Graphene as a Manufactured Product: A Look Forward

by

Stephen T. Frost

Submitted to the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering

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ABSTRACT

Graphene's unique electrical and mechanical properties have brought it into the spotlight in recent years. With the number of patents increasing rapidly every year, production of the material is becoming more and more important. We evaluate various production methods of Graphene, including Chemical Vapor Deposition, Exfoliation, SiC synthesis, and Nanotube Unzipping. Key findings report CVD having the largest potential for large-scale production for most applications with lower quality requirements, while exfoliation of graphite produces lower quality graphene for applications that do not need large sheets of graphene. Currently, CVD has been able to produce sheets of graphene with diagonal sizes of 40", with high transparency. Using the roll-to-roll method, these sheets have proven viable on flexible touchscreen devices.

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Chapter 1

Introduction

Graphene has existed ever since graphite has existed

-Sean C. O'Hern

1.1 Focus of the Paper and Motivation

1.1.1 Focus and Motivation

The focus of this paper is on the manufacturing and use of graphene as a manufactured product, and the large scale viability of graphene. Focus will be put on the current production methods of graphene, as well as the potential limitations of these processes, including Liquid Phase, Chemical Vapor Deposition (CVD), SiC Synthesis, and other smaller methods. Additionally, the applications of graphene will consider the current demands of the material, and how the material should be produced to reach these applications. Finally, the paper will touch upon which uses of graphene are the most viable in products in the foreseeable future.

Graphene research has taken off substantially in recent years. New papers are produced on a nearly daily basis, and the growing interest in graphene is enormous.¹ As shown in Figure 1.1, graphene patents have more than tripled from 2010 to 2012. From its optical and electronic properties, to the flexibility and strength of the material, the possibilities for graphene seem endless. Thus far, the focus has been in the field of fundamental physics and electronic devices, but there current potential is reaching into various other fields. One major concern right now is how to produce graphene readily and efficiently, and when will it be able to become a viable product in the future. By looking into various demands of the material, and what processes can produce a sufficient quality for those demands, graphene can take another step towards being a real product. One major question remains on the minds of researchers: will graphene's unique electrical and physical properties be useful enough to justify the switch to this new material, and will the manufacturing processes become more affordable and less lengthy to justify this jump?



Figure 1.1: Worldwide Graphene patents per year (Red bars indicating recent

data taken)²

Patents in recent history for graphene have been primarily in research institutions, thought a few companies are also beginning to patent technologies and be the first into the field. All of this attention leads to a big push from companies to develop methods to produce graphene in the most cost efficient way.



Figure 1.2: Patents granted in the Graphene industry by group in 2010²⁰

1.2 Background Information and Technical Information

1.2.1 What is Graphene?

Carbon is the basis of all living things, and the basis of all of organic chemistry. Carbon is extremely flexible with its bonding, and can form nearly limitless possibilities with carbon-based systems, all with varying physical properties. From tubes of carbon atoms to soccer ball-shaped shells of carbon, the element varies substantially when the geometric makeup changes. ¹ One of the most interesting all-carbon substances is currently graphene. Graphene is a two-dimensional crystal – a single atom thick sheet of carbon arranged hexagonally in a honeycomb structure (shown in Figure 1.3).³ Graphene is separate from the rest of the environment and is free-standing, making it rare, as it is the first readily known and highly researched singleatom thick material. The material is the structure of Carbon Nanotubes, and graphite is composed of multiple layers of graphene bonded together, meaning that graphene has existed naturally in a multi-level version in nature. Graphene has a number of unique properties, most importantly its high mobility, flexibility, conductivity, strength, and durability that have sparked the recent trend of research on the material.³



