11-2014

To Study the Effect of Catalyst on the Physical Parameters of Carbon Spheres

Tejas Shailesh Mehta
Embry-Riddle Aeronautical University - Daytona Beach

Follow this and additional works at: https://commons.erau.edu/edt

Part of the Aerospace Engineering Commons

Scholarly Commons Citation
https://commons.erau.edu/edt/170

This Thesis - Open Access is brought to you for free and open access by Scholarly Commons. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of Scholarly Commons. For more information, please contact commons@erau.edu.
To Study the Effect of Catalyst on the Physical Parameters of Carbon Spheres

By

TEJAS S. MEHTA

A Thesis Submitted to the College of Engineering, Department of Aerospace Engineering for the partial fulfillment of the requirements of the degree of Master of Science in Aerospace Engineering

Embry-Riddle Aeronautical University

Daytona Beach, Florida

November 2014
To Study the Effect of Catalyst on the Physical Parameters of Carbon Spheres

By

Tejas Mehta

This thesis was prepared under the direction of the candidate’s Thesis Committee Chairman, Dr. Virginie Rollin, Professor, Department of Aerospace Engineering, and has been approved by the members of thesis committee. It was submitted to the Department of Aerospace Engineering in partial fulfillment of the requirements for the degree of Master of Science in Aerospace Engineering

Thesis Committee:

Dr. Virginie Rollin
Committee Chair

Dr. Sathya Gangadharan
Committee Member

Dr. Sirish Namilae
Committee Member

Dr. John Mathis
Committee member

Dr. Yi Zhao
Graduate Program Coordinator

Dr. Robert Oxley
Associate Vice President for Academics

Date: 12-4-14
ACKNOWLEDGEMENTS

I would like to thank all my faculty and student mentors who have helped me during my pursuit of my Master’s of Science degree.

I would like to thank my thesis advisor, Dr. Virginie Rollin for letting me join the Nano Research Group (NRG) and letting me choose my topic of interest. She has provided me constant support and encouragement throughout the course of my thesis research.

I would like to express my sincere gratitude to the committee members, Dr. Sirish Namilae, Dr. Sathya Gangadharan and special thanks to Dr. Mathis for helpful discussions on carbon nanotubes and many discussions about the chemistry involved in this thesis.

I would also like to thank my NRG group mates who have helped me in the process of this thesis. I also appreciate the financial support of Embry-Riddle Aeronautical University to conduct the experiments and provide the space for storage of materials. The use of Scanning Electron Microscope was made possible through NSF grant 1337742.

Finally, I would like to thank my brother and sister-in-law, Deven and Nidhi Mehta for their support in the United States and my parents for supporting me through my two years of study.
The discovery of fullerenes has opened up modern studies in carbon materials. Carbon nanoparticles have a large surface area and demonstrate good conductivity. Their unique properties has gained attention in many areas such as water filtration, hydrogen storage and battery electrodes. In this research, carbon spheres with high specific area and uniformity were grown using the Chemical Vapor Deposition (CVD) process with silicon substrates, ethylene ($\text{C}_2\text{H}_4$) as a carbon precursor and argon as the inert gas. We observe that the morphology of carbon spheres largely depend on the experimental conditions, including CVD time duration, temperature, catalyst and flow of gases. This thesis discusses the synthesis and effects of catalyst on carbon spheres.
Table of Contents

LIST OF FIGURES ______________________________________________________ ii

LIST OF TABLES ______________________________________________________ ii

DEFINITIONS __________________________________________________________ 1

CHAPTER I: INTRODUCTION ______________________________________________ 3

  1.1 Carbon Spheres _____________________________________________________ 3

  1.2 Sphere Morphology _________________________________________________ 7

  1.2.1 Diameter _________________________________________________________ 7

  1.2.2 Surface Areas ____________________________________________________ 8

  1.2.3 Shape ___________________________________________________________ 9

  1.2.4 Arrangement of Carbon Layers _______________________________________ 10

  1.3 Applications of Carbon Spheres ______________________________________ 11

CHAPTER II: SYNTHESIS OF CARBON SPHERES ________________________________ 13

  2.1 Arc discharge method _______________________________________________ 14

  2.1.1 Inert gas ________________________________________________________ 16

  2.1.2 Optical plasma control _____________________________________________ 16

  2.1.3 Catalyst _________________________________________________________ 16

  2.2 Laser ablation ______________________________________________________ 17
2.2.1 Continuous wave laser-powder method .............................................. 18
2.2.2 Ultra wave laser-powder method ...................................................... 19
2.3 Chemical Vapor Deposition .................................................................. 20
  2.3.1 Plasma enhanced chemical vapor deposition ..................................... 21
  2.3.2 Aero gel-supported CVD ................................................................. 22
  2.3.3 Alcohol catalytic chemical vapor deposition .................................... 22
2.4.1 Vapor phase growth ......................................................................... 22
2.4.2 Thermal chemical vapor deposition .................................................. 23

CHAPTER III: EXPERIMENTATION ................................................................. 26

  3.1 Substrate Preparation. .......................................................... 27
  3.2 Catalyst Preparation. ................................................................. 28
  3.3 Deposition of Catalyst ................................................................. 31
  3.4 Carbon Sphere Growth ................................................................. 34

CHAPTER IV: RESULTS ................................................................................. 38

  4.1 SEM Analysis ..................................................................................... 38
    4.1.1 Carbon spheres with Molybdenum as catalyst (Sample 10) ............. 38
    4.1.3 Growth of carbon spheres with no catalyst (Sample 1) ....................... 40
    4.1.4 Growth of carbon spheres with Cobalt + ethanol as catalyst (Sample 3) 41

