making it extremely unattractive for large scale production. Other methods try to solve this problem. One such method is using chemically derived graphite oxide. Graphite is oxidized and diluted with water, and since water is hydrophilic, the graphite-oxide exfoliates automatically (into individual sheets). Then hydrazine hydrate is added to the solution under high temperature, de-oxidizing Graphite Oxide into Graphene. Though once deoxidized, the Graphene sheets can congregate into bulk Graphene (graphite) but optimizations to this process can counteract this effect. [5]

GRAPHENE CHARACTERIZATION

Once created, it is important to characterize the products created. In other words figure out how thin the Graphene is and thus its properties. Scanning probe microscopy is one method to measure the thickness of the created samples. However, due to Graphene’s uniquely high conductivity at low thicknesses, it can interfere with the measurements of such devices. As such, Raman Spectroscopy is used to determine thickness by measuring the frequency/wavelength shift of reflected light. Because Graphene’s properties rely heavily on its thickness and crystalline quality, characterization is of utmost importance. [5]

CONCLUSION

Graphite and graphene have a hexagonal crystal structure combined with sp2 atomic bonding. Diamond on the other hand, has a cubic crystal structure, with sp3 atomic bonding. Diamond is currently used in high technology thermal and tribological coatings and is not too difficult to manufacture of characterize, but getting a good quality seed layer is difficult, and transistor technology doesn't seem to be getting much attention, and costs are high. Graphene is currently being researched for its Ability to improve transistors and sensors, with the potential for reducing costs because of its vast abundance. The current challenges with graphene is it's difficult to manufacture and difficult to characterize. While both diamond and graphene are vastly different versions of the same element, they both have a tremendous potential for improving future technology and we predict strong future growth and opportunity.

REFERENCES

[1] Wei, L.; Kuo, P. K.; Thomas, R. L.; Anthony, T.; Banholzer, W. (1993). "Thermal conductivity of isotopically modified single crystal diamond". Physical Review Letters 70 (24): 3764–3767. Bibcode 1993PhRvL..70.3764W. doi:10.1103/PhysRevLett.70.3764. PMID 10053956

[2] Walker, J. (1979). "Optical absorption and luminescence in diamond". Reports on Progress in Physics 42 (10): 1605–1659. doi:10.1088/0034-4885/42/10/001

[3] Yarnell, A. (2004). "The Many Facets of Man-Made Diamonds". Chemical and Engineering News 82 (5): 26–31

[4] Collins, A.T. (1993). "The Optical and Electronic Properties of Semiconducting Diamond". Philosophical Transactions of the Royal Society A 342 (1664): 233–244. doi:10.1098/rsta.1993.0017

[5] Honeycomb Carbon: A Review of Graphene, Matthew J. Allen, Vincent C. Tung, and Richard B. Kaner, Chemical Reviews 2010 110 (1), 132-145

[6] Kobashi, Koji (2005), "2.1 Structure of diamond", Diamond films: chemical vapor deposition for oriented and heteroepitaxial growth, Elsevier, p. 9, ISBN 9780080447230

[7] G. Braunstein, R. Kalish, Channelling analysis of high temperature ion-implanted diamond, Nuclear Instruments and Methods, Volumes 182-183, Part 2, 15 April-1 May 1981, Pages 691-697, ISSN 0029-554X, 10.1016/0029-554X(81)90797-7. <http://www.sciencedirect.com/science/article/pii/0029554X81907977>

[8] P. G. Read (1999). Gemmology (2nd ed., available on Google Books). Butterworth-Heinemann, Great Britain. pp. 52, 53, 275, 276. ISBN 0-7506-4411-7

[9] Bhushan, Bharat Subramaniam, Vish V. Malshe, Ajay Gupta, B. K. Ruan, Juai

[10] Department of Mechanical Engineering, The Ohio State University, Columbus, Ohio 43210-1107, Sept. 1993 Journal of Applied Physics, <http://ieeexplore.ieee.org/xpl/freeabs_all.jsp?arnumber=5147106>

[11] Koizumi, S.; Nebel, C. E. and Nesladek, M (2008). Physics and Applications of CVD Diamond. Wiley VCH. pp. 200–240. ISBN 3527408010

[12] "Basic Properties of Diamond". DiamondBladeSelect.com.

[13] Takano, Y. et al. (2007). "Superconducting properties of homoepitaxial CVD diamond". Diam. Relat. Mater. 16 (4–7): 911. doi:10.1016/j.diamond.2007.01.027

[14] Takano, Y. (2006). "Overview". Sci. Technol. Adv. Mater. 7 (S1): S1. Bibcode 2006STAdM...7S...1T. doi:10.1016/j.stam.2006.06.003

[15] Anthony, T. R.; Banholzer, W. F.; Fleischer, J. F.; Wei, Lanhua; Kuo, P. K.; Thomas, R. L.; Pryor, R. W. (1989-12-27). "Thermal conductivity of isotopically enriched 12C diamond". Physical Review B 42 (2): 1104–1111. Bibcode 1990PhRvB..42.1104A. doi:10.1103/PhysRevB.42.1104

[16] Wei, Lanhua; Kuo, P. K.; Thomas, R. L.; Anthony, T. R.; Banholzer, W. F. (1993-02-16). "Thermal conductivity of isotopically modified single crystal diamond". Physical Review Letters 70 (24): 3764–3767. Bibcode 1993PhRvL..70.3764W. doi:10.1103/PhysRevLett.70.3764. PMID 10053956

[17] Read, P. G. (2005). Gemmology. Butterworth-Heinemann. pp. 49–50. ISBN 0-7506-6449-5.

[18] B. G. Streetman, S. K. Banerjee, Solid State Electronic Devices M. Horton, Ed. (Prentice Hall, 2006; http://www.ncbi.nlm.nih.gov/pubmed/21842288).