Figure 1.3: The Honeycomb Structure of Graphene. ⁴

1.2.2 History of Graphene

Along with the huge spike in graphene came a large amount of public attention for the material. Graphene's name stems from the composite of graphite and the suffix '-ene', which indicates the structure of graphene. Graphene's true 2D structure was thought to be unstable entirely until it was discovered in 2004.⁵ Research in nano-materials and nanoscience are part of a developing field that has been booming in recent years. Nanoscience in the 70s-90s was a developing field that was discovering that the size, not just the composition, of a material could change the properties of the material substantially. Beginning research on fullerene (materials made entirely of carbon) molecules was difficult at the time, and progress was seen in other forms of carbon-based materials, such as the Buckminsterfullerene developments in the 80s. ⁶ However, as research progressed, the ideas began to grow of the potential for sp² carbon. Carbon nanotubes (CNT), which are cylindrical graphite structures on a nano-scale, began to find relevance when Sumio lijima discovered that these CNTs behaved very similarly to metals and semi-conductors, which would mean that carbon could be used to produce both transistors and the wires connecting them.¹ Since these CNTs were so small, this would allow for electronics functioning on an extremely small scale, and bring life to the field of microelectronics. Funding began to come in for CNTs, but growing these tubes in a high enough density, in a chosen geometry, and with dimensions large enough to prove useful became a bit difficult, and their viability as a commercial good still struggles to come to fruition.⁶



Figure 1.4: An outlined History of the production of Graphene. 7

Graphene began as a description of the single-layer sheets of carbon in graphite materials, and then in carbon nanotubes. However, graphene research made substantial leaps in 2001, when Walt de Heer realized that Carbon Nanotubes, if unrolled, would retain a large number of their physical and electric properties.⁸ This was a large development, as carbon nanotubes were difficult to manufacture in a consistent and well-controlled way, and scaling the nanotubes from their single-tube transistors to larger scale applications in circuits was nearly impossible, and there was a possibility that graphene could reach a state of commercial use since it was easier to use in general surfaces of products. Because there was such a large amount of research already done on CNTs, many of the seemingly strange but outstanding properties (such as the quantum hall effect that allowed for CNTs to act as metals and semi-conductors) could be accurately predicted in graphene. The first real characterization of graphene came in 2004 when Andre Geim and Kostya Novoselov of Manchester University were able to finally extract (with Scotch tapes) single layer sheets of graphene from large pieces of graphite. Since then, graphene has continued to be a point of popular discussion in the scientific world, with 2010 Nobel Prizes in Physics being given to Geim and Novoselov for their work.5

1.2.3 Physical Properties of Graphene

Graphene's electrical properties garner most of the attention due to the possibilities for microelectronics such as flexible display, but graphene is also an incredibly interesting material from a physical standpoint as well. Graphene's unique physical properties raise a few questions about its potential as a structural material. Graphene is transparent, and extremely flexible. Graphene is exceptionally strong, with a breaking strength of over 100 times that of steel film, given the same thickness with fracture strength of 125 GPa.⁹ In fact, it is the thinnest material currently known, and the strongest. The Young's Modulus of graphene in tension has been measured to be 1 TPa, three times that of steel, and is extremely light, weighing a fraction of a percent of the weight of other materials, with a specific surface area of 2630m²/g.⁹ Graphene is also known for its thermal properties, specifically its thermal conductivity of ~5000 W/mK, which allows for it

Additionally, holes in graphene can actually be fixed by simply having materials around the sheet that contain carbon. When pure carbon surrounds the material, holes are fixed entirely, with the carbon "snapping" into the lattice structure of the sheet. Also nano holes (defects) may be used to selectively pass ions and atoms, which may be used to make superefficient membranes for desalination and atomic sieving.

Many crystals cannot grow in a stable state when in their 2D arrangement due to the requirement of high temperature and the instability that thermal fluctuations can cause for 1D and 2D objects. Crystals on a nanometer-scale can exist, but as the size increases, the 2D crystals naturally converge to a more stable 3D object in nature. However, this is not necessarily true in a laboratory setting, as the crystals can be handled at a low enough temperature so as to not cause these thermal fluctuations to break the existing ionic bonds.

1.2.4 <u>Electronic properties of graphene</u>

Perhaps the most exciting properties of graphene are the electronic properties. These properties are what make graphene have such high potential as the future of electronic devices, just as silicon changed the scope of the entire electronics world years before. Graphene is a semi-metal, differing greatly from 3D crystals of graphite. Because of its specific lattice structure, it acts as a zerobandgap semi-conductor and has exceptionally high electron mobility at a resting temperature (up to 200,000 cm²/(Vs)).¹⁰ This information was highlighted in 2008 by researchers at Columbia University, who found that the electron mobility of graphene was substantially higher when suspended 150nm above a Si/SiO₂ gate electrode. ¹⁰ This work showed the potential of graphene as a conducting ultrathin material, and reduce Dirac peak widths 10 fold compared to sheets that were not suspended.¹⁰