  4.2. Amount of spheres grown ................................................................. 42
CHAPTER V: DISCUSSION

5.1.1 Carbon spheres grown with cobalt and ethanol as catalyst

5.1.2 Silicon wafer with molybdenum as catalyst

5.1.3 Carbon spheres grown with cobalt as catalyst

CHAPTER VI: CONCLUSION & FUTURE WORK

CHAPTER VII: BIBLIOGRAPHY

APPENDIX A
LIST OF FIGURES

Figure 1: Carbon Spheres ........................................................................................................ 5
Figure 2: Carbon Spheres attached together by Van der Waals force ......................................... 7
Figure 3: Dependence of specific surface area values measured on heat treatment temperature (HTT) (Michio Inagaki) .......................................................................................................................... 8
Figure 4: Schematic representation of carbon black (Pergamon) .................................................. 10
Figure 5: Arc discharge technique (Rigaku) .................................................................................. 14
Figure 6: Laser ablation technique (Iop Science) .......................................................................... 18
Figure 7: Chemical vapor deposition (Goteborg University) ............................................................. 20
Figure 8: Plasma enhanced chemical vapor deposition (Dow Corning) ............................................. 21
Figure 9: Thermal CVD set-up (Royal Society of Chemistry) ........................................................ 23
Figure 10: Substrate in a flat plate .................................................................................................. 27
Figure 11: Molybdenum acetate getting stirred at 1000 rpm ............................................................ 33
Figure 12: Sonicating Catalyst ....................................................................................................... 33
Figure 13: CVD set-up (furnace) .................................................................................................... 34
Figure 14: Argon gas at 80 psi ........................................................................................................ 35
Figure 15: View of carbon spheres on substrate ............................................................................ 36
Figure 16: Diameter of carbon spheres (catalyst- molybdenum) ...................................................... 38
Figure 17: Diameter of carbon sphere (Catalyst-Cobalt) ................................................................. 39
Figure 18: Cluster growth of carbon spheres (no catalyst) .............................................................. 40
Figure 19: Cluster growth of carbon sphere (catalyst- Cobalt + ethanol) ......................................... 41
Figure 20: Top view of carbon spheres grown with cobalt as catalyst (sample 9) ......................... 44
Figure 21: Projected thick layer of carbon spheres on substrate (sample 9) ................................. 45
Figure 22: (a) Top view of carbon spheres grown on substrate with cobalt and ethanol as catalyst (b) EDX analysis of carbon spheres grown on substrate with cobalt and ethanol as catalyst ............................ 51
Figure 23: Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with cobalt and ethanol as catalyst

Figure 24: (a) Top view of carbon spheres grown on gold plated substrate with molybdenum as catalyst and (b) EDX image of carbon spheres

Figure 25: Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with molybdenum and ethanol as catalyst on gold plated silicon wafer

Figure 26: (a) Side view of carbon spheres grown with cobalt powder as catalyst

Figure 27: Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with molybdenum and ethanol as catalyst on gold plated silicon wafer
LIST OF TABLES

Table 1: Diameters of carbon spheres synthesized by different techniques .......................................................... 25

Table 2: List of substrate and catalyst used ............................................................................................................ 30

Table 3: Process for growth of carbon sphere where Co- Cobalt, Mo- Molybdenum and H2O is water .......... 37

Table 4: Amount of carbon spheres grown using with different catalyst ............................................................. 43

Table 5: Average diameter of carbon spheres with different catalyst ................................................................. 47
DEFINITIONS

Fullerenes: A fullerene is any molecule made of carbon in any shape.

Nanotubes: Hollow tubes of very small diameter. The name is derived from their size as their diameter is approximately 50,000 times smaller than a human hair.

Megatubes: Larger in diameter than nanotubes and prepared with walls of different thicknesses and they are mostly used for electrical applications.

Polymers: Polymers are molecular long chains made up of a unit monomer repeated many times.

Van der Waals force: Van der Waals forces are secondary forces that define the attractive potential between molecular chains.

Pyrolysis: In this process, an organic material is decomposed by heat and in the absence of oxygen. This process is generally conducted at high pressure and high temperature.

Macroscopic: Visible to the naked eye.

Microscopic: So small as to be visible only with a microscope.

Plasma: Unique phase of matter and collection of charged particles. Since these particles are electrically charged, it is also called ionized gas.
Catalysis: Acceleration or deceleration in the rate of a chemical reaction due to the participation of an additional substance called catalyst.

Tribology: Science and engineering of interacting surfaces in relative motion.

Polyethylene terephthalate: Thermoplastic polymer resin of the polyester family. Its application are generally in the areas of synthetic fibers, food, beverages and in engineering resins.
CHAPTER I: INTRODUCTION

1.1 Carbon Spheres

The study of carbon properties dates back to prehistoric times. From hardened firewood to modern day nanotubes and nanospheres, this element has been used for many applications. Life on earth depends upon this element to obtain energy and provide for its very structure. It plays a role in solar fusion and has been indirectly observed in the vast reaches of interstellar space [1]. Carbon has the unique ability to combine with various other elements to form very complex structures. The discovery of fullerenes in the mid-1980s led to an upsurge interest in the structure and shape of carbon containing materials, in particular when carbon is in the ‘nano’ regime [1]. During the past three decades, the availability and ready approach to characterization techniques at the nano-scale has led to a more detailed investigation of well experienced and novel materials.

The discovery of fullerenes expanded the research and knowledge of carbon allotropes, which, until now, was limited to only graphite, diamond and charcoal; graphite being one of the softest solids and diamond being one of the hardest ones. Lightweight structures with very high stiffness and good electrical conductivity are expected to find applications in the fields of space, medicine and
various engineering streams. In the past few decades, many different types of carbon materials such as buckyball clusters, nanotubes, megatubes and polymers have been synthesized and their properties have been studied [2]. The study of carbon nanotubes (CNTs) has provided a strong focus for much work in the area of ‘Shaped Carbon Material’. The other breed of edifice that has a long history of study and has again become a fresh focus of attention is carbon spheres. A spherical shape is the shape adopted by materials during synthesis (growth, nucleation) and is determined by consideration of energy minimization [3]. Spherically-shaped carbon materials have been known for decades and their properties have been exploited in many arenas (tires, batteries, printer ink, etc.) [4,5]. Carbon spheres are known by many names; carbon spheres, carbon balls, carbon nanospheres, carbon microbeads, carbon blacks, onions, mesophorous microbeads, etc. [4], while the sizes, distribution and density vary with the use of different catalysts.
The growth of carbon spheres can be controlled by the flow of gases. The spherical shape is not peculiar to carbon; numerous studies of spherical silica have indicated the wide range of synthetic strategies and approaches that can be used to make spherical materials [3].

Many carbon spheres have shown to be made of carbon that aggregated to form a necklace-like structure or bunch of grapes. Carbon spheres are attached together by strong Van der Waals forces and this force leads to the accumulation of carbon spheres as shown in figure 2. Carbon spheres having a diameter less than 1000 nanometer (nm) also tend to bond together to make a necklace or bead-like structure [6, 7]. These chains are formed during the synthesis process with ethylene or any alcoholic gas.
The study of carbon spheres can be categorized in four different ways. First, spheres can be described as solid, core-shell or hollow [3]. Second, they can be classified according to their ‘nanometric texture’, i.e. in terms of whether the spheres are made of concentric, radial or random layers [7, 8]. Third, it has also been proposed that spheres can be categorized in terms of their size, in particular their diameter [5].

