Engineering Graphene Films from Coal

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ABSTRACT

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Engineering Graphene Films from Coal

Director of Dissertation: Gerardine G. Botte

Graphene is a unique material with remarkable properties suitable for a wide array of applications. Chemical vapor deposition (CVD) is a simple technique for synthesis of large area and high quality graphene films on various metal substrates. Among the metal substrates, copper has been shown to be an excellent support for the growth of graphene films. Traditionally, hydrocarbon gases are used for the graphene synthesis via CVD. Unconventional solid carbon sources such as various polymers and food waste have also shown great potential for synthesis of graphene films. Coal is one such carbon enriched and abundantly available unconventional source. Utilization of coal as a carbon source to synthesize large area, transparent, and high quality few-layer graphene films via CVD has been demonstrated in the present work.

Hydrocarbon gases are released as products of coal pyrolysis at temperatures \( \geq 400 ^\circ C \). This study hypothesized that, these hydrocarbon gases act as precursors for the synthesis of graphene films on the copper substrate. Hence, atmospheric pressure CVD and low temperature of 400 °C were utilized initially for the production of graphene films. These conditions were suitable for the formation of amorphous carbon (a-C) films but not crystalline graphene films that were the objective of this work. The synthesized a-C films on the copper substrate were shown to be uniform and transparent with large surface area. The thickness and surface roughness of the a-C films were determined to
have typical values of ~5 nm and 0.55 nm, respectively. The a-C film has >95 % optical transmittance and sheet resistivity of 0.6 MΩ sq⁻¹. These values are comparable to other carbon thin films synthesized at higher temperatures. Further, the a-C films were transferred onto any type of substrate such as silicon wafer and titanium foil, and can be utilized for diverse applications.

However, crystalline graphene films were not produced by implementing atmospheric pressure CVD and low temperature operation. Annealing of copper support was required to remove the oxide layer present on its surface and low pressure operation was demonstrated to be suitable for crystalline graphene film formation. The CVD system and the synthesis procedure were modified to address these issues. This was done by increasing the synthesis temperature, incorporating a vacuum pump for low pressure operation, and implementing two step procedure of annealing the copper substrate followed by subsequent coal pyrolysis for the synthesis of crystalline graphene films. The synthesized few layer graphene films were uniform and continuous with thickness in the range of 3-7 nm. The optical transmittance and electrical conductivity measurements demonstrated that the graphene films have >95 % transparency and sheet resistivity of 5.0 kΩ sq⁻¹, respectively.

An investigation of growth mechanism of coal derived graphene films synthesized via CVD was conducted utilizing spectroscopy, microscopy, and chromatography techniques. Gas collection was performed at the graphene synthesis conditions utilizing the CVD reactor without vacuum in operation. Various gases released as products of coal pyrolysis in the CVD reactor were collected and analyzed using gas chromatography. The
analysis showed the presence of methane, ethane, ethene, propane, propene, carbon monoxide, and carbon dioxide as coal pyrolysis products. The hydrocarbon gases act as precursors for graphene growth. Raman spectroscopy, selected area electron diffraction (SAED), and X-ray photoelectron spectroscopy (XPS) confirmed the formation of crystalline graphene films at 1055 °C and 18-30 min synthesis. The growth mechanism involves copper catalyzed reaction to produce amorphous carbon film within the first few minutes of synthesis. Raman spectroscopy and SAED validated that lower synthesis times (6-12 min) produced hybrid amorphous carbon films. This is followed by hydrogen catalyzed graphitization of the underlying carbon film to form graphene domains. Optical microscopy and Raman spectra demonstrated the formation of these oval shaped graphene domains as synthesis time was increased (18-30 min). The graphene films are formed by growth and merging of these graphene domains on the copper substrate. The growth mechanism of coal derived crystalline graphene films is presented in the current work.
DEDICATION

Dedicated to my family
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CHAPTER 1 : INTRODUCTION

1.1 Project Significance

Graphene films have gained significant importance and attention among scientific community due to their unique physical and chemical properties, opening a wave of research targeting applications such as solar cells, capacitors, sensors, batteries, protective coatings, LCDs, LEDs, and medical devices [1-6].

Graphite is a conventionally used carbon source for the synthesis of graphene. Hydrocarbon gases (methane, acetylene, etc.) are alternatively used depending on the synthesis technique [7, 8]. However, the United States relies on other countries mining graphite such as China and Canada for its need of natural graphite. Further, an increase/decrease in demand of hydrocarbon gases for energy related applications creates market fluctuation. Moreover, hydrocarbon gases require pressurized systems for transportation. These are thus unreliable for steady supply as carbon sources for large scale and low cost synthesis of graphene.

Alternate sources of carbon need to be investigated for economical synthesis of graphene. In one such attempt, researchers have converted food waste to graphene [9]. There are opportunities to explore other possible naturally occurring low cost carbon rich source to grow high quality graphene, which might prevent the dependence on other traditional carbon sources, reduce cost, and increase reliability towards steady supply of carbon source for scalable graphene synthesis.
Coal is a solid source with high carbon content, which is stable at room temperature and atmospheric pressure, and is easy to transport. The United States has large reserve of coal. Coal is a composite of aromatics and low molecular weight species, which are networked to form highly complex polymeric structure [10]. This complexity is illustrated in Figure 1.1, which is one of the several molecular representations of sub-bituminous coal (such as Wyodak coal used in this work) structure, as proposed by Shinn [11].

![Figure 1.1: Molecular representation of the complex structure of sub-bituminous coal as proposed by Shinn [11].](image)

Originally published in Preprints of papers- American Chemical Society (ACS) Division of Petroleum Chemistry, Inc.; (1996), 41 (2) 510-515; 211th National meeting, Proceedings of a meeting held in 1996, Orlando, Florida, USA. Image has been re-drawn.
The synthesis of carbon nanotubes and fullerenes using coal as a carbon source has been demonstrated previously [12, 13]. However, not much effort has been directed towards the synthesis of graphene films from coal. Within this context, the significance of this research is the conversion of coal to graphene films. The utilization of coal to produce graphene could open a new market for coal as non-conventional carbon source and provide reliability for scalable synthesis of graphene. Furthermore, an investigation of the growth mechanism in the proposed work could bring new opportunities to grow graphene films using different types of coal such as bituminous and anthracite. Moreover, utilizing coal to produce value added product such as graphene could also significantly impact the economy and provide environmental benefits during efficient scale up of the process.

1.2 Statement of Objectives

The low-cost and abundant availability of carbon enriched coal makes it a promising source for nanocarbon synthesis. Coal has been used to synthesize various forms of nanocarbon materials such as carbon nanotubes [12], fullerenes [13], microballs [14], and bamboo-shaped carbon tubes [15]. Recently, anthracite coal was utilized to produce graphene sheets [16]. However, a complex procedure involving high temperature graphitization (2400 °C) and chemical conversion was employed in order to produce graphene sheets [16]. There is a tremendous potential to develop graphene films using coal as carbon source by employing a facile technique. This motivation leads to the primary specific objectives incorporated in the present work as follows:
a) Synthesis of graphene films using coal as the carbon source via a facile and low cost chemical vapor deposition (CVD) technique

Synthesis was performed by a conventional chemical vapor deposition (CVD) technique, which is easy to implement and economically viable for large scale production, as well as for conducting fundamental study.

b) Physical characterization of the synthesized graphene films to determine the properties

Surface characterization techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were used to investigate the quality and properties of the graphene films. Other characterization techniques implemented were optical transmittance spectroscopy and electrical conductivity measurements.

The growth mechanism of the graphene films using coal with the facile CVD approach is certainly appealing. The coal pyrolysis in an inert environment produces various gases including hydrocarbon gases at different temperatures [17]. It can be hypothesized that similar to hydrocarbon gases such as methane used for the synthesis of graphene films, the mixture of hydrocarbon gases released during the coal pyrolysis act as precursors for the synthesis of the graphene films. These hydrocarbon gases undergo thermal decomposition and chemisorptions on the copper surface which is used as a substrate for the CVD growth [18-20]. The copper acts as a catalyst and assists in the formation of active surface carbon species [18-20]. The carbon species deposit onto the
surface of copper, nucleate and grow to produce graphene films [18-20]. To validate this hypothesis, the third primary objective was:

c) To investigate the growth mechanism of coal derived graphene films

   Understanding the growth mechanism will aid in the synthesis of high quality graphene films using different types of coal. Optical microscopy images assisted in determining the growth rate of the graphene films. Gas chromatography was used to identify the gases released during the coal pyrolysis. The spectroscopy and microscopy techniques assisted in the growth study by determining the phase transformation of carbon occurring during the growth.

1.3 Project Overview

   Carbon is sometimes referred as “The King of the Elements” due to its diverse applications and existence in various forms with each having distinct characteristics. Carbon is one of the most abundantly available materials on earth [21] with over 95% of all chemical compounds as “carbon compounds” [22]. It has the ability to bond with itself as well as with “electro-positive” and “electro-negative” elements, employing any hybridization combination (sp\(^1\), sp\(^2\), and sp\(^3\)) [22, 23]. This yields a plethora of materials with diverse properties and hence could be used in a wide variety of applications.

   Graphite, diamond, and amorphous carbon were the only forms of carbon known until the 1980s. Kroto et al. discovered a novel form of carbon consisting of 60 carbon atoms that came to be known as fullerenes [24]. Fullerenes are high value products due to their stability and ability to formulate various derivatives [24]. In 1991, Iijima
synthesized tubular carbon nanostructure known as carbon nanotubes (CNT) [25]. CNTs have intrigued researchers due to their unique physical and chemical properties. Graphene, a two dimensional nanostructure has been a recent addition to the nanocarbon family.

Graphite and hydrocarbon gases have traditionally been used to grow carbon nanostructures. Alternately, the United States has vast coal reserves, which makes it an inexpensive carbon source to synthesize various carbon nanostructures [12-15, 26, 27]. CNTs were the first nanocarbon to be produced using coal [12, 13]. Carbon nanostructures have been synthesized via arc-discharge and plasma techniques, using coal as a source [28-32]. These techniques require high temperature operation and include complex procedure, thus limiting their use for large scale production. Furthermore, in most cases, a catalyst is required for the synthesis of carbon nanostructures. These factors limit the economic viability of using coal for the synthesis of carbon nanostructures. Consequently, it is necessary to utilize a suitable synthesis technique that is economically feasible for large scale and high quality production of carbon nanostructures, while using coal as a carbon source. Further, there is a huge potential to develop various other forms of nanocarbon, using coal.

Within this context, the primary goal of the present work was to develop graphene films using coal via an inexpensive technique such as chemical vapor deposition (CVD). Hydrocarbon gases are released at temperatures ≥400 °C. Hence, the synthesis was initially performed at 400 °C. It was observed that low temperature and atmospheric pressure (AP) CVD synthesis produced amorphous carbon films with excellent properties
as presented in Chapter 4. AP CVD did not yield crystalline graphene films even at high
temperatures. However, literature demonstrated that low pressure and high temperature
operation produced crystalline graphene films. Therefore, low pressure and high
temperature operations were implemented to produce coal derived graphene films with
excellent physical and chemical properties, as discussed in Chapter 5. Further, the growth
mechanism of coal-derived graphene films, a fundamental aspect associated with this
project, was investigated and a mechanism proposed in Chapter 6.
2.1 Graphene

Graphene resembles a flattened honeycomb lattice which is composed of sp² hybridized carbon atoms that are compactly packed. In 2010, the Noble prize in Physics was awarded to A. K. Geim and K. S. Novoselov for their discovery of 2D graphene material. They demonstrated the structure and excellent properties of graphene. Graphene can be "enveloped to form a 0D fullerene, rolled to form 1D nanotubes and arranged in layers to form 3D graphite" [1] as represented in Figure 2.1 [1].

Figure 2.1: Graphene is designated as “mother” of all graphitic forms. Image is reproduced from Geim and Novoselov [1].

Graphene has a large specific surface area and exhibits exceptional mechanical, thermal, electrical, optical properties and excellent chemical stability [1, 6, 33, 34]. These remarkable properties make graphene suitable for a wide variety of applications such as in solar cells, batteries, sensors, capacitors, electronic and optical devices [4-6, 8, 33, 35-39].

2.2 Synthesis Techniques

Traditional techniques for graphene synthesis include mechanical exfoliation, chemical derivation, total organic synthesis and chemical vapor deposition (CVD) [6, 36, 40]. Mechanical exfoliation of graphite produces high quality graphene sheets, though with low yield due to the intricacy in limiting the layers in the final products [36]. Consequently, this method is viable only for conducting fundamental studies. Chemically derived graphene colloidal suspensions have poor electrical conductivity which can be attributed to structural defects induced by chemical oxidation and reduction. Further, total organic synthesis produces side reactions which limits the size of graphene films [36, 41]. Among the above mentioned techniques, CVD shows great potential for high quality, large area, and scalable synthesis of graphene films [7, 8].

2.3 Carbon Source for Graphene Synthesis

2.3.1 Traditional carbon sources

Graphite has traditionally been used as a carbon source for the synthesis of graphene. Hydrocarbons, which includes solids (polymethyl methacrylate, polystyrene,
etc.) [19, 42], gases (methane, ethylene, acetylene, etc.) [8, 43-45] and liquids (methanol, ethanol, benzene, etc.) [19, 46] are also used as a carbon source for the synthesis of graphene films. Recently non-conventional solid carbon sources (food waste, insects, etc.) have shown promising results for graphene film growth which brings new opportunities to explore other non-traditional carbon feedstocks to synthesize graphene films [9, 19, 20, 42].