Graphene has been found to have a band gap tunable between 0 and .25 eV, which is substantially lower than Si with a band gap of 1.17 eV at 0K and 1.11 at 300K.¹¹ Uniquely, the mobility of graphene is relatively unchanged in a large temperature range. Additionally, the conductivity is higher than that of copper, with values of 4e²/h being reported. However, impurities in graphene can reduce electron mobility and conductivity substantially, which requires more precise manufacturing to avoid. Many production methods produce lower quality graphene, which can serve purposes in more simple applications.¹¹

One major concern with graphene is the lack of current technology to produce large sheets of the material, meaning that multiple pieces may need to be stitched in order to obtain a sheet large enough. Stitching at the boundaries can cause the electronic properties to suffer, depending on the quality of the stitching. Researchers have found that growing graphene at a more rapid rate led to tighter stitching between sheets of the graphene, which led to higher quality graphene. This was tested using electrodes on top of a substrate to measure the specific boundaries and determine ways to reduce electron mobility losses.¹²

Chapter 2

State of Production: Challenges and General Information

2.1 Current Processes

2.1.1 Mechanical Exfoliation and Micromechanical Exfoliation

Mechanical exfoliation is the most basic way of acquiring graphene sheets, first demonstrated by Novoseloc and Geim.¹ Nicknamed the "scotch tape" method, it can be replicated at home with a piece of graphite and scotch tape by simply sandwiching a small piece of graphite in the tape, pulling it apart, and repeating the process, removing excess as necessary. Eventually, what remains is a very thin layer of graphene, which can be transferred onto a piece of silicon. This results in relatively inconsistently shaped graphene, which may be more than one layer thick. However, it is incredibly inexpensive, and is practical for applications requiring low degrees of precision or quality.¹



Figure 2.1: A piece of Graphite, A roll of Scotch Tape Signed by Andre Gein, and a graphene transistor.¹

Some micromechanical exfoliation, however, is an incredibly precise procedure. These more advanced procedures involve precisely cleaving off sheets of graphene from pieces of graphite under a high resolution microscope, and with high precision.¹³ This is a time intensive method, but was one of the first ways that graphene was able to be removed in a high level of quality. This procedure, while producing quality results, is generally used in a laboratory setting due to its high degree of accuracy and low volume of graphene produced, the method isn't currently viable on a large scale.³

2.1.2 <u>Chemical Vapor Deposition</u>

Chemical Vapor Deposition (CVD) is the most reliable source of large sheets of graphene. CVD generally consists of a clam-shaped furnace, and transition metal surface, and a pump or exhaust that connects to the gas inlet and provides the process with a carbon-based precursor, such as ethanol, methane, etc. As the precursor passes over the heated substance, in many cases copper, the graphene is deposited on the surface and then the copper is removed, as depicted in Figure 2.1. The process can produce square meters of graphene sheets at a time, and can be used to provide graphene to applications that require large sheets, such as transparent conductive applications (Touch screens, Photovoltaics, etc). Additionally, the properties that come from CVD are comparable to those produced and exfoliated by other methods.



Figure 2.2: CVD Growth Process of Graphene.14

The one substantial downside to CVD is the current cost of production. The primary concern for this is the high cost of energy required to keep the temperature of the process so high. Research is being done to reduce the necessary temperature of the process, which would make the method substantially more viable in large scale production. Another issue that needs to be addressed is the issues with transferring the sheets of Graphene after they have been produced, as this is the major source of quality issues with the method. Since copper is a conductive material, producing electronic devices on the surface of the material can lead to a shorting of those devices, so the material must be moved to a non-conducting substrate, which drive up the energy costs and cause many problems withstanding the growth temperature.

CVD is not a flawless growth model, however. Studies have been conducted on the method, and there have been significant growth defects in relatively large quantities despite the graphene being considered continuous without properly accounting for them. A few of the ways to reduce these defects are to: ensure the copper foil is free of surface imperfections before using it, clear the copper of any dust particles before use, and to ensure the copper is free of impurities that can becomes released during heat treatment.