If the diameter of the sphere is between 2-20 nm then we classify it as a well-graphitized sphere. If the diameter of the sphere is between 20-1000 nm, then we classify them as less graphitized spheres and, finally, if the diameter is greater than 1000 nm, then it is classified as carbon beads. Finally, it is also possible to classify the carbon spheres based on the synthesis used. There are various procedures such as chemical vapor deposition (CVD), arc-discharge, laser ablation, pyrolysis of carbon sphere, reduction of supercritical carbon dioxide with bimetallic lithium and potassium, hydrothermal reaction, etc. by which spherical carbon spheres can be grown. In the ‘synthesis’ section, I will be discussing a few of these synthesis techniques in detail.
1.2 Sphere Morphology

A wide variety of carbon spheres have been researched and a few comments on the morphology of carbon spheres follow.

1.2.1 Diameter

Carbon spheres vary from a range of a few nanometers to many microns. The diameter of carbon spheres mainly depends upon the synthesis technique and
carbon precursor used during growth technique. Control of the diameter of spheres differs depending on the method used to synthesize carbon spheres and from literature it seems there is no common technique by which size of carbon spheres can be controlled. Diameters obtained by various synthesis methods are listed in chapter 2.

1.2.2 Surface Areas

The surface areas of carbon spheres varies from very low (< 2mg$^2$/g$^{-1}$) to very high values (>1200m$^2$/g$^{-1}$) [6, 10, 11]. The dependence of specific surface area on carbonization temperatures in different gas atmosphere is shown below.

![Figure 3: Dependence of specific surface area values measured on heat treatment temperature (HTT) (Michio Inagaki)
From the graph above it can be noticed that up to 800 °C, there is no effect of atmosphere during heat treatment on surface area, but different areas are determined by using CO₂. The surface area can also be controlled with the use of inert gases. For instance, high-purity argon gas decreases the surface area with increase in high treatment temperature (HTT), which is said to be due to shrinkage of pores by carbonization [8, 12]. However using CO₂, the surface area increases abruptly due to the increase of pores by oxidation.

1.2.3 Shape

The Chemical Vapor Deposition (CVD) technique generally produces smaller carbon spheres in the form of a necklace. The sphere linkage appears early in the synthesis process and involves graphite layers compressing spheres into a necklace [8, 12]. The spheres are thus chemically linked. Larger spheres normally form as discrete carbon structures that can interact with other spheres through Van der Waals bonding [6].

Figure 4 shows the effect of heating discrete carbon spheres (a) to form amalgamated structure via sphere coalescence (carbon-like structure) (b) that can take place at high temperatures (aggregate of carbon-onion like structure) [7]. Indeed, it has been shown that when carbon balls (CBs) are used as an electrode in an arc-discharge reaction, the spheres accrete at high temperature to eventually
give multi-walled CNT’s [7]. In figure 4 b, the arrow indicates a neck between two spheres.

![Diagram of carbon black spheres](image)

*Figure 4: Schematic representation of carbon black. (Pergamon)*

### 1.2.4 Arrangement of Carbon Layers

The unique subtlety in bonding configurations that results from the carbon’s ability to adopt almost any imaginable combination of sp, sp$^2$ and sp$^3$ hybridization in a broad scope of materials results in an immensely diverse range of structures and morphologies [8]. Spheres can be made with their carbon chains or carbon layers or carbon flakes perpendicular or parallel to the main core of carbon. Chemical and physical properties of these carbon spheres can be heavily influenced with the arrangement of their layers.
The size of the flakes or their orientation can be determined using a Scanning Electron Microscope (SEM). To determine the orientation of carbon spheres using SEM, sample is tilted between 5-30 degrees and a stationary beam is focused upon the sample. A number of the incident electrons are slightly inelastically scattered within the sample, and subsequently elastically backscattered electrons produce a pattern on the screen which is characteristic of both the orientation and structure of the sample [9]. More graphitic structures can be generated with the help of pyrolysis of carbon spheres [7].

1.3 Applications of Carbon Spheres

Carbon spheres have wide range of applications. Mesocarbon microbeads have been widely used in batteries and electrochemical cells. Carbon spheres have been extensively used in electrolysis. After molding and heat treatment, carbon spheres have been used as sealants [10]. Due to ease of synthesis and ability to control carbon spheres, they are used like most carbons as a catalyst support [5]. There are many reports on the use of carbon spheres to make composites. Composites made with carbon spheres and carbon sources can be made by either mixing or by inducing a chemical reaction between two components [4]. The spherical shape carbon spheres suggests that they will be useful for tribological coatings or as lubricant additives [11]. Hollow spheres made by templating/polymerizing phenol on silica spheres have been used for removal of traces of ethylene in agribusiness
environments [12]. They can be used to modify the electronic properties of insulating materials [1, 20-21]. Mesocarbon microbeads when combined with other carbons (naphthalene pitch) can give materials with a compressive strength of 420 mPa [13]. Platinum and ruthenium loaded on carbon spheres have shown very promising results in the direct methanol fuel cell [23, 24]. Given the high strength associated with the carbon spheres and the use of carbons where strength is required it may be possible to use carbon spheres in shock wave protection materials [14].
CHAPTER II: SYNTHESIS OF CARBON SPHERES

The last few decades have experienced a rapid growth in research and application of carbon nanotubes in various sectors. This led to (often accidentally) the synthesis of many other differently shaped carbon materials including carbon spheres. The synthesis of carbon spheres can be classified into two categories, depending on the growth temperature.

The first category is based on high temperature decomposition of carbon containing materials in an inert atmosphere. Arc-discharge, laser ablation, chemical vapor deposition, fall under this category. The second category is based on low temperature pyrolysis and catalytic decomposition of organic compounds by heat treatment.

The influence of carbon precursor, catalysts, flow rates, pressure, gases, duration, all play a very important role in influencing the properties (surface area, density, size, etc.) of the carbon spheres. It has been suggested that new carbon spheres must be distinguished from carbon blacks in terms of microstructures and approaching scheme [15] and are not the same as carbon blacks [16].
Nevertheless, many of the high temperature techniques to grow carbon spheres have led to similar properties to carbon blacks, suggesting that there may certainly be abundant similarities between carbon blacks and many of the carbon spheres reported in the literature.

Carbon spheres have been synthesized in matrices by procedure that do not presently lead to their extraction and use [17]

### 2.1 Arc discharge method

The carbon arc discharge method was primarily used for growing Buckminsterfullerene (C\textsubscript{60}) [18]. Later, this process, with slight modifications was used for growing carbon nanotubes. The first carbon nanotubes were grown using the arc discharge method.