2.3.2 Coal as carbon source

Abundant availability of inexpensive coal makes it a viable alternative as a carbon source to produce nanostructures [47-49]. Coal is a complex heterogeneous organic rock [10] consisting of a system with low molecular weight species and another system with a macromolecular network [10]. The network is composed of various aromatic structures which are grouped and connected by bridges [10]. This complex structure with weak bonds and rich mineral matter content might play an important role in the growth of carbon nanostructures [47]. Further, coal is classified into various types based on the ascending order of maturity, each having distinct characteristics. Lignite, the lowest ranked coal, contains the highest moisture content, and is followed by sub-bituminous and bituminous coal. Anthracite is the highest ranked coal with the lowest moisture content [50]. The use of different types of coal (bituminous, sub-bituminous, etc.) might impact the yield and purity of the graphene films.

Synthesis of carbon nanotubes and fullerenes using coal as a carbon source has previously been demonstrated [12-15, 26, 27]. Pang et al. were the first to demonstrate the production of carbon nanotubes using coal [12, 13]. They used an electrical arc...
deposition for synthesis of carbon nanotubes [13]. Electrical arc deposition is a widely implemented technique to grow carbon nanostructures using coal as source material [28-32]. Recent studies highlight the production of carbon nanotubes from coal using radio frequency plasma technique [26, 27] and catalytic deposition techniques such as chemical vapor deposition (CVD) [51, 52]. In addition, anthracite coal has been used to produce graphene sheets [16]. However, a complex procedure was employed, wherein the coal is catalytically graphitized at high temperatures of 2400 °C, then subjected to chemical oxidation and dielectric barrier discharge plasma-assisted deoxygenation to produce graphene sheets [16].

Coal pyrolysis in an inert atmosphere yields mixtures of various gaseous products at different temperatures [17, 53]. This can be explained by the fact that different activation energy is required to break the carbon-hydrogen linkages, aliphatic and aromatic carbon-carbon linkages, and oxygen-containing complexes [17]. At temperatures of 200 °C or lower, gases adsorbed on the surface of coal and water vapors are released [17, 53]. Gaseous species with low molecular weights are released when the coal is further heated from 200 °C to 400 °C [17, 53]. Carbon monoxide, carbon dioxide, hydrogen, nitrogen oxides along with various hydrocarbons gases such as methane, ethane and propane are released at temperatures over 400 °C [17, 53], thus making coal a highly prospective carbon rich source. There is an opportunity to develop graphene films using coal via the CVD technique.
2.4 Graphene Growth Mechanism Studies

Graphene growth mechanism on metals with high carbon solubility, such as iridium and ruthenium, have been investigated thoroughly [54]. However, very few studies have been directed towards investigating the graphene growth kinetics on metals with low carbon solubility such as copper [45, 55]. Further, copper foils are covered with cupric and cuprous oxide, which hinders the catalytic activity of the copper as a substrate for the graphene growth [56]. However, annealing of copper was observed to increase the grain size, reduce the structural defects, and remove contaminants and volatile impurities from the surface of copper [45, 56-58]. Furthermore, it was observed that the low solubility of carbon on the copper substrate facilitated the formation of monolayer graphene films [45, 55]. Moreover, relative to iridium and ruthenium, copper is less expensive and more readily available in the United States.

Graphene growth on copper surface using methane as a carbon source involves the following elementary surface reactions which has been previously reported in literature [59-62].

\[
\begin{align*}
CH_4 & \rightarrow CH_3 + H \\
CH_3 & \rightarrow CH_2 + H \\
CH_2 & \rightarrow CH + H \\
CH & \rightarrow C + H
\end{align*}
\]
Li et al. used sequenced doping of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ on the copper substrate and studied the distribution of $^{12}$C and $^{13}$C graphene domains, which were determined using Raman spectroscopy [55, 56]. This isotope labeling technique showed some regions of $^{12}$C, some of $^{13}$C, and some regions with the presence of $^{12}$C and $^{13}$C, which suggested that the mechanism of graphene growth on copper is surface adsorption process [55, 56]. The schematic of the surface adsorption process as proposed by Li et al. is represented in Figure 2.2 [55].

![Figure 2.2](image-url)  
Figure 2.2: Schematic representation of surface adsorption process of graphene film formation on copper substrate utilizing isotope labeling technique as illustrated by Li et al. [55].

Similarly, various studies have demonstrated that the kinetics of graphene growth on copper substrate is determined by the adsorption, diffusion, dehydrogenation, nucleation, growth, and merging of graphene domains [56, 60, 63-65]. Literature suggests a surface mediated process with no change in graphene formation with increase in synthesis time once graphene covers the surface of copper [55, 56, 64].

Kim et al. have investigated a growth mechanism of graphene on copper using methane as the carbon source and provided more accurate understanding of this surface mediated process [64]. The concentration of carbon species ($C_{Cu}$) reaches saturation ($C_{nuc}$) by decomposition of methane on the copper surface through dissociative chemisorptions thus undergoing nucleation and subsequent growth of graphene domains [64]. The growth of domains either stops after consumption of all the carbon species or when these domains merge together to form graphene film and cover the surface of copper [64]. Kim et al. correlated their growth mechanism to monomolecular-like Avrami growth model and determined that the attachment of carbon species to the graphene edges is the rate limiting step [64]. The graphical representation of growth mechanism as developed by Kim et al. is represented in Figure 2.3 [64].
Figure 2.3: Graphene growth mechanism as illustrated by Kim et al. utilizing methane as the hydrocarbon source [64].


Alternately, Celebi et al. used Gompertz sigmoidal function to investigate the growth mechanism of graphene using ethylene as the carbon source [63]. The graphical illustration of graphene growth as predicted by the authors is shown in Figure 2.4 [63]. The authors determined that the catalytic reactions of ethylene to undergo dissociation and dehydrogenation is the possible rate-determining step for the growth of graphene on the copper surface [63].
Figure 2.4: Graphene growth mechanism as illustrated by Celebi et al. utilizing ethylene as the hydrocarbon source [63].


Different reaction cascades involved during the methane and ethylene based graphene growth (methane by Kim et al. and ethylene by Calebi et al.) lead to disparity between the associated mechanistic studies [63, 64]. Hydrocarbon gases (such as methane and ethylene) have different decomposition temperatures [66]. Ethylene has a lower decomposition temperature as compared to methane [66]. The decomposition temperature of the hydrocarbon gases is critical for the growth of graphene films. The hydrocarbons with higher decomposition temperature are suitable for the formation of monolayer graphene films on copper substrate [66]. Multilayer graphene are formed from larger aliphatic hydrocarbons [67]. The high carbon content from high molecular weight hydrocarbons such as ethane generate few layer to multilayer graphene films [67]. The secondary growth occurs by the reaction of carbon species from larger hydrocarbon
molecules with the pre-grown layer of graphene sheet [66, 68]. The boundaries, edges, defects, and impurities of pre-existing layer of graphene film acts as active sites for carbon adsorption and thus leads to formation of few layers to multilayers of graphene film [67, 69]. Higher aliphatic hydrocarbons have weaker bond energies associated with C-C and C-H linkages than methane [67]. These hydrocarbons dissociate more rapidly leading to the formation of active carbon species [67]. The suspended carbons from the pre-existing layer can bond with these additional carbon species forming nucleation seeds for additional graphene layers as represented in Figure 2.5 [67].

![Secondary or templated growth of graphene on the pre-grown graphene sheet as illustrated by Wassei et al. [67](9): p. 1415-1422. Copyright (2012) John Wiley and Sons; DOI: 10.1002/smll.201102276.](image)

The secondary growth demonstrates that there is no need of the copper catalyst in this growth step [70]. Hydrocarbon gases with high decomposition temperatures are favorable for the formation of few to single layer graphene as they suppress the templated or secondary growth step to produce monolayer or few layer graphene [66]. Further, it has been shown that the reduction of hydrocarbon gas flow rate effectively suppressed
the nucleation density [71, 72] and thus restricting the secondary growth step of graphene on the copper substrate [66]. High hydrogen flow rate was also found beneficial in suppressing the templated or secondary growth step [66]. Growth temperatures and time are critical towards formation of graphene films [63, 64]. The increase in growth temperature decreased the nucleation density thus favoring monolayer graphene formation [71].

The partial pressure of hydrocarbon gas is shown to be an important kinetic growth factor which is crucial in controlling the growth rate and uniformity of the graphene domains [65, 71, 73, 74]. The graphene domains were observed to increase in size with increase in the growth time [74-76]. An integral part of growth mechanism investigation is to analyze the formation of graphene domains. The graphene domains have been directly analyzed on the copper substrate utilizing high resolution scanning electron microscopy [63, 64]. The graphene domains have an inherent property of protecting the surface of copper from oxidation [72, 76, 77]. The non-domain areas oxidize in air as soon as the copper foil is removed out of the CVD furnace [63, 64]. Thus, the domains can be visible under high resolution scanning electron microscopy [63, 64]. Alternately, it was demonstrated that graphene domains can be made optically visible by heating the copper foil in air at low temperatures [72, 76, 77]. The areas with graphene domains remain unaffected, whereas other areas oxidize. The color contrast was then viewed under optical microscope as illustrated in Figure 2.6.
Figure 2.6: Growth of graphene domains on the copper substrate as viewed under optical microscope after low temperature treatment of the copper substrate in air. The graphene domains merge together to produce continuous graphene films.

Most of the graphene growth mechanism studies on copper surface have used hydrocarbon gas, such as methane or ethylene, as the carbon source [59-61, 63-65, 78]. There is not much effort directed towards mechanistic studies using solid carbon sources. It is hypothesized for solid carbon sources such as polymethyl methacrylate and polystyrene that the polymers directly decompose on the copper surface to form active carbon species and then undergo nucleation and growth [19]. While using amorphous carbon (a-C) films as the carbon source, the a-C film reacts with hydrogen to form methane which acts as the precursor for graphene formation [20].

The growth mechanism of graphene using coal is certainly unique and intriguing. Unlike using single hydrocarbon gas such as methane or ethylene as the carbon source in graphene growth, a mixture of various hydrocarbon gases are released during coal
pyrolysis with varied concentrations [17]. Further, these gases have different decomposition temperatures on the copper substrate [66]. Growth kinetics is greatly influenced by the hydrocarbon source as is evidenced from the studies by Kim et al. and Celebi et al [63, 64]. A growth mechanism of coal derived graphene film is proposed and the details are discussed in Chapter 6.
3.1 Experimental Methods

3.1.1 Chemical vapor deposition (CVD) for synthesis

Chemical vapor deposition (CVD) is a traditional technique used to grow thin films directly on any desired metal substrate through chemical reactions involving the vapor species and the metal substrate [79]. A typical CVD system incorporates a high temperature furnace where the chemical reaction occurs and a thin film is deposited on the metal substrate as a product of the reaction [79]. A gas delivery system with flow controllers are connected to the inlet of the furnace in order to deliver the reactive gases [79]. In addition to precursor gases for thin films, the delivery system also provides gases which act as a reducing agent for the reaction to proceed [79]. The non-reacted gaseous species are vented out through the exhaust, which may or may not have a vacuum pump system connected [79]. The CVD can thus be operated at atmospheric pressure or low pressure depending on the need of the reaction. A CVD system with a high temperature furnace and gas delivery system is shown in Figure 3.1.
CVD has been demonstrated to be a suitable technique to grow large area and high quality graphene films on various metal substrates such as copper [7, 8]. Copper has low solubility to carbon and can thus aid in growing uniform, large area, and high quality graphene films [45, 55]. Copper foil, 0.025 mm thick, 99.8 % (metals basis) was purchased from Alfa Aesar and used as the substrate. Wyoming [Wyodak (DECS-26)] coal obtained from the Penn state coal bank was used as a carbon source. The procured coal was ground, sieved, and mixed to obtain particle size of <44 µm. Argon (99.999 % purity) was used as the carrier gas and hydrogen (99.999 % purity) was used as the reducing agent/carrier gas for the synthesis. The synthesis was performed in a controlled CVD furnace.

3.1.2 Gas collection during coal pyrolysis

Coal pyrolysis releases numerous gaseous species including hydrocarbon gases. It is proposed that the hydrocarbon gaseous species act as reactive species to undergo
chemisorptions on the copper catalyst leading to formation of graphene films on the copper substrate [60, 63, 64]. Therefore, it is vital to analyze the gases released during the coal pyrolysis process.

A 5 L tedlar gas sampling bag with SS fittings purchased from SKC Inc., was connected to the end of the CVD tube furnace to collect the gases released during the coal pyrolysis process. Finally, the gases were analyzed using gas chromatography.