2.1.3 Large Scale Production of Graphene Through CVD

In what may be the most recent advances in CVD growth, researchers at the Oak Ridge National Laboratory (ORNL) have found that large scale production of graphene may be possible at atmospheric pressure. Samples of up to 40" in diagonal measurement have been produced by using a large scale 67 foot long furnace with gases of a low H_2 and CH_4 that reduced their flammability at atmospheric temperatures.¹⁵ The copper foil was electropolished before the growth, and it was found to produce graphene with lower frequencies of defects than that produced by unpolished or etched copper.¹⁵ Transferring the graphene with a large, commercial lamination machine allowed for easy and usable transferring, which allows for this method to function for many applications.

Additional work is has researched the possibility of using roll-to-roll production methods of large sheets of graphene film, some up to 30" in size. ¹⁶ The concept undergoes a relatively standard CVD synthesis on a copper (Cu) foil, but the transfer method is where the method differs. The graphene sheet on the Cu foil is laminated with a polymer support between two metal rollers before being run through a secondary series of rollers with an etching solution for the copper, leaving only the graphene and polymer. Finally, the graphene is run through a final series of rollers with the target substrate, leaving the graphene on the desired surface. Figure 2.3 illustrates the process.



Figure 2.3: The roll-to-roll method of producing large areas of graphene.¹⁶

This method allows for the successful production of graphene on flexible substrates, rather than the previously required rigid substrates. By reducing the chance of error during the transferring of the graphene, it allows for a more consistently high quality graphene, with sheet resistances of ~125 Ohms and exhibiting the quantum Hall effect. With production of stacked graphene, sheet resistances of ~30 Ohms were observed with 4 sheets of graphene. These two methods were able to produce sheets with 97.4% and 90% transparency respectively. ¹⁶

2.1.4 Liquid Phase and Thermal Exfoliation

Liquid Phase production is a simple method for acquiring graphene. The procedure involves submerging a graphite block in a liquid medium and rubbing the graphite block while applying an ultrasonic treatment to the medium and the rubbing agents.¹⁷ Liquid phase production of graphene is currently very viable for production in the near future. However, liquid phase typically produces graphene flakes rather than larger, more consistently sized, graphene sheets.¹⁷ This limits the usefulness of this production method for applications that require large sheets, but lends to a high chance of success in the world of conductive ink and paints, since those applications would not require sheets of graphene. Recent developments with rod-coating techniques have been found to, in combination with the liquid phase exfoliation, produce thin, flexible, and conducting films. ¹⁷ This method involves rolling a rod through the liquid medium with the graphene, and producing a thin sheet along

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the surface of an object, and then letting it rest. This process can result in the production of multi-layer graphene, which can be problematic if that is not the desired product.



Figure 2.5: Unzipping of Carbon Nanotubes. 18

Additionally, Thermal Exfoliation can be used to unzip CNTs in order to produce a most consistent a higher quality product, but this results in a relatively higher cost. Unzipping nanotubes can result in relatively small sheets of graphene (the length of the tubes), which doesn't necessarily solve the issues of liquid exfoliation.¹⁸ This produces narrow width graphene nanoribbons (GNRs), which can be useful for their controllable widths and lengths, and smooth edges for electronic applications. In 2009, researchers at Instituto de Ciencia de Materiales de Madrid found that these nanotubes can be unzipped in a few different way, but among the primary methods are chemical exfoliation, and synthetic exfoliation, though these methods remained to be relatively small means of production, and with very similar properties to those of the original CNTs, allowing them to work as fillers as CNTs as well.¹⁹

2.1.5 Synthesis using Silicon Based Substrates

Silicon Carbide (SiC), a material that is currently very common in the electronics world, can be used to grow graphene. Graphene can be synthesized on the surface of SiC, which could allow for electronics and graphene to be manufactured together or more fluidly. Synthesis on SiC or Si wafers was thoroughly researched at the Leibniz Institute for Solid State and Materials research.¹⁹ While synthesizing graphene on the surface of cubic B-SiC, they were able to find that they were able to produce high-quality graphene with only negligible interactions with the SiC substrate.¹⁹ By saturating the area around the substrate with carbon, the researchers observed a production of a film of graphene onto the annealed surface of the SiC, fitting within the lattice structure of the SiC as shown in figure 2.4.



Figure 2.4: Graphene's placement on the SiC surface. 19

Production via this method yields very high quality graphene, with large crystallites having next to no issues with impurities or imperfections, with some research being done However, again, this process comes at a very high cost, primarily due to the >1000° C required temperature of production and the high cost of SiC wafers. However, this growth method also has the possibility of applications with high-frequency transistors capable of ~1 THz. One issue of quality of the production comes from the multi-layered graphene have terraces in the second and third layers.