![Arc discharge technique (Rigaku)](image)

Figure 5: *Arc discharge technique (Rigaku)*
X. He et al. have described a procedure for the synthesis of carbon spheres using acetylene and coke powder as a carbon source in the DC arc discharge method [19]. As the anode, a carbon rod containing nickel and iron was used. On the other end as the cathode a graphite rod with high purity was used. The diameter of this rod was 30 mm x 20 mm. A current of 70-90 amperes was passed through two electrodes in an acetylene medium at a pressure of 0.05-0.06 MPa while the voltage between the two electrodes was in the range of 30-35 volts. The spheres formed by this method varied in size between 50-100 nm.

W.M. Qiao et al. synthesized carbon spheres using polymers as carbon source [15]. They used polyethylene terephthalate (PET) resin from recycled bottles for growing carbon spheres at a pyrolysis temperature of 1100 °C using the arc discharge technique. They placed two hundred carbon balls, having a diameter of 3 cm each at the bottom of a furnace near two electrodes. The carbon balls were heated in the presence of inert gas argon until the resistance of the carbon balls reached its highest level. Pieces of polyethylene terephthalate were then introduced into the furnace. The carbon balls were heated to 1100 °C. After achieving the reaction temperature, the resistance of the carbon balls was increased and arc-discharge occurred among carbon balls. At the same time the polyethylene terephthalate pyrolyzed and was converted to a solid product. The resultants were characterized by SEM (scanning electron microscope), TEM (transmission electron microscope), Raman Spectroscopic techniques and X-ray
Diffraction (XRD). The diameters of the grown carbon spheres was observed to be 100 nm.

Depending on the selective growth of carbon spheres, the procedure required in arc discharge can be modified. A couple of ways to improve the process of arc discharge are stated below:

2.1.1 Inert gas

It appears that argon with lower thermal conductivity and diffusion coefficient gives carbon spheres a very low diameter. Literature review reveals that a carbon sphere diameter decreases by 0.2 nm per 10% increase in ratio of helium and argon gas [18].

2.1.2 Optical plasma control

Carbon sphere formation is improved due to enhanced anode vaporization. Macroscopic and microscopic parameters of carbon spheres can be controlled simultaneously by combined control of argon helium mixture [18].

2.1.3 Catalyst

We know that catalysts are widely used in chemical vapor deposition (CVD) for growth of carbon spheres and carbon nanotubes. Researchers tried to use the same catalyst in arc discharge technique and they found that not all catalysts used for
the chemical vapor deposition technique appeared to result in carbon spheres for arc discharge. But there appeared to be similarities of diameter of carbon spheres produced by CVD and arc discharge [6, 8, 11]. The diameter of carbon spheres was reduced drastically by using the mixture of cobalt and molybdenum in high concentration as a catalyst.

Apart from this, techniques such as magnetic field synthesis, synthesis in presence of nitrogen and various other techniques can be used to improve the synthesis by arc discharge method.

### 2.2 Laser ablation

In 1995, Rice University reported the first growth of carbon nanotubes by laser vaporization [11, 27-28]. This technique was later modified to grow carbon spheres. Laser ablation uses pulsed or continuous laser to vaporize a carbon precursor in the presence of a metal catalyst [20]. In this technique, a pulsed laser vaporizes a graphite target in a high temperature reactor with an uninterrupted supply of inert gas into the chamber. Carbon nanoparticles are obtained from the cooler surface of the reactor due to condensation of vaporized carbon. Generally for laser ablation technique, water or oil is used as the cooling solvent [11, 27].
There are a lot of similarities between arc discharge technique and laser ablation technique, as the catalyst mixture and background gas used are similar in both methods. The reaction conditions needed to conduct both experiments are also very similar.

The laser ablation technique is further classified into two techniques, namely:

1) Continuous wave laser-powder method
2) Ultra-fast pulses from free electron laser (FEL) method

2.2.1 Continuous wave laser-powder method

This method is a novel continuous, highly productive laser method. A Ni/Co mixture is used as catalyst, the temperature is 1100 °C [18]. Using the continuous
wave laser-powder method, carbon spheres with a mean diameter of 1.2-1.3 nm were obtained [11, 29].

2.2.2 Ultra wave laser-powder method

Ma et al. reported the synthesis of carbon coated iron particles using a laser-induction heating evaporation technique. In this technique, they placed an iron cake in a graphite crucible in an evacuated chamber with pressure less than 10 Pascals and the system was then flushed with argon gas to remove impurities. He then increased the pressure to 2KPa with argon. A high frequency induction power of 40 kW was then applied to melt the iron cake. Simultaneously, a continuous wave CO$_2$ laser (power of 4-4.5kW) was used to irradiate and vaporize the molten iron. Methane gas was introduced with a pressure of 5kPa for a total duration of one hour. Using this technique, they successfully grew core-shell iron-carbon nanospheres with a varying diameter of 5 to 50 nm.

Yang et al. synthesized amorphous hollow carbon spheres (HCSs) using radio frequency plasma enhanced CVD from methane/H2 in the presence of MgO and Ni nanoparticles supported silica. A radio frequency power of 220 W was used. The temperature of the reactor was maintained between 700 °C - 800 °C. The carbon spheres produced had a diameter ranging between 100 and 800 nm.
2.3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) synthesis is accomplished by placing a carbon source in the gas phase at a high temperature [21]. In this process a carbon source such as methane, ethylene or acetylene is used. A high temperature is applied to split the molecules into responsive atomic carbon. The carbon diffuses near the substrate, which is heated and layered with the catalyst where it will grow. Growth rate can also be controlled by chemical vapor deposition.

Chemical Vapor deposition was invented by Endo, Shinshu University, Nagano, Japan. Using this technique, carbon spheres can be synthesized with a diameter ranging from a few nanometers to micrometers. It is the most convenient and simple technique to scale up to industrial output.

Figure 7: Chemical vapor deposition (Goteborg University)
There are many different techniques by which carbon sphere can be synthesized with CVD, such as plasma enhanced CVD, aero gel-supported CVD, laser-assisted CVD, alcohol catalytic CVD, vapor phase [11,30].

2.3.1 Plasma enhanced chemical vapor deposition

This is a procedure applied to deposit thin films from a gas state to a solid state on a substrate. The chemical response is involved in the operation, which occurs after the institution of plasma of the reacting gases.