3.2 Physical Characterization

3.2.1 Raman spectroscopy

Raman spectroscopy is a traditional tool to investigate the structural properties of graphene films [80, 81]. It is considered to be the most robust and non-destructive technique to perform various analysis of graphite and graphene materials [80, 81]. Raman spectra of carbonaceous materials exhibit the G band (1508-1600 cm\(^{-1}\)) and the D band (1350 cm\(^{-1}\)). The G band is attributed to tangential vibration of carbon atoms and the D band to the structural defects and disorder [80]. The 2D band, an overtone of the D band, is usually observed around 2700 cm\(^{-1}\) [80], which originates from the double resonance process and is indicative of the band structure of graphite layers [80]. Raman spectra of different types of carbon films are represented in Figure 3.2 [82].
Phase transformation of carbon was investigated through the evolutions of the D, the G, and the 2D band. Raman spectroscopy was further used to evaluate the uniformity and quality of the graphene domains [72, 76]. Raman mapping was utilized to determine the quality of graphene films and graphene domains over a large area. The Raman spectra and mapping were obtained using a Bruker Senterra Raman spectrometer and microscope with a 532 nm laser.
3.2.2 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) is traditionally used to investigate the elemental composition of any material by performing a survey analysis [84, 85]. Once elements are identified from the survey spectra, the XPS can assist in chemical analysis of the individual spectra. XPS can thus determine the elemental and chemical composition of carbonaceous materials [84, 85]. The XPS of carbonaceous materials typically show a broad peak for the C1s spectra in the range of 282 – 290 eV. C1s spectra of various carbon are represented in Figure 3.3.

![Figure 3.3: XPS C1s spectra of different carbon types reproduced from Mérel et al. [86].](image)

XPS assisted in the assessment of sp\textsuperscript{2}/sp\textsuperscript{3} ratio and carbon-oxygen components in the carbon films. The XPS characterization was requested from the Edwards Accelerator laboratory at Ohio University. The spectra was analyzed using Kratos software at the Center for Electrochemical Engineering Research (CEER) at Ohio University.

3.2.3 Selected area electron diffraction (SAED)

Selected area electron diffraction (SAED) is utilized to investigate the nature and phase change in carbonaceous materials. The presence of a high intensity ring is an indication of amorphous nature; whereas the presence of diffraction spots is an indication of crystalline nature in carbonaceous materials. A combination of an amorphous ring and diffraction spots reveals the hybrid nature of carbonaceous materials [87]. SAED patterns of carbonaceous materials are depicted in Figure 3.4, adapted and reproduced from Cui et al. [87]. SAED of the carbon and graphene films were obtained using a JEM 2100F Transmission Electron Microscope (TEM).

![SAED patterns](image)

Figure 3.4: SAED pattern of carbon films showing amorphous nature (A), crystalline nature (C), and a hybrid amorphous-crystalline nature (B) of carbon films as adapted and modified from Cui et al. [87].

3.2.4 Optical microscopy

The graphene domains prevent oxidation of the underlying copper substrate. Thus, optical detection of these graphene domains can be used as a swift technique to investigate their evolution during progressive experimental conditions [72, 76, 77]. To facilitate optical detection, the copper foils were exposed to flash heating on a hot plate at 100 °C as shown in Figure 3.5.

![Figure 3.5: Procedure for optical detection of graphene domains utilizing optical microscopy.](image)

The optical microscopy was conducted utilizing an Alicona® Infinite Focus Optical Microscope (IFM) managed by the Institute of Corrosion and Multiphase Technology (ICMT) at Ohio University.

3.2.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was used to investigate the crystal structure and surface morphology of graphene films. The number of layers in the
graphene films were also determined from high magnification TEM images. TEM analysis was performed utilizing JEM 2100F Transmission Electron Microscope (TEM).

3.2.6 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) was used to investigate the surface morphology and height profile of the carbon and graphene films. The surface roughness of the carbon films were also determined utilizing AFM. AFM images were obtained using an Agilent Technologies 5500 Atomic Force Microscope in AC mode.

3.2.7 Optical transmittance

CVD grown graphene films are transparent. The transparent nature of these films is suitable for various applications such as touch screen devices. Optical transmittance measurements quantify the transparency of the carbon and graphene films. Optical transmittance spectra were measured using an Agilent 8453 UV-Visible spectrophotometer.

3.2.8 Electrical conductivity

Graphene films are electrically conductive. The conductivity depends on several factors such as quality of film, defects and disorders in the films, and thickness of the films. A standard four probe technique was implemented to measure the electrical conductivity of the carbon and graphene films. The electrical conductivity measurements were performed with assistance from Dr. Savas Kaya in the Department of Electrical Engineering and Computer Science at Ohio University.
CHAPTER 4 : THE GROWTH OF TRANSPARENT AMORPHOUS CARBON THIN FILMS FROM COAL

The contents of this chapter have been published in Carbon, a peer-reviewed journal: Vijapur, S. H.; Wang, D.; Botte, G. G., The growth of transparent amorphous carbon thin films from coal. Carbon 2013, 54, 22-28 [88].

4.1 Introduction

4.1.1 Coal pyrolysis

The thermal decomposition of coal in an inert atmosphere yields mixtures of several gaseous products at different temperatures [17, 89, 90]. Decomposition of coal below 200 °C produces water and some adsorbed gases. Species with low molecular weights are evolved when the coal is further heated in the range of 200 °C to 400 °C. Hydrocarbon gases are released at temperatures over 400 °C. The distribution of volatile species of sub-bituminous coal from Wyodak has also been well investigated by various researchers. For example, Miknis et al. investigated low temperature (375 °C, 400 °C and 425 °C) pyrolysis of Wyodak coal [53, 91]. They observed a net increase in aromatic carbon content in the pyrolysed coal, which was primarily attributed to the splitting and release of small portion of aliphatic carbon species with light and high hydrogen content such as CH₄, C₂H₂, etc. The remaining carbon is predominantly due to CO₂ and small amount of CO. Campbell J. H. investigated the gas evolution during the pyrolysis of Wyodak coal from 500 K to 1300 K[92]. He reported that small amounts of methane,
ethane, propane and ethylene are released at low temperatures of 650 K and peak at 750 K-800 K; whereas, CO\textsubscript{2} and CO are released at low temperature of 550 K. Similar pyrolysis products of Wyodak coal were reported by Westmoreland and Forrester [93].

As mentioned earlier, the hydrocarbon gases released as products of coal pyrolysis at temperatures over 400 °C can act as precursors for formation of graphene films. Hence, initially low synthesis temperature of 400 °C and an atmospheric pressure were maintained to verify the possibility of graphene synthesis. However, it was determined that low temperature synthesis produced amorphous carbon films and did not yield crystalline graphene films. Within this context, this chapter reports a low temperature chemical vapor deposition towards the synthesis of large area, uniform, and transparent amorphous carbon thin films on copper foils with few nanometer thickness. The properties of the carbon thin films were characterized and investigated by atomic force microscopy (AFM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and optical transmittance spectroscopy.

4.1.2 Amorphous carbon (a-C) thin film

Amorphous carbon (a-C) thin film is a network of disordered carbon phase consisting of short and medium range order [94, 95]. Amorphous carbon thin films exhibit remarkable chemical, mechanical, thermal, and opto-electrical properties, which are attributed to the versatility of the concentrations of sp\textsuperscript{1}, sp\textsuperscript{2}, and sp\textsuperscript{3} hybridization sites and the atomic connectivity within the carbon network [94-98]. The disordered structure of amorphous carbon is represented in Figure 4.1 [99].
Carbon thin film can be synthesized using different methods such as chemical vapor deposition (thermal and plasma), pulsed laser deposition, and sputtering (radio frequency, magnetron and ion beam) [43, 94, 100]. Most of the synthesis techniques that are implemented either operate at high temperatures (> 600 °C) and/or entails complex procedures [101]. Chemical vapor deposition (CVD) is a promising method for growing high quality and large area carbon thin films. However, the CVD methods usually require hydrocarbon gas as a carbon source [43, 44], which limit the applications of this
technology to various potential carbon feedstocks. Coal is a complex structure rich in mineral matter content and often considered to be a two component system [10]. While one system is the mobile phase which consists of low molecular weight species, the other system is the macromolecular network composed of cyclic aromatic rings which are clustered and linked together by bridges [10]. In addition, coal is an inexpensive and abundantly available resource with high carbon content.

Amorphous carbon films have excellent conductivity and transparency, exceptional chemical stability and corrosion resistance, high hardness, and high melting point [94, 100, 102-106]. Additionally, these films have demonstrated great potential in applications ranging from solar cells, protective coatings in magnetic storage and biomedical implants, light emitting diodes (LED) to photodiodes etc. [94, 98, 100, 102, 103, 105-114]. Thus, it is interesting to extend the application of coal to produce carbon thin film.

4.2 Experimental

4.2.1 Chemicals and materials

Sub-bituminous coal (Wyodak coal seam, Wyoming) was obtained from the Penn state coal bank and database. The elemental analysis obtained from the database reported carbon (69.74 %), hydrogen (5.55 %), nitrogen (0.94 %), organic sulfur (0.35 %), oxygen (14.83 %), and mineral matter (8.59 %) for the sub-bituminous coal. The proximate and ultimate analysis of the Wyodak coal is given in Table 4.1.
Table 4.1: The proximate and ultimate analysis of Wyodak coal obtained from the Penn state coal bank and database

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Ultimate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % (dry basis)</td>
<td>Wt % (dry basis)</td>
</tr>
<tr>
<td>Ash</td>
<td>7.57</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>44.86</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>47.57</td>
</tr>
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<td></td>
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Acetone (> 99 %), Cupric sulfate (> 95 %), and Hydrochloric acid (6 N) were obtained from Fisher Scientific. Copper foils (99.8 %, 0.025 mm thickness) and titanium foils (99.99 %, 0.127 mm thickness) were purchased from Alfa Aesar. Quartz slides (1 mm thickness) were purchased from Ted Pella. Si wafers (SSP 0.025 mm VSI stock wafers) were procured from Virginia Semiconductor Inc.

4.2.2 Sample preparation

Copper foils were cut into ~1 cm × 1 cm pieces and rinsed with acetone, and finally dried with a flow of Argon (99.999% purity) to be used as substrates for the synthesis of carbon thin films. The coal was ground, sieved and shuffled to attain a uniform particle size distribution of < 44 µm. Approximately, 1 mg of coal samples were
placed on the copper foils. The copper foils with the coal were then placed inside a quartz tube for CVD synthesis in a tube furnace.

4.2.3 CVD synthesis

The carbon thin films were fabricated in a controlled CVD furnace under ambient pressure. A schematic of the CVD system used for the synthesis of the carbon thin films is shown in Figure 4.2A. The CVD system consists of a furnace with a 3 foot long alumina tube. One end of the tube with gas input was positioned away from the heating zone for performing a fast heating and fast cooling process. The fast heating and cooling processes were accomplished by moving a 1 cm diameter quartz tube inside the alumina tube. A magnet was attached to the quartz tube which assisted in the movement for the fast heating and fast cooling stages of the process. This process facilitated the separation of carbon thin film from the substrate in an efficient manner [8]. Copper foils with coal samples were placed inside the quartz tube. The edges of the copper foils were folded to hold the coal on the foils thus avoiding any spillage, and also to fit into the quartz tube. The tubes were positioned initially as represented in Figure 4.2A in such a way that the substrates were out of the heating zone.
Figure 4.2: Equipment and process used for the synthesis of carbon thin films from coal. (A) Schematic of the CVD system. (B) Operating conditions for the synthesis of the carbon thin films from coal: temperature, time, and flow rates.

Figure 4.2B shows the process used for the synthesis of the carbon thin films: synthesis time, temperature, and gas flow rate. The tube furnace was first purged with 300 sccm Argon for 30 min in order to create an inert atmosphere. The furnace temperature was then stepped to 400 °C in 15 min. Once the furnace reached 400 °C, the quartz tube was shifted inside the heating zone using a magnet. The synthesis temperature
was kept at 400 °C for 15 min. After 15 min, the quartz tube was shifted out of the heating zone for performing the fast cooling process. Finally, the furnace was cooled down to room temperature and carbon thin films were synthesized on the copper foils. Coal residues were observed on the copper foil even after the synthesis. Coal is a complex heterogeneous organic material and contains non-carbonaceous elements associated with it [10]. At temperatures lower than 400 °C, when coal is subjected to thermal annealing in an inert atmosphere, most of the non-carbonaceous elements do not undergo decomposition and hence a residue is observed. In order to obtain pure carbon thin films, the copper foil substrates were dissolved in Marbles reagent (10 g CuSO$_4$, 50 ml HCl, 50 ml DI water) [42]. The copper dissolved in the Marbles reagent in approximately 2 hours, leaving the carbon thin films floating in the solution.

4.2.4 Physical characterization

The surface morphology and the height profile of the carbon thin films on Si wafers were characterized using atomic force microscopy (AFM). The AFM images were acquired under ambient conditions using an Agilent 5500 AFM/STM microscope in AC mode with NSC 15/AlBS probes (resonant frequency of 325 kHz) from MikroMasch USA (Wilsonville, OR). The root mean square (rms) roughness of the carbon thin film was determined using the WSxM Scanning Probe Microscopy Software [115]. Transmission electron microscopy (TEM) images and the energy dispersive X-ray spectroscopy (EDX) of the carbon thin film were acquired using the Tecnai F20 system. The carbon thin film was transferred onto a TEM grid for the characterization. The Raman spectra of the carbon thin films on titanium foils were obtained using a Bruker
Senterra Raman spectrometer and microscope through a 20X objective lens. 532 nm laser excitation with 20 mW power, 3-5 cm\(^{-1}\) of resolution and 20 s of integration time were used for Raman spectra collection. The X-ray photoelectron spectroscopy (XPS) analysis of the carbon thin film was conducted using Kratos XSAM 800 electron spectrometer. Monochromated 1484 k\(\alpha\)Al X-ray source with an operating power of 120 W and pass energy of 40 eV was used for the analysis. Optical transmittance spectra of the carbon thin films on quartz slides were measured using an Agilent 8453 UV-Visible spectrophotometer in the region from 350 nm to 900 nm.