2.1.6 Other Growth Methods

There are a number of other growth methods, but many of them are not commercially viable due to the very high cost or low potential for scaling. These methods are generally higher quality, but on a smaller scale. Many times the methods can be replicated to a very similar degree with a substantially lower cost (IE Spray coating an object vs using Laser Abalation). As research continues with graphene, it is likely these methods will remain used in a laboratory setting when production numbers are not as important as in a commercial setting.

2.1.7 Comparing the Various Growth Methods

Each of the various growth methods have different advantages and disadvantages, but there are a few key criteria that can be used to evaluate the growth methods against each other. Among these criteria are the following: Maximum Area Produced, Defect Occurrence, Energy Required, Rate, and Cost.

Growth	<u>Maximum</u>	<u>Relative</u>	<u>Scalability</u>	Energy	Cost
CVD	Up to 40" Diagonally ¹⁵	High Quality	Moderate scalability, but with recent advances the scalability is possible	High energy Requirement due to temperatures over 1000°C	High Cost
Liquid Phase	Nanosheets: from nm to a few µm	Moderate Quality, but with impurities	High Scalability	Moderate Energy Cost	Low Cost
CNT Unzipping	Nanotubes: <10 μm generally	High Quality	Moderate scalability	Moderate Energy Cost	Potential for low cost, but currently has a higher cost
SiC Synthesis	Thin films: >50 μm	High Quality	Moderate Scalability	High Energy Requirement, Temperature requirement of over 1000°C	High Cost due to expensive substrate
Micromechani cal Exfoliation	Flakes: 5 to 100 μm	High Quality but with uneven films	Small Scalability	Low Energy Cost	High Cost
Chemical Reduction of Graphite Oxide	Nanoflakes or Powder: nm to a few µm	Low Purity w/ a high defect density	High Scalability	Relatively Low Energy Requirement	Low Cost

Table 2.1: A Comparison of the Different production methods of graphene 15.20

Chapter 3

Applications of Graphene and Their Demands

3.1 Electronic Applications

3.1.1 <u>Flexible Electronics</u>

The combination of graphene's flexibility and its electronic properties have given rise to the possibility of making electronics in the future that are able to bend to high degrees than what are currently possible. Flexible and transparent conductors (FLC) offer a large range of interesting options for unique products, such as flexible touchscreen devices, thin film photovoltaics, printable electronics, and flexible transistors. Aside from graphene's flexibility, it also has the ability to stretch up to 20% of its original dimensions. ¹⁰ Currently, the most common FLC is indium-doped tin oxide (ITO), however, this conductor is incredibly expensive, and in short supply. Additionally, the material can behave as a ceramic, leaving the possibility of fracturing in the products. This leaves the need for a better FLC, and graphene might just be that FLC.¹⁷

Flexible electronics, however, require relatively large sheets of graphene that must be produced separately and later applied to the electronic. These requirements seem to point to CVD as the best option, as a large sheet can be produced in a high-temperature zone separately, and then applied to the electronic during production. However, transferring the graphene after CVD can still be difficult, as can problems in the sheet of graphene. One alternative solution in development is coming from liquid phase exfoliation. In this rodcoating method, a liquid medium saturated in the graphene flakes can be used to produce a FTC by rolling the medium into a thin and flexible sheet.¹⁷ If this process proves to be viable, it will likely mean that flexible electronics may be able to be produced at a more reasonable cost level than CVD can currently provide.²¹ However, until this point is reached, CVD remains as the most viable production method for touchscreen devices.

In fact, with the recent success of the CVD production methods, particularly the roll-to-roll method, the production of these screens is quickly becoming a reality. By rolling the graphene onto the polymer supports, the researchers were able to transfer the graphene onto touchscreen device surfaces, leading to a functioning touchscreen device using graphene, as shown in Figure 3.1.¹⁶



Figure 3.1: An overview of the roll-to-roll method being applied, including the flexibility of the film after transferring (c) and the functioning device (f). ¹⁶