![Figure 8: Plasma enhanced chemical vapor deposition (Dow Corning)](image)
2.3.2 Aero gel-supported CVD

Carbon spheres are grown by disintegrating carbon on an aero gel-supported catalyst. There are many significant factors that affect the yield and quality of carbon spheres. The productivity of the catalyst is much higher compared to any other methods. By simple acidic treatment and oxidation process, high purity spheres can be maintained [18].

2.3.3 Alcohol catalytic chemical vapor deposition

Alcohol catalytic CVD is a technique that can be used for large-scale production of carbon spheres at very low cost when compared to other techniques [21]. During this process, evaporated alcohols, methanol or ethanol are used. Temperature ranges from 500 to 1000 °C. The diameter of the carbon spheres synthesized is about 1 nm.

2.4.1 Vapor phase growth

Vapor phase growth is a synthesis method of carbon spheres. For this process two furnaces are placed in the reaction chamber. In the first furnace, a carbon precursor is maintained at a comparatively low temperature [22]. In the second furnace, decomposed carbons are absorbed and diffused [21] and carbon spheres are produced. The diameters of the carbon spheres obtained using vapor phase growth are in the range of 2 to 100 nm [21].
2.4.2 Thermal chemical vapor deposition.

In this process, metals such as iron (Fe), nickel (Ni), cobalt (Co) or an alloy of catalytic metals are placed on a substrate. In a diluted hydrofluoric acid (HF) solution with distilled water, the substrate is etched [6]. The specimen is then placed in a quartz boat. The boat is later placed in a CVD reaction furnace. Additional etching of the catalytic metal is done using ammonia gas at a temperature ranging from 750 to 1050 °C.

The chemical vapor method can be used to make smooth single shell, deformed single shell and nitrogen doped shell carbons using silica spheres [17] [21].

*Figure 9: Thermal CVD set-up (Royal Society of Chemistry)*
The table below gives the list of carbon spheres diameter synthesized by different techniques.

<table>
<thead>
<tr>
<th>Catalyst/ Carbon Source</th>
<th>Synthesis conditions</th>
<th>Carbon Sphere Size</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ARC DISCHARGE</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>Carbon balls were heated to 1100 C; Arc-discharge</td>
<td>100nm</td>
<td>[15]</td>
</tr>
<tr>
<td>Carbon rod containing Fe-Ni; acetylene</td>
<td>A current of 70-90 A passed through two electrodes in an acetylene medium at a pressure of 0.05-0.06 MPa</td>
<td>50-100nm. The material showed that the cell electrode has a high reversible capacity</td>
<td>[19]</td>
</tr>
<tr>
<td>Ni; coal</td>
<td>40-50 V and a current of 50-70 A were used; under helium at a pressure of 500-700 Torr</td>
<td>10-20 um. Exist in different forms such as balls, net-like structures and plate like materials</td>
<td>[23]</td>
</tr>
<tr>
<td><strong>LASER ABLATION</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe cake; CH\textsubscript{4}</td>
<td>An iron cake was molten under argon at a 40kW frequency. Afterwards CH\textsubscript{4} gas at 5 kPa was introduced</td>
<td>5-50 nm</td>
<td>[24]</td>
</tr>
<tr>
<td>Co, Ni; carbon aerosol</td>
<td>1700-2400 C</td>
<td>50-100nm</td>
<td>[25]</td>
</tr>
<tr>
<td>MgO-Ni supported on Si; CH\textsubscript{4}</td>
<td>700-800 C, 1600 pa CH\textsubscript{4}, radio frequency 220 W</td>
<td>100-800nm</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>900-1100 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------</td>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Iron; CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td>1.2-35um</td>
<td>[27]</td>
</tr>
<tr>
<td><strong>NON CATYLYTIC</strong></td>
<td><strong>CHEMICAL VAPOR</strong></td>
<td><strong>DEPOSITION</strong></td>
<td></td>
</tr>
<tr>
<td>Toluene/Acetylene</td>
<td>1000 C for 20 min</td>
<td>200nm</td>
<td>[28]</td>
</tr>
<tr>
<td><strong>CATALYTIC</strong></td>
<td><strong>CHEMICAL VAPOR</strong></td>
<td><strong>DEPOSITION</strong></td>
<td></td>
</tr>
<tr>
<td>Zn-Se; toluene</td>
<td>1100 C for 3 hours</td>
<td>40-120 nm</td>
<td>[29]</td>
</tr>
<tr>
<td>Si, benzene and</td>
<td>900 or 1000 C</td>
<td>Single, Double</td>
<td>[30]</td>
</tr>
<tr>
<td>acetonitrile</td>
<td></td>
<td>Shelled, and</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>nitrogen doped</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>spheres were</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>synthesized</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ranging from 460</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>to 1600 nm</td>
<td></td>
</tr>
<tr>
<td>Co/MgO; CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>600 C</td>
<td>50-200 nm</td>
<td>[31]</td>
</tr>
<tr>
<td>Fe or Ni particles,</td>
<td>1000 C</td>
<td>Carbon nanobeads</td>
<td>[32]</td>
</tr>
<tr>
<td>kerosene</td>
<td></td>
<td>about 250-850 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>covered with</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>graphite shell</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>of 80-100 nm</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1: Diameters of carbon spheres synthesized by different techniques*
CHAPTER III: EXPERIMENTATION

The synthesis of carbon spheres was carried out in the Nanomaterials lab (COAS-423) and Prep room (Lehman 170-A) using Chemical Vapor Deposition with a tube furnace. We selected the chemical vapor deposition technique since it was the best suited, the most flexible and most economical. The fabrication of carbon spheres constitutes the main part of this thesis and will be elaborated in this chapter.

For carbon spheres, there are 5 sections; each covering one step of the process:

1. Substrate preparation
2. Catalyst preparation
3. Deposition of catalyst
4. Carbon spheres growth
5. SEM analysis
3.1 Substrate Preparation.

We selected a P type boron doped silicon wafer with an orientation of <100>, resistivity of 0.001-0.005 ohm and diameter of 50.8 mm [42, 43]. This substrate was purchased from University Wafer, Inc. The silicon substrate provided the base for growth of carbon spheres. The wafer, being too large to fit in our tube furnace (di-19 mm), had to be cut it into smaller pieces. This substrate was rinsed with acetone and distilled water a couple of times to get rid of impurities on the surface of the wafer. After rinsing, it was allowed to dry at normal room temperature. Some substrates were coated in gold using a sputter coater at a current of 30 mA for 40 seconds with an argon pressure of 0.08 mbar.

*Figure 10: Substrate in a flat plate*
3.2 Catalyst Preparation.