The electrical conductivity of the carbon thin film was measured using the standard four probe technique. Measurements were performed under ambient conditions using Tungsten probe tips. The resistance was measured using Agilent 34401A digital multimeter. The electrode contacts were formed by sputtering a 20 nm conducting layer of gold/palladium on a silicon substrate masked with Metrigraphics deposition mask (0.254 mm lines and spaces). The carbon thin film was then placed onto the conducting layer. A total of ten measurements were acquired and average value of electrical conductivity was calculated.

4.3 Results and Discussion

Figure 4.3A shows the photographic image of a copper foil after the CVD synthesis floating in the Marbles reagent solution, while in Figure 4.3B, the copper foil is dissolving and a transparent thin film is visible in the background. The floating carbon thin film was transferred to DI water using a clean glass slide, in order to clean its surface
and prevent the formation of copper sulfate crystals on the film. After cleaning in the DI water, the carbon thin films were transferred to various substrates including glass and quartz slides, silicon wafers, titanium foils, and flexible plastics by directly lifting the films from the DI water using the desired substrates. Figure 4.3C and Figure 4.3D show the uniform and transparent carbon thin films transferred to a titanium foil and to a silicon wafer, respectively.

Figure 4.3: Images of the carbon thin films on different substrates. Photographs of (A) Copper foil after the synthesis floating on the Marbles reagent solution. (B) Copper foil dissolving in the reagent leaving behind a transparent carbon thin film as seen in the background. (C) Carbon thin film transferred to a titanium substrate. (D) Carbon thin film transferred to a silicon substrate.
The size of the carbon thin film is limited by the diameter of the quartz tube. The synthesis of any desired size of carbon thin films can be obtained using large copper substrates and with larger quartz tubes during the CVD synthesis.

The synthesis of carbon thin films at different temperatures were also investigated. There was no formation of film when the synthesis was performed at temperatures lower than 400 °C. It is hypothesized that the hydrocarbons released during the coal pyrolysis are the precursors for the growth of the carbon thin films and are adsorbed on the surface of copper. The copper acts as a catalyst and assists in the decomposition of these hydrocarbons to form active surface species of carbon [63, 64, 66]. These carbon species then diffuse onto the copper surface, thus increasing in concentration. Finally, the carbon species merge together and undergo nucleation producing carbon thin films [18-20].

The morphology and thickness of the carbon thin films were characterized by atomic force microscopy. Figure 4.4A reveals a typical carbon thin film on a silicon substrate. The brighter stripes designating thicker areas on the carbon thin films are either due to formation of wrinkles, overlapping of edge, or back-folding of edge during the transfer process. Figure 4.4B shows that the thickness of the films was about 5 nm as measured by AFM at the edge.
Figure 4.4: (A) AFM image of the carbon thin films on Si substrates. (B) Height profile of the carbon thin films indicating the thickness to be ~5 nm.

The roughness of the carbon thin film was further investigated by higher magnification AFM imaging (Figure 4.5A). The 3D representation in Figure 4.5B further reveals troughs and peaks in the carbon thin film, which are in agreement with the continuous peaks and depressions in the height profile (Figure 4.4B). The root mean square (rms) surface roughness was determined to be ~0.55 nm suggesting that the carbon thin films have smooth surfaces. The rms surface roughness value for the carbon
thin films is within the range and in some cases less than previously reported data on a-C films synthesized using other techniques [102, 103, 105, 116].

![AFM image of carbon thin films](image)

Figure 4.5: (A) Large magnification AFM image of the carbon thin films. (B) 3D representation of the carbon thin films.

The surface morphology and structure of the carbon thin film was further characterized by TEM as shown in Figure 4.6. The low magnification image (Figure 4.6A) shows continuous carbon thin film with the formation of wrinkles, back-folding
and overlapping of edge due to the transfer process and is consistent with the observation from the AFM characterization. The high magnification TEM image (Figure 4.6B) does not show any graphitic ordering, suggesting the amorphous nature of the carbon thin film.

![Figure 4.6: (A) Low magnification TEM image of the carbon thin film. (B) Large magnification TEM image of the carbon thin film.](image)

Chemical element analysis of the carbon thin film was determined by energy dispersive X-ray spectroscopy (EDX). EDX (Figure 4.7) analysis reveals that the thin film consists of C (98.97 atomic %), O (0.88 atomic %), Cu (0.14 atomic %), and trace amounts of S. The Cu signal observed in the spectrum results from the residual CuSO$_4$ reagent for Cu foil etching process. Trace amounts of S and O can be attributed to the impurities of coal and/or the residual CuSO$_4$ reagent.
Figure 4.7: The EDX spectrum of the carbon thin film revealing 98.97 % as atomic carbon.

Raman spectrum of the carbon thin films is shown in Figure 4.8. The thin film exhibit the D band at 1368 cm$^{-1}$ and the G band at 1594 cm$^{-1}$. The D band is attributed to the carbon defects and disorder, and the G band relates to the tangential vibration of the carbon atoms [80]. The widening of the bands observed in the Raman spectrum is characteristics of amorphous nature due to the short range order [117]. The featured bands in the Raman spectrum verified that the thin film consists of amorphous carbon, which is consistent with TEM characterization.
The carbon thin film was further characterized by X-ray photoelectron spectroscopy (XPS). As shown in Figure 4.9, the XPS spectrum reveals the C1s peak centered at 285.2 eV, which is in agreement with the reported XPS spectrum of amorphous carbon thin films [94, 95].

Figure 4.8: Raman spectrum of the carbon thin film showing broad D and G bands.
Figure 4.9: XPS spectrum of the carbon thin film revealing a C1s peak centered around 285.2 eV indicating formation of amorphous carbon film.

In addition, the XPS survey spectrum of carbon thin film (Figure 4.10) reveals the presence of copper, oxygen, and carbon. The XPS survey did not show any other impurities present in the carbon thin film. This further validates the discussion regarding the presence of impurities in the carbon thin film (revealed in the EDX analysis), suggesting that the impurities originate from the Marbles reagent used in the transfer process.
Figure 4.10: XPS survey spectrum of the carbon thin film revealing C, O, and Cu peaks from the carbon thin film grown on the copper surface.

The carbon thin films were also transferred onto quartz slides for the optical transmittance measurements. The optical transmittance spectrum of the carbon thin film is depicted in Figure 4.11. The synthesized carbon thin films have > 95 % optical transmittance over the spectral range from 350 nm to 900 nm. This transmittance is higher than previously reported data of optical transmittance of a-C films [106, 110, 118].
Figure 4.11: Optical transmittance spectrum of the carbon thin films indicating the transmittance to be > 95 % over the spectral range of 350 nm to 900 nm.

The standard four probe technique was implemented to measure the electrical conductivity of the carbon thin film. The sheet resistivity of amorphous carbon thin film was calculated to be 0.61 MΩ sq\(^{-1}\), and corresponding electrical conductivity was calculated to be \(3.28 \times 10^2\) S m\(^{-1}\). The sheet resistivity is in agreement with two layer carbon nanosheet synthesized at 1100 K by Nottbohm et al. (0.38 ± 0.13 MΩ sq\(^{-1}\)) [119] and carbon nanosheets synthesized at 1100 K by Turchanin et al. (0.1 MΩ sq\(^{-1}\)) [120]. The electrical conductivity is in agreement with ultrathin conducting carbon film synthesized by Schreiber et al. (3.9×10\(^2\) S m\(^{-1}\)) at 750 °C [110]. Lower resistivity of carbon thin films is observed with increase in the synthesis temperature [110, 119-122].
4.4 Conclusion

Inexpensive and abundantly available sub-bituminous coal was used as a solid carbon source for the synthesis of carbon films via low temperature CVD. The conditions investigated were not suitable for the production of crystalline graphene films. However, large-area and transparent amorphous carbon thin films with few nanometer thickness were obtained. The carbon thin films were characterized by AFM, Raman spectroscopy, TEM, EDX, XPS, optical transmittance spectroscopy and electrical conductivity measurements. The synthesized carbon thin film was ~5 nm thick with a surface roughness of ~0.55 nm demonstrating a smooth surface, a high transparency of >95 %, and good compatibility with various substrates, and thus show great potential in tribological applications, solar cells, and electronic devices.
CHAPTER 5 : RAW COAL DERIVED LARGE AREA AND TRANSPARENT GRAPHENE FILMS


5.1 Introduction

Although coal has been used as a carbon source for the synthesis of carbon nanotubes [47] and fullerenes [26], few studies have been carried out on the synthesis of graphene films using coal. Recently, anthracite coal has been used for graphene growth through a complicated and multi-step process, which involves catalytic graphitization at 2400 °C, chemical oxidation, and dielectric barrier discharge plasma-assisted deoxygenation [16]. Graphene has a large specific surface area with remarkable physical and chemical properties [1, 6], demonstrating huge potential for a variety of applications such as sensors [6], batteries [3], and super capacitors [2]. Transparent and conducting graphene films have inspired increasing interest in terms of practical applications of graphene such as solar cells [4], field effect transistors [6], and electronics [5]. Thus, it becomes necessary to develop a facile and economic method for growing graphene films from raw coal. Chapter 4 demonstrated that low temperature and atmospheric pressure CVD failed to yield graphene films, but only amorphous carbon (a-C) thin films. Low pressure CVD has been verified to be an ideal technique for the synthesis of graphene
films [61, 71, 124-126]. Further, there are oxide films on copper substrate, which needs to be removed by thermal annealing. Thermal annealing of copper in presence of hydrogen is conducted prior to graphene growth [45, 55, 56, 63, 64, 71]. Hydrogen acts as a reducing agent to remove the oxide layer and creates a surface ideal for graphene growth [45, 55, 56, 63, 64, 71]. Accordingly, the system and the synthesis procedure described in Chapter 4 was modified to integrate low pressure and hydrogen environment. Within this context, Chapter 5 reports the synthesis of graphene films using abundant and inexpensive raw coal as solid carbon source via a modified CVD setup and procedure.

5.2 Experimental Details

5.2.1 Chemicals and materials

Sub-bituminous coal (Wyodak coal seam, Wyoming) was purchased from the Penn state coal bank and database. The elemental analysis of the Wyodak coal was provided by the coal bank reported carbon (69.74 %), hydrogen (5.55 %), nitrogen (0.94 %), organic sulfur (0.35 %), oxygen (14.83 %), and mineral matter (8.59 %) content.

Acetone (> 99 %), Cupric sulfate (> 95 %), and Hydrochloric acid (6 N) were purchased from Fisher Scientific. Copper foils (99.8 %, 0.025 mm thickness) were obtained from Alfa Aesar. Flexible plastic substrates were obtained from Grafix Plastics. Quartz slides (1 mm thickness) were procured from Ted Pella. Silicon wafers (SSP 0.025 mm VSI stock wafers) were purchased from Virginia Semiconductor Inc.
5.2.2 Sample preparation

Copper foils were used as substrates for the synthesis of graphene films and cut into pieces of 1 cm × 1 cm. The copper foils were rinsed with acetone and dried with a flow of Argon (99.999 % purity). The coal was ground, sieved, and mixed to obtain particle size of < 44 μm. The copper foil was placed on one end of a semicircular quartz boat. Approximately, 10 mg of coal was placed on one end of another semicircular quartz boat. The quartz boat with copper foil was placed inside a quartz tube (2” diameter and 66” long) and was positioned inside the heating zone; whereas, the semicircular quartz boat with coal was placed inside the quartz tube and initially positioned out of the heating zone. Magnets were attached to both of the semicircular quartz boats as shown in Figure 5.1. An external magnet was used to move both of the semicircular quartz boats in and out of the heating zone. The schematic of the CVD setup is illustrated in Figure 5.1.

![Figure 5.1: Schematic of the modified CVD set up demonstrating vacuum tubular furnace with two quartz boat. Quartz boats are utilized as support for coal and copper substrate each. The setup and procedure was modified to perform a two step process of annealing the substrate followed by subsequent synthesis by performing coal pyrolysis.](image-url)
5.2.3 Graphene synthesis

The sub-bituminous Wyodak coal was used as solid carbon source. Coal was placed on one end of a quartz boat and the copper foil was placed on one end of another quartz boat as represented in Figure 5.1. While the quartz boat with copper foil was positioned inside the heating zone, the CVD quartz tube was evacuated to 100 mtorr and backfilled with hydrogen gas (99.999 % purity) at a flow rate of 100 sccm, thus maintaining a pressure of 2-5 torr in the system. The furnace was ramped to 1050 °C in 40 min and kept at 1050 °C for the whole graphene synthesis process. After 15 min of annealing the copper foil, the quartz boat with coal was shifted inside the heating zone using an external magnet, for the growth of graphene films on the copper foil. The growth time was maintained for 30 min. After the synthesis, both the quartz boats were shifted out of the heating zone for a fast cooling to room temperature. The furnace was cooled down to room temperature, the vacuum pump and the gas flow turned off before opening the tube furnace. The synthesis procedure showing operating parameters for the growth of graphene films using raw coal is represented in Figure 5.2.