3.1.2 Field Effect Transistors

The potential to manufacture graphene-based transistors is a large part of the reason that graphene is such an exciting potential product. Because of its high

carrier mobility, graphene could form some of the best high performing transistors for radio-frequency applications. Transistors with high cut-off frequencies, some as high as 155 GHz, have been made using the material in 40 nm transistor lengths.²² However, these applications require a high degree of quality and consistency. In recent work, graphene has been grown on a copper film via CVD for these applications, and then transferred onto a diamond-like piece of carbon, where it was able to act as a suitable high frequency transistor. ²²

As a logic transistor, however, graphene finds a bit of a struggle. Graphene works well because of its high mobility and quantum-hall effect, but the fact that it lacks a band-gap means that it's less effective for digital switching in a logic transistor. However, the industry potential for a graphene would be pretty substantial, as other semi-metal transistors are currently the only major players in the market. One way that that has been overcome has been through the introduction of edge effects and quantum confinement of narrow width GNRs, created by unzipping nanotubes. This means that thermal exfoliation could be one of the more effective ways of producing graphene for these applications. Synthesizing graphene on SiC is also a possibility for the production of graphene for transistors, but the substrates used are relatively expensive.

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3.2 Materials Applications

3.2.1 Energy Applications

In addition to other, more commercial, applications, graphene also has applications in the world of clean energy. Graphene's high specific surface area $(\sim 2600 \text{m}^2/\text{g})$ and ability to quickly transfer electrons, the material is being assessed in energy applications. A few of the possibilities for the material currently include graphene-based electrodes for lithium ion batteries and for some capacitor applications.²³ Graphene currently helps to increase the recharge capacity of some of these batteries in a laboratory setting, and could help increase the capacity of conductors and reduce the losses in electrochemical double layer capacitors (EDCLs) by using graphene as spacers within the capacitors themselves. For these applications, liquid based exfoliation techniques work well, due to the need for a moderate level of quality, but at a relatively low price to keep the price of these batteries and capacitors down.²⁴ Solar panels also have graphene in their potential future, the electronic properties of graphene make it highly functional in solar applications. Additionally, since graphene is transparent, solar cells could be built into windows, allowing for buildings to regain lost energy through solar power. These applications, however, would require large sheets of the material, at a relatively high quality. This kind of scaling and quality would have to come from CVD developments, especially with windows and solar panels being so dependent on size.

3.2.2 Sensors

Because graphene has a conductance that changes with the extent of the surface absorption, the large specific area of the material, and the low Johnson noise, the material shows promise for detecting various molecules. These molecules can include gases, biomolecules, and other materials. When the other materials are absorbed, the interaction and charge transfer between the two creates a chemical response.²⁵ When there are changing carrier densities and Fermi level, as well as the resistance of the graphene, the graphene is likely being doped with the molecules, allowing for detection of them. For these applications, the chemical reduction of graphene production allows for the best reactions from the sensors. The low cost, despite the relatively low quality, allow for this growth method to work well with sensor applications.²⁵

Chapter 4

Conclusions and Areas for Potential Progress

4.1 Conclusions

4.1.1 Most viable Production Methods for large scale graphene

Of the various production methods, the two that stick out most clearly are Chemical Vapor Deposition and exfoliation based techniques. Between the two techniques, they provide methods for producing large volumes of lower quality (via exfoliation), as well as large sheets of high quality (via CVD) and seem to cover the vast majority of applications for graphene. It seems as though many of the technologies currently being pursued are based on these two methods. In fact, the vast majority of graphene patents in recent years have been based in CVD growth and exfoliation research, as shown by Figure 4.1. Moving forward, it appears that these two synthesis techniques will be the major players in the graphene industry, and are the most viable production methods on a large scale. The primary applications of graphene will likely focus on the material's unique potential in electronics, specifically transistors and in flexible touch screen devices.



Figure 4.1: A breakdown of the number of patents in various growth

methods.20

4.2 Looking Forward

4.2.1 Current work Being done and considerations for future work.

From the research being done with large-scale furnaces and synthesis on large scales to the work being done with development of 3D graphene nanonetworks from mass CVD synthesis, the industry is in a clear move towards viability as a product. As the price of graphene continues to fall, the scalability of the material will have to be the focus of research, and products will see graphene as more of a realistic goal, and not just a miracle material that is out of reach. Within the next couple of years, it is clear the graphene will continue to be a hot topic in the world of physics, manufacturing, and the overall scientific community. Once a large scale production of the material is achieved, it will appear in everyday devices with higher and higher degrees of frequency.