There are many nano-sized transition metal particles such as nickel, iron, cobalt, molybdenum and copper that can be used as a catalyst while implementing the chemical vapor deposition technique. There are several articles on growth of carbon spheres using different compositions of catalyst, size and preparation methods. Catalysts are used for their ability to catalytically decompose carbon precursors.

Some of our substrates were gold plated using a sputter coater prior to depositing the catalyst. We used cobalt powder (purity of 99.8%), molybdenum powder (purity of 99.99%), cobalt acetate in the form of powder and chunks (purity of 99.999%) and molybdenum acetate in needle form (purity of 98%) as catalysts [44, 45]. All these chemicals were supplied by Sigma-Aldrich. To study the effect of catalyst on carbon spheres, we used 11 different combinations of substrate and catalyst. Table 2 lists out the different catalysts and substrates used for the synthesis of carbon spheres.

According to the mechanism explained by Baker et al. hydrogen and carbon is released on the foremost part of the metal particle due to the disintegration of hydrocarbon gas (ethylene). This liberated hydrogen and carbon is then dissolved in the metal particle. The dissolved carbon is precipitated at the rear end on getting diffused through the particle [33].
## Table 2: List of substrate and catalyst used

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>SUBSTRATE</th>
<th>CATALYST</th>
<th>Amount mg;ml</th>
<th>Deposition technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silicon wafer</td>
<td>None</td>
<td></td>
<td>---------</td>
</tr>
<tr>
<td>2</td>
<td>Gold plated silicon wafer</td>
<td>None</td>
<td></td>
<td>---------</td>
</tr>
<tr>
<td>3</td>
<td>Silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>84;160</td>
<td>Dip</td>
</tr>
<tr>
<td>4</td>
<td>Gold plated silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>84;160</td>
<td>Dip</td>
</tr>
<tr>
<td>5</td>
<td>Silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>50;210</td>
<td>Dip</td>
</tr>
<tr>
<td>6</td>
<td>Gold plated Silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>50;210</td>
<td>Dip</td>
</tr>
<tr>
<td>7</td>
<td>Silicon wafer</td>
<td>Cobalt acetate + ethanol</td>
<td>54;160</td>
<td>Drop</td>
</tr>
<tr>
<td>8</td>
<td>Silicon wafer</td>
<td>Molybdenum acetate + ethanol</td>
<td>50;210</td>
<td>Drop</td>
</tr>
<tr>
<td>9</td>
<td>Silicon wafer</td>
<td>Cobalt powder</td>
<td>42</td>
<td>Manually</td>
</tr>
<tr>
<td>10</td>
<td>Silicon wafer</td>
<td>Molybdenum powder</td>
<td>25</td>
<td>Manually</td>
</tr>
<tr>
<td>11</td>
<td>Silicon wafer</td>
<td>Cobalt powder + water</td>
<td>54;200</td>
<td>Spin</td>
</tr>
</tbody>
</table>

Where,
Dip- Dip coating technique; Drop- Drop casting technique; Spin- Spin coating technique
When the catalyst powder is mixed to a liquid, the amount of catalyst is measured with a scale of precision of 1 mg. The powder is then added to a specified amount of liquid, stirred at 1000 rpm for 10 minutes (except for cobalt, which is magnetic and for which stirring was done by hand). The mixtures was then sonicated between 1 and 2 hours prior to deposition of the catalyst.

Table 2 summarizes the quantities used.

### 3.3 Deposition of Catalyst

We used different techniques for depositing catalyst on the substrate.

Spin Coating technique: In this technique substrate was placed on the rotating disc (vacuum). The substrate was then rotated at a high speed and the mixture of catalyst was introduced using dropper on this substrate. Rotation was continued till the fluid spins off the edges of substrate. This procedure was used to deposit uniform thin film of catalyst on substrate.

Drop casting technique: The metallic acetate solution was deposited by applying 7-10 droplets of the solution using a disposable dropper, resulting in complete coverage of the substrate surface. The substrate was then allowed to sit on a flat plate to let ethanol evaporate completely. Finally this substrate was placed in the furnace for 550 °C for 7 minutes for annealing.
Dip coating technique: The substrate piece was submerged vertically into a prepared metallic acetate solution for different time duration (approx. 7-11 minute). We left the upper 3mm of substrate above the solution level to prevent the solution from getting contaminated by the tweezers. This substrate was then drawn up from the solution very slowly. This was then dried at normal room temperature. After this process, substrate was placed in the furnace and maintained at 550 °C for 7 minutes for annealing.

Table 2 summarizes the technique used for each substrate /catalyst combination.
Figure 11: Molybdenum acetate getting stirred at 1000 rpm

Figure 12: Sonicating Catalyst
3.4 Carbon Sphere Growth

In this section, a step by step procedure for the growth of carbon spheres is described. For the growth process of carbon spheres, we used ethylene gas as a carbon precursor and argon as the inert gas. To avoid the backflow of impure gases, we connected the appropriate tubing on the outlet of the tube furnace to direct the waste / impure gases in a water beaker.

Step 1 - Argon gas was introduced in the reactor tube with a flow rate of 200 sccm for 10 minutes and the temperature of the furnace was maintained at 950 °C.

This step was conducted to flush out all the impurities.
Step 2- Ethylene gas was introduced in the reactor tube with a flow rate of 200 sccm for 7 minutes.

The temperature of the furnace was maintained at 950 °C.

During this step, a large amount of ethylene gas was supplied so that a good amount of carbon can be introduced in the reaction chamber.

Step 3- Two gases were introduced in the reactor tube at the same time.

i) Argon was introduced with a flow rate of 200 sccm

ii) Ethylene was introduced with a flow rate of 25.8 sccm
Step 3 was carried out for 30 minutes and the temperature was maintained at 950 °C. After 30 minutes, the furnace was cooled down and the specimen was removed from the reactor tube and taken for SEM testing.

This step was carried out to reduce carbon by approximately one-tenth the initial supply before the growth process was stopped by cutting off the supply of ethylene gas.