The obtained graphene films were then characterized by Raman spectroscopy, UV-Visible spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED).
5.2.4 Graphene transfer process

The graphene films were obtained by dissolving the copper foil in the Marbles reagent \((10 \text{ g CuSO}_4, 50 \text{ ml HCl}, 50 \text{ ml DI water})\) [42]. The copper foil was dropped in the Marbles reagent for \(~2 \text{ h}\), thus etching the copper and a graphene film was observed to be floating in the solution. The floating graphene film was then transferred to DI water using a clean glass slide. This process was repeated three times in order to clean the surface of the graphene film and remove any contamination from the Marbles reagent. The floating graphene film in the DI water can be directly lifted onto the desired substrates such as silicon wafer, glass and quartz slides, and flexible plastic substrates.
5.2.5 Physical characterization

The graphene films were transferred onto quartz slides for obtaining the transmittance spectra. Optical transmittance spectra were measured using an Agilent 8453 UV-Visible spectrophotometer in the region from 400 nm to 900 nm. The Raman spectra of the graphene films on silicon wafer were acquired using a Bruker Senterra Raman spectrometer through a 50X objective lens. Raman spectra were measured using an argon laser ($\lambda=532$ nm) with 20 mW power, resolution range of 3-5 cm\(^{-1}\) and integration time of 20 s. Atomic force microscopy (AFM) was used to characterize the surface morphology and height profile of the graphene film. The graphene film was transferred onto a silicon wafer and used for the AFM characterization. The images were obtained at ambient conditions using an Agilent 5500 AFM microscope in AC mode with NSC 15/AlBS probes (resonant frequency of 325 kHz) from MikroMasch USA (Wilsonville, OR). Transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) of the graphene films were acquired using the Hitachi H-7600 Transmission Electron Microscope (TEM). The graphene film was transferred to a lacey carbon TEM grid for the characterization. A standard four probe technique was implemented to measure the electrical conductivity of the graphene film at ambient condition. Silicon wafer was masked with Metrigraphics deposition mask and sputtered with 20nm conducting layer of gold/palladium. Graphene film was then transferred onto the conducting layer which acted as electrode contacts for the measurements. Measurements were performed using four tungsten probe tips and an Agilent 34401A digital multimeter. The resistance was directly measured on the Agilent 34401A digital
multimeter and corresponding sheet resistance was calculated based on the measurements acquired.

5.3 Results and Discussion

Figure 5.3A and Figure 5.3B show photographs of uniform and transparent graphene films ~1×1 cm² in size supported on a glass slide and flexible plastic substrate, respectively. Larger size of graphene films can be obtained by increasing the size of the copper substrate and the tube furnace. The glass slide and flexible plastic substrate with the graphene films are placed over the letterings “COAL” and “CEER”, respectively, in order to demonstrate the transparency.

Figure 5.3: (A) Photograph of transparent graphene film on a glass slide, and (B) Photograph of graphene film on a flexible plastic substrate. The size of graphene films is about 1 cm × 1 cm.
The transparency of the graphene film was further determined by optical transmittance spectroscopy. The graphene films have over 95% transmittance in the spectral range of 400-900 nm as shown in Figure 5.4A.

![Optical transmittance spectra](image1)

![Raman spectra](image2)

Figure 5.4: (A) Optical transmittance spectra of graphene film with over 95% transmittance in the spectral range of 400 nm to 900 nm, and (B) Raman spectra of raw coal (curve 2) and few layer graphene films (curve 1) obtained from the raw coal.

As shown in Figure 5.4B (curve 1), the film exhibited the D band at 1360 cm\(^{-1}\), a zone-boundary phonon mode in first order Raman spectra attributed to defects in the graphene films; the G band at 1585 cm\(^{-1}\), associated with the tangential vibrations of sp\(^2\) bonded carbon atoms; and the 2D band at 2700 cm\(^{-1}\), a boundary phonon mode in second order Raman spectra associated with graphene [70]. As a comparison, the raw coal only exhibits a broad D peak at 1365 cm\(^{-1}\) and the G peak at 1582 cm\(^{-1}\) (Figure 5.4B, curve 2), which are the characteristics of amorphous carbon showing defects and disorder [127].
The D band is related to defects or disorder such as subdomain boundaries and point defects in the graphene films [66, 128, 129]. The D band has low intensity or is inactive for single layer graphene and the intensity increases for multilayer graphene [129]. These defects or disorder are attributed to the breaking of hexagonal structure of graphene caused by the sp\(^3\) hybridized carbons and/or by the abundance of carbon species from the precursor [42, 130]. It is also noted that coal pyrolysis produces various gaseous mixtures such as CO, nitrogen oxides apart from hydrocarbons, which may induce some defects in the coal derived graphene films. Previous studies have demonstrated that the intensity of the G/2D ratio is about 0.3-0.5 for monolayer graphene [42, 45, 131], and increases to 2.4 for few-layer graphene films [70, 128, 131]. Further, it has been reported that the full width at half maximum (FWHM) of the 2D peak for 3-5 layer graphene films is between 45-85 cm\(^{-1}\) [70, 128, 131]. The FWHM of the 2D peak and the intensity of the G/2D ratio of coal derived graphene films are \(\sim\)57 cm\(^{-1}\) and 1.33, respectively. These values of FWHM and the G/2D intensity ratio indicate coal derived graphene films are few layer rather than monolayer.

The AFM image (Figure 5.5A) shows the continuous graphene film on silicon substrate. Line scans were performed on the various regions of graphene films to determine the thickness, as depicted in the AFM image (Figure 5.5A). The corresponding height profiles (Figure 5.5B) show that the thickness is \(\sim\)3-7 nm across the line scans (1, 2, 4, and 5) suggesting the formation of few layer graphene films, which is in agreement with the Raman spectra measurements. The brighter areas in the AFM image are caused by the back-folding and/or overlapping and due to the formation of wrinkles during the
graphene film transfer process. This can be evidenced in the AFM image and the corresponding height profile for line scan 3, which reveals the thickness to be \(~10\) nm for the brighter region.

![AFM Image](image)

**Figure 5.5:** (A) AFM image reveals a continuous graphene film on silicon wafer with some brighter spots exhibiting wrinkles and overlapping. Line scans were performed to determine the thickness of the graphene films. (B) Corresponding height profile of the various line scans revealing the thickness of graphene film to be \(~3-7\) nm demonstrating formation of few layer graphene films.

The nature of the graphene film was further confirmed by TEM. The image (Figure 5.6A) reveals continuous graphene film over a large area on the TEM grid.
Wrinkles can be observed in the TEM image, which is in compliance with the AFM image. The SAED pattern (Figure 5.6B) demonstrates the typical hexagonal crystalline structure of graphene. Further, the SAED pattern clearly reveals six diffraction spots, thus confirming crystalline nature of graphene film [70, 132].

Figure 5.6: (A) TEM image of large area and continuous graphene film. (B) SAED of the graphene film showing hexagonal pattern with six diffraction spots demonstrating crystalline nature of the graphene film.

A standard four probe technique was implemented to measure the sheet resistance of the graphene film at ambient conditions. The sheet resistance of the graphene film was determined to be 5.0 kΩ sq⁻¹, which is close to the reported value of graphene films synthesized using solid carbon sources [42].
The mechanism of the growth of graphene film using coal is appealing. Coal consists of species with low molecular weights and a macromolecular complex of aromatics, which are networked together [88]. The pyrolysis of coal in an anaerobic atmosphere yields various gaseous mixtures at different temperatures due to the different activation energy for breaking of the aliphatic carbon-carbon linkages, carbon-hydrogen linkages, oxygen-containing complexes, and aromatic carbon-carbon linkages [17]. Water and some adsorbed gases are produced below 200 °C. In the range of 200 °C-400 °C, low molecular weight species are released. Hydrocarbon gases (such as methane and ethylene), CO$_2$, CO, nitrogen oxides, and hydrogen are evolved when the temperature exceeds 400 °C [17, 53]. The pyrolysis of Wyodak coal and distribution of volatile species has been reported by various researchers [53, 92, 93]. Similar findings of hydrocarbon gas evolution such as methane, propane, ethane, and ethylene during the Wyodak coal pyrolysis has been determined [53, 92, 93]. It can be proposed that like other solid carbon sources used for the graphene synthesis [19, 20], the hydrocarbons released during pyrolysis of Wyodak coal work as precursors for the synthesis of graphene films. The released hydrocarbons are adsorbed on the copper surface thus forming active surface carbon species. The concentration of the carbon species on the copper surface increases. These species undergo nucleation and growth producing graphene films [19, 20]. Different hydrocarbon precursor gases affect the graphene layer formation [130]. The higher concentration of carbon from larger aliphatic hydrocarbons such as ethane and propane produce thicker graphene films [130]. The growth of additional layers of graphene occurs by supplementary carbon species from high carbon
concentration, reacting on the pre-grown graphene sheet [66, 130]. The impurities, boundaries, defects or edges of the pre-existing graphene layer can act as nucleation sites for these reactive species and thus grow to form additional layers of graphene [130]. Thus, larger aliphatic hydrocarbons such as propane, ethane, and ethylene formed during Wyodak coal pyrolysis might cause an increase in nucleation density leading to formation of few layer graphene films.

5.4 Conclusion

In conclusion, few layer graphene films were synthesized using abundant and inexpensive raw coal as the carbon source via CVD. The large area graphene films were uniform and continuous with thickness of ~3-7 nm as revealed from the TEM and AFM images. The graphene films were >95 % transparent and conductive with sheet resistance of 5.0 kΩ sq⁻¹ as determined by optical spectroscopy and electrical conductivity measurements, respectively. The coal derived graphene films thus exhibit great potential in various applications such as electronics and energy storage applications.

An investigation of graphene growth mechanism was required in order to validate the growth mechanism hypothesis and also to make the synthesis process applicable to other various types of coal. The growth mechanism was investigated utilizing various techniques and is discussed in the Chapter 6.
CHAPTER 6 : AN INVESTIGATION OF GROWTH MECHANISM OF COAL DERIVED GRAPHENE FILMS


6.1 Introduction

The discovery of graphene has created an immense interest in developing an efficient synthesis route for high quality and large-scale production opening a new wave of research in targeting its use in diverse applications [4-6, 35-37, 133, 134]. Chemical vapor deposition (CVD) is a promising technique for high quality, large area, transparent and scalable graphene synthesis [7, 8, 128]. Non-conventional carbon sources such as food waste and amorphous carbon films have been utilized for graphene production via CVD [9, 135]. Similarly, Chapter 4 and Chapter 5 have demonstrated the utilization of coal as a non-conventional carbon source to grow amorphous carbon and graphene films, respectively [88, 123, 136]. The current market price of CVD grown graphene stands at roughly $10-12 per cm$^2$ [137, 138]. Current laboratory scale production of graphene via CVD and utilizing coal as a carbon source brings down the cost of graphene to ~$4.50 per cm$^2$. The cost analysis of coal derived graphene film is included as appendix A (The analysis includes the cost of supplies, source, services, personnel cost, and other indirect cost to produce coal derived graphene films). The reduction in cost from the preliminary
economic analysis inspires the initiative of utilizing coal for graphene production, although this process needs to be optimized for efficient scale up.

The studies on the growth mechanism of graphene are critical for the optimization process and also to tailor the graphene films as desired for various applications. The graphene growth mechanism is influenced by not only the synthesis conditions such as temperature, pressure, and time, but also by the solubility of carbon in the metal substrate [45, 55, 63, 64, 70, 71, 74, 139]. The low carbon solubility in the copper substrate has been demonstrated to be ideal for the synthesis of graphene [45, 55]. Previous studies on graphene growth mechanism on the copper substrate focused on the formation of graphene films utilizing pure hydrocarbon sources such as methane and ethylene [45, 55, 63, 64, 71]. Graphene growth studies show that the growth mechanism involves copper catalyzed surface adsorption of carbon species from the pure hydrocarbon source, which undergoes nucleation to form graphene domains. These graphene domains grow and merge together to form graphene film on the copper substrate [55, 71]. Interestingly the surface mediated graphene growth mechanism is revealed to be self-limiting, which is attributed to the low solubility of carbon species on the copper substrate [45, 55]. However, various studies have demonstrated a change in graphene growth kinetics depending on the growth conditions leading to formation of bilayer or multilayer graphene films [65, 70, 140]. This confirms the self-limiting graphene growth mechanism does not hold for all the growth conditions. Furthermore, there is little focus on investigating the graphene growth mechanism using solid carbon sources such as coal. Unlike pure hydrocarbon gases, coal pyrolysis releases a mixture of various gases
including hydrocarbons with different molecular weights. Moreover, the partial pressure of gaseous hydrocarbons, which presumably influences the graphene growth [65, 73, 74] is challenging to control while utilizing a complex solid carbon source such as coal. Consequently, it is essential to elucidate the carbon nucleation, growth of domains, and coal pyrolysis products to better understand the growth mechanism of coal derived graphene films. An understanding of the graphene growth mechanism using coal could have a significant impact on the optimization of the synthesis conditions, economics, and environment during the efficient scale up of the process.