5. References

- ¹ Geim, A. K. & Novoselov, K. S. The rise of graphene. Nature Mater. 6, 183–191 (2007)
- ² United Kingdom. Intellectual Property Office. Graphene: The Worldwide Patent Landscape in 2013. March, 2013.
- ³ Geim, A. K., Graphene: Status and Prospects, Science 19, June 2009: 324 (5934), 1530-1534. [DOI:10.1126/science.1158877]
- ⁴ AlexanderAIUS. Wikimedia Commons, http://commons.wikimedia.org/wiki/File:Graphen.jpg
- ⁵ Geim, A. K.; Novoselov, K. S.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. Electric Field Effect in Atomically Thin Carbon Films. Science 306
- ⁶ Choi, H.; Mody, C. C. M., The Long History of Molecular Electronics: Microelectronics Origins of Nanotechnology. Soc Stud Sci 2009, 39 (1), 11-50.
- ⁷ M. Noel, R. Santhanam, Electrochemistry of graphite intercalation compounds, Journal of Power Sources, Volume 72, Issue 1, 30 March 1998, Pages 53-65
- ⁸ Grigorieva, I. V.; Firsov, A. A., Electric field effect in atomically thin carbon films. Science 2004, 306 (5696), 666-669.
- ⁹ Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 321, 385–388 (2008)
- ¹⁰ Bolotin, K. I. et al. Ultrahigh electron mobility in suspended graphene. Solid State Commun. 146, 351–355 (2008)
- ¹¹ Kittel, C., Introduction to Solid State Physics, 6th Ed., New York: John Wiley, 1986, p. 185.
- ¹² Park, Jiwoong. "Tighter 'stitching' Means Better Graphene." ADVANCED MATERIALS & PROCESSES July (2012): 12. Web.
- ¹³ Zhang, Yuanbo, Small, Joshua P., et all. Fabrication and Electric Field Dependent Transport Measurements of Mesoscopic Graphire Devices. Columbia University.
- ¹⁴ Yarris, Lynn. Graphene Films Clear Major Fabrication Hurdle. Lawrence Berkeley National Laboratory. April, 2010.
- ¹⁵ Vlassiouk, Ivan, Pasquale Fulvio, Harry Meyer, Nick Lavrik, Sheng Dai, Panos Datskos, Sergei Smirnov, Large scale atmospheric pressure chemical vapor deposition of graphene, Carbon, Volume 54, April 2013, Pages 58-67
- ¹⁶ Bae, Sukang, Kim, Hyeongkeun, et all. Roll-to-roll production of 30-inch graphene films for transparent electrodes. Nature Nanotechnology. June 2010, 574-578.

- ¹⁷ J. Wang et al., "Rod Coating: Towards Large-Area Fabrication of Uniform Reduced Graphene Oxide Films for Flexible Touch Screens", Advanced Materials, 24 (21) (2012) 2874-2878
- ¹⁸ Santos, H. Chico, L. Carbon Nanoelectronics: Unzipping Tubes into Graphene Ribbons. Physical Review. Aug, 2009.
- ¹⁹ Victor Yu. Aristov, Grzegorz Urbanik, Graphene Synthesis on Cubic SiC/Si Wafers. Perspectives for Mass Production of Graphene-Based Electronic Devices. Nano Letters 2010 10 (3), 992-995
- ²⁰ Sivudu, K.S., Mahajan, Y.R., Challenges and opportunities for the mass production of high quality graphene: an analysis of worldwide patents Nanotech Insights, 3 (2012), pp. 6–19
- ²¹ Xuesong Li, Yanwu Zhu, Weiwei Cai, Mark Borysiak, Boyang Han, David Chen, Richard D. Piner, Luigi Colombo, and Rodney S. Ruoff Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes Nano Letters 2009 9 (12), 4359-4363
- ²² Wu, Yanqing, Lin, Yu-ming, Bol, Ageeth A., Jenkins, Keith A.. Xia, Fengnian, High-frequency, scaled graphene transistors on diamond-like carbon. Nature 2011/04/07
- ²³ J. Yao, X. Shen, B. Wang, H. Liu, G. Wang, Electrochem. Commun. 2009, 11, 1849.
- ²⁴ B. E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Plenum Publishers, New York 1999.
- ²⁵ Y. B. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, Nature 2005, 438, 201