![Image of carbon spheres on substrate]

*Figure 15: View of carbon spheres on substrate*

The table in the next page summarizes the process involved for growth of carbon spheres on each substrate.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon wafer</td>
<td>-----------</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>-----------</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Co</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>Co</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Mo</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>Mo</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Co acetate</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Mo acetate</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Co powder</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200, 22.5</td>
<td>30</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Mo</td>
<td>150</td>
<td>10</td>
<td>150</td>
<td>3</td>
<td>150,10</td>
<td>15</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Co+ H₂O</td>
<td>200</td>
<td>7</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3: Process for growth of carbon sphere where Co- Cobalt, Mo- Molybdenum and H₂O is water
CHAPTER IV: RESULTS

4.1 SEM Analysis

4.1.1 Carbon spheres with Molybdenum as catalyst (Sample 10)

Figure 16: Diameter of carbon spheres (catalyst- molybdenum)

Figure 16 shows the carbon spheres grown with the molybdenum catalyst. When we analyzed the sample we found that some nanotubes were grown along with carbon spheres. Spheres were attached to carbon nanotubes and not many spheres were synthesized. The flow rate used here was less as compared to flow rate we used for growth of carbon spheres using different catalysts.
4.1.2. Carbon Spheres with Cobalt as Catalyst (Sample 9)

Figure 17 shows carbon spheres with cobalt as catalyst. When we analyzed the sample, we saw random clusters of carbon spheres grown on the substrate.
4.1.3. Growth of carbon spheres with no catalyst (Sample 1)

Using chemical vapor deposition we successfully synthesized carbon spheres on a bare substrate in the form of a nano-necklace like structure or bunch of grapes. The results indicated that a catalyst is not required for synthesis of carbon spheres.

*Figure 18: Cluster growth of carbon spheres (no catalyst)*
4.1.4 Growth of carbon spheres with Cobalt + ethanol as catalyst (Sample 3)

Using cobalt and ethanol as catalyst we observed that dense compacted forests of carbon spheres were synthesized. The diameter of these spheres was very small as compared to the diameter of spheres grown with different catalysts under the same operational conditions.

Figure 19: Cluster growth of carbon sphere (catalyst- Cobalt + ethanol)
4.2. Amount of spheres grown

The growth of carbon spheres is due to the decomposition of carbon from the carbon precursor on the substrate. This growth was influenced by carbon source, flow rate, temperature and catalyst. Due to the high temperature we used for growth process, the carbon source decomposed into fragments and radicals. It was observed that the amount of carbon spheres grown depends on the catalyst used for the growth process.

The table on the next page lists the amount of carbon spheres formed on a substrate with different catalysts.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Weight (g)</th>
<th>Area (cm²)</th>
<th>Amount (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold plated silicon</td>
<td>Cobalt + ethanol</td>
<td>0.044</td>
<td>0.84 ± 0.04</td>
<td>0.0524</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt acetate + ethanol</td>
<td>0.089</td>
<td>2.04 ± 0.015</td>
<td>0.0436</td>
</tr>
<tr>
<td>Gold plated silicon</td>
<td>Molybdenum + ethanol</td>
<td>0.032</td>
<td>0.80 ± 0.021</td>
<td>0.04</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt powder</td>
<td>0.021</td>
<td>1.05 ± 0.036</td>
<td>0.02</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>0.054</td>
<td>3.3225 ± 0.061</td>
<td>0.0179</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum acetate + ethanol</td>
<td>0.051</td>
<td>3.80 ± 0.057</td>
<td>0.0134</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>0.017</td>
<td>1.68 ± 0.028</td>
<td>0.0101</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>--------------------------</td>
<td>0.005</td>
<td>0.6 ± 0.029</td>
<td>0.0083</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + water*</td>
<td>0.021</td>
<td>2.575 ± 0.041</td>
<td>0.0082</td>
</tr>
<tr>
<td>Gold plated silicon</td>
<td>--------------------------</td>
<td>0.009</td>
<td>1.2 ± 0.054</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

*Table 4: Amount of carbon spheres grown using with different catalysts*
Carbon spheres grown on a substrate with cobalt and water as a catalyst was damaged while taking it out from tube furnace; hence there is a high possibility that this value is incorrect and it has been marked with *. 

Figure 20: Substrate with a layer of cobalt as catalyst (sample 9) 

Figure 21: Top view of carbon spheres grown with cobalt as catalyst (sample 9)
Typically the carbon source is polymerized at high temperature. In the CVD process, spheres were synthesized with the carbon layers horizontal to the substrate. When we synthesized carbon spheres with cobalt and water as catalyst, we got a film of spheres which could easily be pulled, separating that layer from substrate. It is interesting to note that even though the catalyst was not on the entire surface (figure 20), the growth was on the entire surface, leading us to believe that with a better substrate preparation, the growth could even be higher.

Figure 22: Projected thick layer of carbon spheres grown with cobalt as catalyst (sample 9)
The diameter of our carbon spheres was measured in table 3. Here the operating condition such as furnace temperature, time and pressure involved for growth of carbon spheres was the same. Only for one experiment (substrate with molybdenum as catalyst) the flow of gas was maintained at 150 sccm and for other experiments the flow of gas was maintained at 200 sccm. We find that there is no significant change in carbon sphere diameter, especially since we only had one experiment for each sample preparation.

Both the results obtained can be termed as preliminary or estimated results as we carried out one experiment on each substrate. Experimental operating conditions was same for all the substrate except for one substrate i.e. silicon wafer with molybdenum as catalyst where flow rate was 150 sccm as compared to 200 sccm for other substrate.

To calculate average diameter we measured 5 diameters of sphere at different location and then calculated its average diameter.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Average Diameter [microns]</th>
<th>Error (standard deviation) [microns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum acetate + ethanol</td>
<td>2.319</td>
<td>0.231</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>2.298</td>
<td>0.186</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>2.182</td>
<td>0.210</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt acetate + ethanol</td>
<td>1.7397</td>
<td>0.168</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>--------</td>
<td>1.658</td>
<td>0.207</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum</td>
<td>1.644</td>
<td>0.198</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>--------</td>
<td>1.5625</td>
<td>0.102</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt</td>
<td>1.277</td>
<td>0.116</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>1.2719</td>
<td>0.200</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + water</td>
<td>1.1982</td>
<td>0.104</td>
</tr>
</tbody>
</table>

*Table 5: Average diameter of carbon spheres with different catalyst*
CHAPTER V: DISCUSSION

We selected transition metals such as Cobalt and Molybdenum as catalyst for the synthesis of carbon spheres by promoting the decomposition of hydrocarbon precursors at a low temperature over that of spontaneous decomposition process [34]. The main reasons for the use of these catalysts were: 1) Carbon’s high solubility in these metals at high temperatures and 2) carbon’s high diffusion rate in these metals. Additionally, cobalt and molybdenum have very high melting points, 1,495 °C and 2,623 °C respectively. Xu et al. have also stated that cobalt as catalyst has produced more ordered carbon structure than any other transition metal catalyst.