Within this context, the objective of the present work is to investigate the growth mechanism of coal derived graphene films, which will facilitate future production of high quality graphene films from various types of coal (anthracite, bituminous, etc.) as a carbon source. Further, characterization of these graphene domains and the graphene films using optical microscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) will assist in developing a growth model for the coal derived graphene films.

6.2 Experimental

6.2.1 Chemicals and materials

The coal used for the experimental work was Wyodak coal (Wyodak coal seam, Wyoming), a sub-bituminous type, which was purchased from the Penn state coal bank. The datasheet provided by the Penn state coal bank reported the elemental analysis of
Wyodak coal as - carbon (69.74 %), hydrogen (5.55 %), nitrogen (0.94 %), organic sulfur (0.35 %), oxygen (14.83 %), and mineral matter (8.59 %) content.

Copper foils (99.8 %, 0.025 mm thickness) obtained from Alfa Aesar were used as substrates for graphene synthesis. Acetone (> 99 %) used for rinsing the copper foils was purchased from Fisher Scientific. Cupric sulfate (> 95 %), and Hydrochloric acid (6 N) used for preparation of the Marbles reagent were also procured from Fisher Scientific. Silicon wafers (SSP 0.025 mm Virginia Semiconductor Inc.) were used as substrates to transfer the graphene films. Copper grids (PELCO® Center-Marked Grids, 300 mesh, 3.0 mm O.D.) and lacey carbon grids (300 mesh, Copper) purchased from Ted Pella were used for transmission electron microscopy (TEM) characterization. 5 L Tedlar sampling bags with stainless steel fittings were purchased from SKC Inc. for gas collection during the coal pyrolysis process.

6.2.2 Sample preparation and synthesis

The sample preparation and synthesis were performed using the experimental procedure and setup demonstrated in Chapter 5 [123]. Briefly, a tubular furnace was evacuated with a vacuum pump and backfilled with hydrogen. The furnace was ramped to the desired synthesis temperature for annealing the copper followed by coal pyrolysis for the growth of graphene on the copper substrate. The carbon and graphene films were synthesized at various temperatures and time as mentioned in Table 6.1. Synthesis was performed in triplicates to determine the uniformity and consistency of the films.
Table 6.1: Synthesis conditions (temperature and time) for the growth of carbon films.

<table>
<thead>
<tr>
<th>Synthesis temperature (°C)</th>
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<td>455</td>
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The copper foils were dissolved in the Marbles reagent and the synthesized carbon films were then transferred onto desired substrates such as silicon wafer and TEM grids for further characterization. The transfer process is also described in Chapter 5 [123].

6.2.3 Gas collection and analysis

The setup used for the graphene synthesis was modified by installing a 'T' valve at the outlet. The coal pyrolysis and gas collection were performed without the vacuum in operation. The schematic of the gas collection setup is shown in Figure 6.1. Each gas sampling bag was connected to the 'T' valve on the exhaust in order to change the bags and collect the coal pyrolysis products for 0-6, 6-12, 12-18, 18-24, 24-30, and 30-45 minutes. Prior to pyrolysis, the six gas sampling bags were purged with argon and hydrogen three times each. Initially, the sampling valve was closed and the exhaust valve
was kept open. The tube furnace was purged with argon for 2 h to remove excess air and to create an inert environment. Further, the argon was turned off with simultaneous purging of hydrogen for an additional 2 h. Hydrogen was used as the carrier gas during the pyrolysis in order to simulate the graphene synthesis conditions. The furnace was ramped to 1055 °C in presence of hydrogen. Once desired temperature was attained, the quartz boat with coal was shifted inside the heat zone for conducting coal pyrolysis. Simultaneously, the exhaust valve was closed and the gas collection valve was opened for collecting the gases released during coal pyrolysis in the sampling bag.

Figure 6.1: Schematic of the coal pyrolysis and gas collection setup.

The collected gases were analyzed using Thermo Scientific gas chromatograph with a packed column (Restek 19808 ShinCarbon ST Packed Column, 100/120 mesh, 2 m length, 1/16” OD, 1 mm ID) coupled with a thermal conductivity detector. Helium was utilized as a carrier gas during the gas chromatography.
6.2.4 Graphene domain visualization

In order to make graphene domains optically visible the copper foils with the graphene films were placed on a hot plate at 100 °C for 1 min [72, 76, 77]. The area with the presence of graphene domains remain unaffected, whereas other areas of the copper foil oxidize. The color contrast between the oxidized region and non-oxidized region was visible under an Alicona® InfiniteFocus Optical Microscope (IFM). The images were collected from three replicate samples to determine the statistical variation and significance.

6.2.5 Physical characterization

The carbon and graphene films synthesized at different temperatures and times were transferred onto silicon wafers for performing Raman spectroscopy and mapping. The Raman spectra of the carbon and graphene films were obtained using a Bruker Senterra Raman spectrometer. A 20X objective lens was used to acquire Raman spectra using an argon laser (λ=532 nm) with 20 mW power, resolution range of 3-5 cm$^{-1}$, and an integration time of 20 s; whereas Raman mapping measurements were obtained utilizing 2 mW power, resolution range of 9-15 cm$^{-1}$, and an integration time of 10 s. Raman mapping over 100 × 100 µm$^2$ area with a step size of 5 µm was selected for measurements. Raman mapping was conducted on the triplicate samples to verify the statistical variation. Transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) of the carbon and graphene films were obtained using the JEM 2100F TEM. The X-ray photoelectron spectroscopy (XPS) analysis of the various carbon and graphene films were conducted using Kratos XSAM 800 electron
spectrometer with a 1484 kαAl X-ray source utilizing 120 W power and pass energy of 40 eV.

6.3 Results and Discussion

The coal derived graphene films were synthesized using low pressure CVD at 1055 °C and 30 min synthesis conditions as demonstrated in Chapter 5 [123]. Raman spectrum of the coal derived graphene film (Figure 6.2A) revealed the D band at 1350 cm\(^{-1}\), the G band at 1575 cm\(^{-1}\), and the 2D band at 2700 cm\(^{-1}\). The presence of the D band in the graphene film is a mode in Raman spectra of first order originating from the disorder and defects such as point defects and subdomain boundaries [66, 70, 80, 81, 128]. These can be due to the breaking of hexagonal graphene structure caused by other functional groups such as C-O, C=O or by the sp\(^3\) carbon [42, 67, 141, 142]. The G band in the coal derived graphene film arises due to the tangential vibrations associated with the sp\(^2\) bonded carbon atoms [70, 80, 81]. Another band at ~2700 cm\(^{-1}\) is designated as the 2D band, which is a mode in Raman spectra of second order and is associated with layers in the graphene films [70, 80, 81]. These bands in the Raman spectra are used to identify the quality and the number of layers associated with the graphene films [80, 81]. The 2D/G ratio is ~1 and the full width at half maxima (FWHM) of the 2D peak is ~31 cm\(^{-1}\), which demonstrates formation of bi-layer to few layer graphene films [42, 45, 70, 80, 128, 131].
Figure 6.2: (A) Raman spectrum of coal derived graphene film synthesized at 1055 °C and 30 min exhibiting the D, the G, and the 2D band. (B) Large area of coal derived graphene films on TEM grid showing wrinkles, overlapping, and backfolding; Inset: SAED with six diffraction spots demonstrating crystalline nature of coal derived graphene film. (C & D) High magnification TEM image with the edge of the coal derived graphene film exhibiting bi-layers to few layers of the film.

TEM image in Figure 6.2B illustrates large area of the graphene film on the TEM grid with wrinkles, back folding and overlapping introduced due to the transfer process. The selected area electron diffraction (SAED - inset in Figure 6.2B) reveals the six diffraction spots depicting the hexagonal diffraction pattern and the crystalline nature of the coal derived graphene films. The edge of the graphene film (TEM image in Figure 6.2C and Figure 6.2D) reveals the layers of the coal derived graphene films, which is in agreement with the Raman analysis.

Energy dispersive X-ray spectroscopy (EDX) was utilized to perform chemical element analysis on the graphene film. EDX (Figure 6.3) analysis on graphene film
reveals the presence of C, O, and Cu with trace amounts of S. The Cu signal observed in
the spectrum can result from the residual CuSO$_4$ reagent for Cu foil etching process
and/or the TEM grid. The oxygen peak can be attributed to various reasons such as
adsorption of air on the graphene films, and/or the oxidation of carbon atoms near the
domain boundaries [84, 85, 143]. The oxygen signal can also result from the residual
CuSO$_4$ reagent for Cu foil etching process. Trace amounts of S can be attributed to the
impurities of residual Marbles reagent, which consists of copper sulfate.

![EDX spectrum of graphene film](image)

Figure 6.3: EDX spectrum of graphene film reveals the presence of C, O, and Cu with
trace amounts of S.

In order to investigate the growth mechanism of coal derived graphene films, the
syntheses were performed at different temperatures and times. Initially, the syntheses
were conducted at different temperatures and 30 min synthesis as mentioned in Table 1. Raman spectroscopy is a powerful tool to investigate the structural properties and growth of graphene films [80, 81]. Raman spectra were utilized to analyze the films synthesized at different temperatures for the 30 min synthesis time. Raman spectra (Figure 6.4) of the low temperature (455 °C, 655 °C, and 855 °C) synthesized films exhibit only the D band and the G band with broad shoulders demonstrating their amorphous nature [117, 127]. As the synthesis temperature is increased to 1055 °C, the 2D peak is also detected along with the D and the G band, confirming the formation of graphene film. The 2D/G intensity and FWHM revealed formation of a bi-layer to few layer graphene film. The presence of the D peak in the Raman spectra of graphene film is the result of defects and disorder due to C-O, C=O, sp³ carbon, etc. within the graphene network of the sp² carbon. As a comparison, the Raman spectrum of raw coal is also included (Figure 6.4), which shows the broad D band at 1365 cm⁻¹ and the G band at 1575 cm⁻¹ indicating amorphous nature of the coal [127].
Figure 6.4: Raman spectra of films synthesized at different temperatures and 30 min synthesis time demonstrating formation of graphene films only when the temperature is increased to 1055 °C.

Further, Raman mapping was conducted in order to validate the results of Raman measurements over large area of carbon films. 100 × 100 μm² area was selected for the mapping. The results were analyzed in terms of the 2D band intensity only, since the purpose was to detect the temperature required for graphene formation. Figure 6.5 shows the 2D band intensity map area of films synthesized at different temperatures with a 30 min synthesis time. It can be observed that the 2D peak intensity is close to zero for films synthesized at 455 °C (Figure 6.5A), 655 °C (Figure 6.5B) and 855 °C (Figure 6.5C)
indicating no formation of graphene films. However, the 2D peak intensity is dominant over large area of films synthesized at 1055 °C (Figure 6.5D) revealing the continuous and large area graphene formation.

Figure 6.5: Raman map measurements showing the 2D band intensity over 100 × 100 μm² area of films synthesized at 455 °C (A), 655 °C (B), 855 °C (C), and 1055 °C (D) demonstrating the presence of the 2D band over large area for films produced at 1055 °C.

Raman mapping (measurements with respect to the 2D peak intensity) was conducted on the replicate samples synthesized at different temperatures in order to
determine the uniformity of the films. Figure 6.6 shows that the 2D peak intensity is negligible for films synthesized at different temperatures without significant variation. Further, the 2D map shows high intensity and uniformity for the replicates synthesized at 1055 °C.

![Graph showing 2D peak intensity vs. synthesis temperature](image)

**Figure 6.6**: Average 2D peak intensity demonstrating no formation of graphene films at low temperatures synthesis and formation of graphene films at 1055 °C.

X-ray photoelectron spectroscopy (XPS) is an ideal technique not only used to determine the elemental composition of carbonaceous materials, but also to provide information regarding the chemical composition [84, 85]. Therefore, XPS was employed to detect the core level C1s carbon spectra directly on the copper surface. Figure 6.7 presents the C1s spectra of the carbon and graphene films synthesized at different
temperatures with a 30 min synthesis time. The C1s spectra of the various carbon films were around 284 eV - 286 eV. The background of the peaks was subtracted using the nine point Shirley background and deconvoluted using the Gaussian fit. The C1s spectra for the various films were deconvoluted into four peaks. The decomposed peaks and their corresponding components are: sp\(^2\) graphitic carbon (284.5 eV), sp\(^3\) amorphous carbon (285.5 eV), C-O (286.5 eV), and O-C=O (288.5 eV) [20, 64, 84, 85, 143-145]. The oxygen related components and the sp\(^3\) carbon are dominant and have high intensity for low temperature film (Figure 6.7A-455 °C, and Figure 6.7B-655 °C). Progressive increase in temperature (Figure 6.7C-855 °C) decreases the peak intensity of oxygen related components and the sp\(^3\) carbon and is found to be lowest for the graphene film synthesized at highest temperature (Figure 6.7D-1055 °C). Conversely, the peak representing sp\(^2\) carbon has low intensity for low temperature films (455 °C and 655 °C). The peak intensity of sp\(^2\) carbon increases with progressive increase in temperature and shows the highest concentration for graphene film.

The XPS analysis is consistent with the results from Raman measurements indicating that the presence of sp\(^3\) carbon within the graphene network induces the defects in the graphene films. Furthermore, the presence of various carbon-oxygen functional groups in graphene films as detected from the XPS analysis are also responsible for the defects and disorder present in the graphene films. The difference in concentrations of sp\(^2\) carbon, sp\(^3\) carbon, and oxygen related components demonstrates the phase change from amorphous carbon (low temperature films - 455 °C, 655 °C, and 855 °C) to crystalline graphene (high temperature films - 1055 °C). The peaks
corresponding to the oxygen components are calculated to occupy an area of ~20% of the total area of the carbon C1s spectra of the graphene film. This can be attributed to various reasons such as oxidation of the copper foil, adsorption of air on the graphene films, and/or the oxidation of carbon atoms near the domain boundaries [84, 85, 143].

Figure 6.7: XPS C1s spectra of carbon films synthesized at 455 °C (A), 655 °C (B), 855 °C (C), and 1055 °C (D) and 30 min synthesis time. C1s spectra of the graphene films (1055°C) show low amounts of sp³ carbon and oxygen related components as compared to carbon films synthesized at low temperatures (455 °C, 655 °C, and 855 °C).

In addition, the XPS survey spectrum of graphene film synthesized at 1055 °C and 30 min (Figure 6.8) reveals the presence of copper, oxygen, and carbon. The XPS
survey did not show any other impurities present in the graphene films. This corroborates the EDX analysis and discussion regarding the presence of impurities in the graphene film, suggesting that the impurities originate from the Marbles reagent used in the transfer process.

![Figure 6.8](image)

Figure 6.8: XPS survey spectrum of graphene film reveals the presence of copper, oxygen, and carbon without presence of any other impurities.

The EDX and XPS analysis of carbon thin film from Chapter 4 and of the graphene film presented in this chapter are in agreement demonstrating that the impurities are related to the Marbles reagent utilized in the transfer process.

Selected area electron diffraction (SAED) was conducted on the films synthesized at different temperatures and 30 min synthesis time for investigating the nature and phase change. Figure 6.9 A-D shows the SAED pattern of the synthesized films. The SAED revealed an intense ring without any presence of diffraction spots for low temperature
films (Figure 6.9A - 455 °C, and Figure 6.9B - 655 °C), indicating their amorphous nature. The SAED pattern of film synthesized at 855 °C (Figure 6.9C) shows a combination of diffraction spots and intense rings indicating a hybrid structure of amorphous and crystalline carbon. A similar SAED pattern was observed by Cui et al., for their low temperature synthesized hybrid films [87]. However, only hexagonal diffraction spots are observed for the graphene films (Figure 6.9D - 1055 °C), demonstrating their crystalline nature. The SAED characterization is in agreement with the Raman and XPS measurements.

Figure 6.9: Selected area electron diffraction of films synthesized at 455 °C (A), 655 °C (A), 855 °C (C), and 1055 °C (D). Amorphous rings present for low temperature films (455 °C and 655 °C), a hybrid film is synthesized at 855 °C, and crystalline graphene film is formed at 1055 °C.
After investigating the synthesis temperature required for graphene formation, it was essential to observe the growth and evolution of the graphene films. This was achieved by increasing the synthesis time from 6 min up to 30 min with every 6 min increment and finally up to 45 min, at the temperature previously demonstrated to be suitable for the formation of graphene films. Figure 6.10 shows the Raman spectra of the graphene films synthesized at 1055 °C and different synthesis times. The 2D peak intensity is negligible for films synthesized at 6 min. However, as the synthesis time is increased the 2D peak becomes sharper and peak intensity increases. This behavior is caused by the increase in graphitization/crystallization of amorphous carbon films and increase in the size of graphene domain with corresponding increase in synthesis time. In order to verify the size of graphene domain optical microscopy was utilized which is discussed later.
Figure 6.10: Raman spectra of films synthesized at 1055 °C and different time demonstrating graphitization and increase in domain size as synthesis time is increased.

The evolution of the 2D band is also evidenced from the map measurements (Figure 6.11 A-F) demonstrating the intensity of the 2D/G ratio over 100 × 100 μm² area of the graphene films. The intensity of the 2D/G ratio is negligible for films synthesized at 6 min (Figure 6.11A). However, with progressively longer time duration the 2D/G intensity ratio increases from ≤0.4 for 12 min (Figure 6.11B), ≤0.6 for 18 min (Figure 6.11C), < 0.8 for 24 min (Figure 6.11D) up to ≥0.8 for 30 min and 45 min synthesis (Figure 6.11E and F). The 2D/G map results indicate that a large fraction of the area is covered with bi-layer to few layer graphene films for 1055 °C and 30/45 min synthesis.
Figure 6.11: 2D/G intensity Raman map over $100 \times 100 \ \mu\text{m}^2$ area of films synthesized at 1055 °C and 6 min (A), 12 min (B), 18 min (C), 24 min (D), 30 min (E), and 45min (F) demonstrating bi-layer to few layer formation of graphene films produced at 1055 °C and 30/45 min.
Raman mapping was also conducted on the replicate samples to validate if the 2D/G intensity ratio is uniform and repeatable across the replicates. The 2D/G intensity ratio increases with increase in synthesis time without significant variation as shown in Figure 6.12.

![Figure 6.12](image)

Figure 6.12: Average 2D/G map intensity of the replicates demonstrating an increase in the 2D/G intensity ratio when the synthesis time is increased from 6 min to 45 min.

Figure 6.13 A-E depicts SAED pattern obtained for the films synthesized at 1055 °C and different times. The SAED for 6 min (Figure 6.13A) and 12 min (Figure 6.13B) synthesis films show intense rings with diffraction spots. These films are hybrid films composed of amorphous and crystalline carbon. However, the films synthesized at 18 min (Figure 6.13C), 24 min (Figure 6.13D), 30 min (Figure 6.13E), and 45 min (Figure
6.13F) reveals only hexagonal diffraction spots indicating the crystalline nature of the graphene films.

Figure 6.13: Selected area electron diffraction of films synthesized at 1055 °C and 6 min (A), 12 min (B), 18 min (C), 24 min (D), 30 min (E), and 45 min (F). Hybrid films with combination of amorphous rings and diffraction spots is observed for 6 min and 12 min synthesis time; while crystalline graphene films obtained for longer synthesis times (18 min, 24 min, 30 min, and 45 min).
Optical microscopy is a simple and direct technique to visualize graphene domains on the copper substrate [72, 76, 77]. Optical detection is a fast approach to observe the development of graphene domains and their growth to form graphene films under various experimental conditions [72, 76, 77]. The domain visualization can be obtained with the assistance of an intrinsic property of the graphene, which is to act as an oxidation barrier [72, 76, 77]. The copper substrate when heated in air gets oxidized, whereas the sites with graphene domains remain unaffected. The copper foils with graphene films synthesized at 1055 ºC and different times were placed on a hot plate maintained at 100 ºC for 1 min to visualize the evolution of the graphene domains. After this exposure, the sites with graphene domains were unaffected, whereas the other region of copper was oxidized. Optical microscopy images (Figure 6.14) show the evolution of these graphene domains synthesized at 1055 ºC and different time intervals. The coal derived graphene domains appears to be oval shaped as seen from Figure 6.14. The graphene domain is similar to one of the many different shapes of graphene domain synthesized by controlling various process parameters [146]. Graphene domains are hardly visible for 6 min synthesis times. The graphene domains grow in size as the synthesis time is increased and eventually merge together to form a continuous graphene film covering the surface of the copper foil.
Figure 6.14: Graphene domains observed utilizing optical microscope. The graphene domains hardly observed for 6 min synthesis (A). With progressive synthesis times, the evolution of graphene domains can be observed for 12 min (B), 18 min (C), and 24 min (D) synthesis. Graphene film is formed by merging of graphene domains for 30 min (E) and 45 min (F) synthesis.
The optical microscopy images demonstrated that the domains increase in size and merge together, thus increasing in coverage on the copper substrate. Optical images were also obtained from the replicate samples to determine the uniformity and consistency of the surface area coverage of graphene films as the synthesis time was increased. The images were analyzed using ImageJ software. Figure 6.15 illustrates this increase in surface area coverage of graphene domains to form graphene films. The graphene film covers ~95 % surface area of the copper substrate at 30 min and 45 min synthesis.

Figure 6.15: Increase in average surface area coverage up to ~95 % for films synthesized at 30 min and 45 min.
Previously, it was observed from the Raman mapping that the 2D intensity increases with increase in synthesis time. This behavior is attributed to an increase in the size of graphene domain with corresponding increase in synthesis time. The optical images obtained from the replicate samples of films synthesized at different times were further analyzed using ImageJ software. The analysis assisted in validating the increase in domain size as synthesis time increased. Figure 6.16 shows that the domain size increases from few micrometers at 12 min synthesis to hundreds of micrometers at 30 min and 45 min synthesis.

![Figure 6.16: The domain size increases from few micrometers at 12 min synthesis to hundreds of micrometers at 30 min and 45 min synthesis. The increase in 2D intensity with increase in synthesis time is attributed to this increase in domain size.](image)
Raman spectroscopy was used to verify the graphene domains. Figure 6.17A shows an isolated oval shaped graphene domain synthesized at 1055 °C and 30 min. Raman spectra obtained from the domain and the non-domain region directly on the copper substrate is illustrated in Figure 6.17B. The Raman spectra of the graphene domain reveals the low intensity D band, the G band observed at 1585 cm\(^{-1}\), and the 2D band at 2700 cm\(^{-1}\). The spectrum of the non-domain region (Figure 6.17B) only show the presence of the D band and the G band, as an indication of an amorphous carbon film surrounding the graphene domain.

![Figure 6.17: Graphene domain on the copper foil (A) with corresponding Raman measurements (B) indicating the presence of the graphene domain and an amorphous carbon in the background.](image)

The mechanism of the graphene growth in this simple coal heating approach is certainly intriguing. The hydrocarbons released during the pyrolysis of coal act as the precursors for the graphene synthesis. In order to determine these hydrocarbon gases, the
Wyodak coal was pyrolyzed at the graphene synthesis conditions and the gases collected in a gas sampling bag using the setup and procedure mentioned in the experimental section of gas collection. The gases were then analyzed using gas chromatography. The chromatography analysis revealed the following gaseous products from the coal pyrolysis after the initial 6 min: Hydrocarbon gases methane, ethane, ethene, propane, and propene, apart from carbon dioxide and carbon monoxide. Further, methane is the only hydrocarbon gas apart from carbon dioxide and carbon monoxide detected after the 6 min coal pyrolysis. Moreover, the concentration of methane decreases with every time increment. The composition of the gases obtained as product of coal pyrolysis for different time intervals are shown in Table 6.2 and the chromatographs are included as appendix B.

Table 6.2: Gas composition (mole %) of products obtained during coal pyrolysis

<table>
<thead>
<tr>
<th></th>
<th>6 min</th>
<th>12 min</th>
<th>18 min</th>
<th>24 min</th>
<th>30 min</th>
<th>45 min</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methane</strong></td>
<td>70±10</td>
<td>49±2</td>
<td>10±2</td>
<td>8±2</td>
<td>2±1</td>
<td>2±1</td>
</tr>
<tr>
<td><strong>Ethane</strong></td>
<td>0.50±0.04</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td><strong>Ethene</strong></td>
<td>1.0±0.5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td><strong>Propane</strong></td>
<td>1.0±0.7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td><strong>Propene</strong></td>
<td>0.5±0.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td><strong>Carbon dioxide</strong></td>
<td>17±11</td>
<td>48±2</td>
<td>87±1</td>
<td>89±2</td>
<td>96±1</td>
<td>96±1</td>
</tr>
<tr>
<td><strong>Carbon monoxide</strong></td>
<td>10±1</td>
<td>3.0±0.1</td>
<td>3.0±0.5</td>
<td>3±1</td>
<td>2.0±0.1</td>
<td>2.0±0.1</td>
</tr>
</tbody>
</table>

*ND: not detected*
Thermogravimetric analysis (TGA) on coal was performed utilizing SDT600 TGA (TA instrument) with argon as a carrier gas. 455 °C, 655 °C, 855 °C, and 1055 °C were selected as target temperature under isothermal conditions (30 min pyrolysis time) in order to mimic the synthesis conditions of amorphous carbon/graphene film. Figure 6.18 shows the TGA curve (weight loss % v/s time), which includes the weight loss occurred during the ramp process as well. Majority of the weight loss occurs during the ramp process itself for all the temperatures albeit at slightly varied time. Majority weight loss occurs within 7 min during the ramp to 1055 °C demonstrating that all the bulk gases are released within the 7 min of the ramp process. This indicates that during the graphene synthesis process (1055 °C) the coal when exposed to flash pyrolysis will release bulk gases within the first 6-7 min. According to the TGA there is no other gases coming out of the coal even with further increase in pyrolysis time after the ramp step.
Figure 6.18: TGA of coal at different temperatures (455°C, 655°C, 855°C, and 1055°C).

TGA was also performed at different ramp rates (5°C, 10°C, and 15°C per minute) to final temperature of 1055°C, which is the graphene synthesis temperature. Figure 6.19 shows the weight loss of coal at different ramp rates. The TGA analysis demonstrates that when coal is pyrolyzed at different ramp rates, the majority of the weight loss concludes at different times. For example, when the ramp rate is 15°C per minute then the majority of weight loss will occur in 37 min. It can be observed that for higher ramp rate (15°C per minute), the majority weight loss of coal takes shorter time (~37 min) as compared to
lower ramp rate (5°C per minute), where the majority weight loss takes longer time (~100 min). The TGA analysis at different ramp rates indicates that flash pyrolysis would release bulk gases within shorter time duration due to sudden exposure to high temperatures.