The basic steps that might have occurred during CVD for the growth process of carbon spheres are: [35]

1. Mass transport of the gaseous reactants from the reactor inlet to the deposition zone
2. Chemical reactions in the gas phase leading to a new reactive species and by products
3. Mass transport of the initial reactants and reaction products to the substrate surface
4. Adsorption of these species onto the substrate surface
5. Surface diffusion of adsorbed species over the surface to the growth center
6. Surface reactions at the growth center
7. Desorption of byproducts
8. Diffusive mass transport of the byproducts away from the surface
9. Mass transport of the byproducts to the outlet of the reactor

![Figure 23: Schematic representation of the basic steps in a CVD process](Springer)

There are numerous mechanisms that have been proposed for the synthesis of carbon spheres. Soot particles are typically spherical in shape and the mechanism of their growth has been extensively studied. The key features are conversion of a carbon source typically into C and H radicals, and finally reaction to give the carbon spheres. The growth of spheres is due to deposition of carbon from the gas phase. This growth is influenced by the carbon source and the reaction conditions. At the typically high temperatures, the carbon
source decomposed into fragments and radicals. This provided the building blocks for the flakes.

According to Ke Xue, success rates of experiment via methane, ethylene and acetylene vary over carbon source flow rate. In statistics, the best success rate is respectively observed in the range of 400-800 sccm for methane, 0-200 sccm for ethylene and 200-600 sccm for acetylene [36].

We selected ethylene as our carbon precursor because the decomposition of ethylene is thermodynamically allowed at all temperatures and occurs readily provided a sufficient activation. Due to their high Gibbs energies of formation, ethylene can self-decompose into carbon, and dihydrogen [37].

The decomposition of ethylene at an elevated temperature is given as

\[ \text{C}_2\text{H}_4 \xrightarrow{\text{Co/Mo}} 2\text{C}(s) + 2\text{H}_2 \] [38]
6.1 EDX analysis

We carried out Energy-dispersive X-ray spectroscopy (EDX) on the carbon spheres grown with cobalt and molybdenum as catalyst.

5.1.1 Carbon spheres grown with cobalt and ethanol as catalyst

Figure 24: (a) Top view of carbon spheres grown on substrate with cobalt and ethanol as catalyst (b) illustrates the element content of the carbon spheres. The images reflect the presence of Aluminum, Oxygen and Nitrogen along with carbon.
Figure 25: Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with cobalt and ethanol as catalyst

We find some oxygen and nitrogen atoms in the spheres, there is a high possibility that these atoms are from the atmosphere since our experiments were not carried out in a vacuum. We also find aluminum in fig 22(b), this aluminum is the stub of SEM. We did not find any traces of catalyst, so the observed spheres are carbon spheres.
5.1.2 Silicon wafer with molybdenum as catalyst

![Figure 26](image_url)

Figure 26: (a) Top view of carbon spheres grown on substrate with molybdenum as catalyst (b) traces of few molybdenum particles (c) illustrates the element content of the carbon spheres. The images reflect the presence of Oxygen, Silicon, Nitrogen and Molybdenum along with carbon.
Carbon spheres, grown with cobalt and ethanol as catalyst, on silicon substrate and carbon spheres, grown with molybdenum and ethanol as catalyst, yield almost the same carbon purity with a difference of 1%. Again here we found oxygen and nitrogen as impurities in the spheres, but no traces of the catalyst.

**Figure 27:** Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with molybdenum and ethanol as catalyst on silicon wafer
5.1.3 Carbon spheres grown with cobalt as catalyst

Figure 28: (a) Side view of carbon spheres grown with cobalt powder as catalyst (b) illustrates the element content of the carbon spheres. The images reflect the presence of Aluminum, Oxygen, Nitrogen and Silicon along with carbon
Figure 29: Energy-dispersive spectrometry (EDS) spectra of carbon spheres grown with molybdenum and ethanol as catalyst on gold plated silicon wafer

Here we observed that purity is the same as it was in carbon spheres grown on silicon wafer with molybdenum as catalyst. We also find aluminum in fig 26 (b), this aluminum is the stub of SEM. But on doing point analysis we found nitrogen and oxygen which
were almost in the same ratio as it was in the spheres grown with molybdenum and ethanol as the catalyst on silicon substrate.

From above analysis it is seen that we obtained carbon sphere with purity of approximately 90% with some impurities of oxygen and nitrogen. The purity can most likely be improved if these experiments are carried out in a vacuum.
CHAPTER VI: CONCLUSION & FUTURE WORK

In summary, carbon spheres have been synthesized using chemical vapor deposition technique, in which ethylene was used as the carbon feedstock. The amount and diameter of carbon spheres was investigated as a function of the catalyst used. We found that there was no significant change in diameter of our spheres using same flow rate but catalysts (Mo and Co) led to higher growth rate.

Moreover, we found that our spheres were about 90% carbon, with some impurities of oxygen and Nitrogen. No catalyst was found to have been pushed off the substrate surface by the growth.

To expand on this work, the growth of carbon spheres can be studied by varying parameters such as the time factor and flow rate of carbon precursor. Effects of the catalyst affecting the carbon spheres material properties such as conductivity and brittleness can be studied in further details.
CHAPTER VII: BIBLIOGRAPHY

# APPENDIX A

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Argon flow rate (sccm)</th>
<th>Time (min)</th>
<th>Ethylene flow (sccm)</th>
<th>Time (min)</th>
<th>Argon , Ethylene flow (sccm)</th>
<th>Time (min)</th>
<th>Diameter (microns)</th>
<th>Amount (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.2719</td>
<td>0.0167</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>2.182</td>
<td>0.0101</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt powder</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.277</td>
<td>0.02</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>Cobalt + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>2.1382</td>
<td>0.052</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt + water</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.1982</td>
<td>0.0082</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum acetate + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>330</td>
<td>2.319</td>
<td>0.0134</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Cobalt acetate + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.7397</td>
<td>0.0436</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Molybdenum</td>
<td>150</td>
<td>10</td>
<td>150</td>
<td>3</td>
<td>150,10</td>
<td>15</td>
<td>1.644</td>
<td></td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>--------</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.658</td>
<td>0.0075</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>-------</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>1.5625</td>
<td>0.0083</td>
</tr>
<tr>
<td>Gold plated silicon wafer</td>
<td>Molybdenum + ethanol</td>
<td>200</td>
<td>10</td>
<td>200</td>
<td>7</td>
<td>200,22.5</td>
<td>30</td>
<td>2.298</td>
<td>0.0101</td>
</tr>
</tbody>
</table>