Figure 6.19: TGA of coal at different ramp rates (5°C, 10°C, and 15°C per minute) to final temperature of 1055°C.

The hydrocarbon gases (methane, ethane, ethene, propane, and propene) lead to the formation of active carbon species, thus acting as an indirect carbon source for the growth of graphene films. Based on the results from the gas chromatography, Raman
spectroscopy, TEM, SAED, and optical microscopy, a growth mechanism of coal derived graphene films is proposed and a schematic is presented in Figure 6.20.

1. Carbons atoms from the various hydrocarbon gases released during coal pyrolysis undergo copper catalyzed adsorption [61, 63, 64].

2. This is followed by catalytic dissociation and desorption to form an amorphous carbon film on the copper substrate within the first few minutes of the synthesis. The carbon film covers the whole area of copper substrate and thus no more active sites of copper are available. Even if more hydrocarbons are released over longer annealing times, no active sites of copper are available for the hydrocarbons to adsorb.

3. As time progresses, the hydrogen catalyzed dehydrogenation and graphitization of the underlying amorphous carbon occurs to form graphene domains.

4. With further increase in time, the graphene domains grow in size and merge together to form a continuous graphene film on the substrate of copper [63, 64].
Figure 6.20: Schematic of growth mechanism of coal derived graphene films showing the formation of amorphous film followed by hydrogen catalyzed graphitization to form graphene domains. As time progresses, the graphene domains grow in size and merge together forming a continuous graphene film on the copper substrate.

Hydrogen plays a key role for the synthesis of graphene on metals with low solubility of carbon and has been investigated [20, 64, 78]. Hydrogen is utilized to anneal the copper surface to remove the oxide layer and passivate the defects present on the copper surface [45, 55, 56, 60, 63, 64, 71]. Atomic hydrogen reacts with the radicals of hydrocarbon and carbon, subsequently etching the hydrogen from the surface by hydrogen abstraction reactions [60]. Hydrogen also assists in the phase transition of sp³ carbon to sp² carbon [60]. It has been described as hydrogen induced graphitization/crystallization of the carbon layer on the copper foil to form graphene [20, 64, 78]. In the present work as the synthesis proceeds with time, hydrogen graphitizes the
underlying hybrid carbon film produced within the first 6 min of the growth process to form graphene domains. In order to confirm the hydrogen induced graphitization; synthesis was performed at the same conditions (1055 °C and 30 min) as graphene growth. Hydrogen was utilized for the initial 15 min for annealing the copper substrate. During the growth step of 30 min, hydrogen was shut off and replaced with 300 sccm of argon. A continuous carbon film was obtained in the absence of hydrogen at the graphene synthesis conditions. Figure 6.21 shows the Raman spectrum of the carbon film revealing the presence of the broad D band and the G band. However, no 2D band was observed, thus validating the copper assisted growth of a-C films and that copper does not induce crystallization as previously confirmed by various studies [20, 147, 148].

Figure 6.21: Raman spectra of a-C film synthesized at 1055 °C and 30 min utilizing 300 sccm argon exhibiting the D band the G band.
The present work demonstrates that hydrogen is not needed to grow amorphous carbon films which is hypothesized to be surface mediated and self limiting process. However, hydrogen is required for the growth of graphene films. The present work shows that graphene film is not formed in absence of hydrogen. Hydrogen plays a vital role in the $sp^3$-$sp^2$ transition by inducing graphitization of the underlying carbon film on the copper surface to produce graphene domains, which merge together to produce graphene films. The results prove that coal derived graphene growth is not just a consequence of copper catalyzed self-limited growth and carbon saturation, but it also involves hydrogen induced graphitization of the carbon films.

An experiment was undertaken to further validate the TGA analysis that bulk gases released within 6 min due to flash pyrolysis are precursors for the initial formation of amorphous carbon in 6 min which leads to the growth of graphene films. The experiment was performed at graphene synthesis conditions of 1055 °C and 30 min. However, the coal was removed outside the heat zone after the initial 6 min coal pyrolysis and the copper foil was maintained inside the heat zone for another 24 min. The copper foil was then removed outside the heat zone for cool down. Raman mapping over an area of $100 \times 100 \ \mu m^2$ was used to investigate the 2D/G peak intensity of the synthesized film. Figure 6.22 reveals the Raman mapping of the synthesized film.
The 2D/G peak intensity was calculated to be $1.0 \pm 0.3$. This value is similar to the graphene film obtained by performing coal pyrolysis for 30 min. The results confirm that the flash pyrolysis of coal releases bulk gases within the 6 min which leads to formation of a carbon film and subsequent formation of the graphene film. Growth of graphene films were attempted by pyrolyzing the coal for 5 min or less. However, no films were formed when the coal was pyrolyzed for 5 min and less.

6.4 Conclusion

Large area and uniform graphene films were obtained utilizing coal as solid carbon source via chemical vapor deposition. The growth mechanism was investigated by implementing Raman spectroscopy/mapping, TEM/SAED, optical microscopy, and gas
chromatography. The results obtained showed that the flash pyrolysis of coal release hydrocarbon gases - methane, ethane, ethene, propane, and propene, which act as precursor. The carbon species from the hydrocarbon gases adsorb on the copper to undergo copper catalyzed reaction to form a hybrid carbon film. This is followed by graphitization of carbon film to form graphene domains with the aid of hydrogen, eventually leading to formation of graphene films.
7.1 Conclusions

The major conclusions of this work are listed below:

1. Atmospheric pressure and low temperature synthesis of carbon films using coal was demonstrated. As per the work presented, atmospheric pressure and low temperature (400 °C) synthesis produces amorphous carbon films and not crystalline graphene films.

2. Low pressure and high temperature synthesis of crystalline graphene films utilizing coal was demonstrated. High temperature and hydrogen environment assisted in graphitization of amorphous carbon to produce crystalline graphene films.

3. The spectroscopy, chromatography, and microscopy analysis demonstrated that the first step of graphene growth involves synthesis of an amorphous carbon film produced due to the surface catalyzed process. Further, the hydrogen catalyzed crystallization of the underlying amorphous carbon to produce graphene domains was validated. As the synthesis time was increased, the graphene domain size increased and the domains merged together to form a continuous graphene film.

The coal derived graphene work discussed here could assist in optimization for efficient scale up of the process. Furthermore, the proposed growth mechanism could have significant impact and could assist in studies of graphene growth utilizing other non-conventional solid carbon sources.
7.2 Future Scope and Recommendations

Copper has been demonstrated to be excellent catalyst for graphene formation [45, 56-58]. Annealing of copper in hydrogen environment to remove the oxide layer is required for the growth of graphene [45, 56-58]. Figure 7.1 shows the XRD pattern of annealed copper in absence of coal and/or hydrocarbons.

![XRD pattern of copper annealed in hydrogen environment in absence of coal and/or hydrocarbons.](image)

**Figure 7.1:** XRD pattern of copper annealed in hydrogen environment in absence of coal and/or hydrocarbons.

The XRD pattern indicates that the annealed copper utilized in the present work is polycrystalline. All the diffraction peaks can be indexed to copper and are consistent with the standard card JCPDS No.01-070-3039.
The graphene domains have been demonstrated to have diverse shapes depending on the crystal structure of the underlying copper support [45, 56]. Different growth rate has also been demonstrated on copper foils with different crystal orientations [149]. Since there is a mixture of hydrocarbons releasing from coal, the dehydrogenation of these hydrocarbons on copper substrates with different crystal orientations can vary and eventually influence the growth rate of graphene formation. Further, various literatures have disagreements over the type of crystal orientation of copper required for graphene formation [56, 124, 149-151]. The influence of crystal orientation of copper on the graphene growth mechanism is thus not well understood. Therefore, the dependence of the growth of graphene on copper substrate with different crystal orientation needs to be investigated for further understanding the reaction mechanism. Single crystal copper substrates such as (1 1 1) and (1 0 0) need to be investigated for the growth of graphene films and compared with the current work.

High resolution Raman mapping provides information about the domain boundaries, defects, and crystal orientation of the graphene films [152, 153]. The Raman spectra of coal derived graphene films revealed the characteristic D band related to defects and disorder (Figure 6.10). More information is required to identify and reduce the defects. This could be achieved by implementing the high resolution Raman mapping. Furthermore, high resolution Raman mapping could also be useful to determine the crystal orientation of graphene during investigating the effect of single crystal and polycrystalline copper on the growth rate and domain shape.
Earlier studies have utilized different techniques such as spectroscopic ellipsometry and low energy electron microscopy (LEEM) for investigating the reaction kinetics of graphene growth in real time [54, 60, 61, 154]. Similarly, these techniques could facilitate the investigation of growth kinetics of coal derived graphene films in more detail. Furthermore, the above mentioned techniques could also assist in determining the rate limiting step.
REFERENCES


APPENDIX A: COST ANALYSIS OF COAL DERIVED GRAPHENE FILMS

Typical graphene synthesis in 2' long and 1/4" diameter tubular CVD furnace produces \(\sim 8 \text{ cm}^2\) of graphene film in 4h of operation. The cost is estimated based on per \(\text{cm}^2\) production of graphene.

<table>
<thead>
<tr>
<th>Supplies</th>
<th>Standard cost</th>
<th>Source of cost</th>
<th>Utilized per 8 cm(^2) graphene synthesis</th>
<th>Utilized per (\text{cm}^2) graphene synthesis</th>
<th>Cost ($) per (\text{cm}^2) graphene synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coal</strong></td>
<td>$20/kg</td>
<td>Penn State coal bank</td>
<td>10 mg</td>
<td>1.25 mg</td>
<td>0.000025</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>$72/261 ft(^3)</td>
<td>Praxair</td>
<td>120000 cm(^3)</td>
<td>15000 cm(^3)</td>
<td>0.0008</td>
</tr>
<tr>
<td><strong>Copper</strong></td>
<td>$34/0.1 m(^2)</td>
<td>Alfa Aesar</td>
<td>8 cm(^2)</td>
<td>1 cm(^2)</td>
<td>0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Services</th>
<th>Rated (kW)</th>
<th>Source $0.10/kWh</th>
<th>Utilized for 4h operation (kWh)</th>
<th>Utilized per (\text{cm}^2) graphene synthesis (kWh)</th>
<th>Cost ($) per (\text{cm}^2) graphene synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vacuum pump</strong></td>
<td>4</td>
<td>eia.gov</td>
<td>16</td>
<td>2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
### Furnace Cost Breakdown

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<th>Furnace</th>
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<th>12</th>
<th>1.5</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow meter</td>
<td>0.0006</td>
<td>eia.gov</td>
<td>0.0024</td>
<td>0.0003</td>
<td>0.00003</td>
</tr>
</tbody>
</table>

### Other Cost Details

<table>
<thead>
<tr>
<th>Other cost</th>
<th>Hours of operation</th>
<th>[$8.10/h] Source</th>
<th>Utilized for 4h operation</th>
<th>Cost ($) per cm² graphene synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Personnel cost</td>
<td>4</td>
<td>ohio.gov</td>
<td>32.4</td>
<td>$4.05</td>
</tr>
</tbody>
</table>

**Direct cost:** $0.39/cm²  
**Indirect cost:** $0.18/cm²  
**Personnel cost:** $4.05/cm²  
**Total cost:** $4.62/cm²
APPENDIX B: GAS CHROMATOGRAPHS FROM COAL PYROLYSIS

EXPERIMENTS

**Procedure:**
GC.RightColumn.FlowMode = FlowCtrl
GC.EquilibrationTime = 0.50
GC.PostRunTempCtrl = Off
GC.RightInlet.Temperature.Nominal = 225
GC.RightInlet.TempCtrl = On
GC.RightInlet.Mode = Splitless
GC.RightInlet.SplitFlowCtrl = Off
GC.RightInlet.GasSaverFlow = 5.0
GC.TCD.Polarity = Positive
GC.TCD.DetTemp.Nominal = 225
GC.TCD.DetTempCtrl = On
GC.TCD.Temp.Nominal = 240
GC.TCD.TempCtrl = On
GC.TCD.FilamentTemperature.Nominal = 350
GC.TCD.MakeupFlow.Nominal = 15.0
GC.TCD.RefFlow.Nominal = 40.0
GC.TempCtrl = On
GC.RightColumn.FlowCtrl = On
GC.RightColumn.Flow.Nominal = 25.0
GC.Temperature.Nominal = 35
GC.TCD.AcqOn
GC.Temperature.Nominal Gradient Start = 35, End = 220, Duration = 4.620
GC.Temperature.Nominal = 220
GC.Temperature.Nominal = 220
GC.RightColumn.Flow.Nominal = 25.0
GC.TCD.AcqOff
Chromatograph for gas collected in first 6 min

Chromatograph for gas collected in between 6 min-12 min
Chromatograph for gas collected in between 12min-18min

Chromatograph for gas collected in between 18min-24min
Chromatograph for gas collected in between 24min-30min

Chromatograph for gas collected in between 30min-45min