"Large Area Graphene Synthesis"

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Abstract
Herein we attempt to synthesize graphene by annealing epitaxial SiC thin films as a carbon source. Three principal methods of synthesis are attempted: 1) Straight annealing of SiC, 2) Annealing of Cu/SiC/Si, 3) Annealing of Ni/SiC/Si.

In the vacuum annealing of SiC/Si structures, an attempt was made to sublimate silicon from the surface of SiC, where remaining carbon reforms into graphene. Subsequent characterization by Raman spectroscopy was inconclusive in identifying any graphitic formation. The second experiment utilizes evaporated nickel thin films, where upon annealing the carbon from the silicon carbide will migrate into the overlaying nickel film and with subsequent cooling, the dissolved carbon will segregate onto the nickel surface and form a graphitic layer. Annealed Ni/SiC/Si structures were characterized with Raman spectroscopy, and showed the presence of nanocrystalline graphite as described by Ferrari et al. [1]. In the final experiment using copper films, carbon from SiC will catalyze at the copper/SiC interface upon annealing. Raman characterization of these structures shows evidence of graphitic formation in only the thinnest copper films used in the experimental matrix.
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1. Introduction

In 2004, the isolation of graphene crystals and subsequent fabrication of highly conductive field effect transistors[2] amazed both the physics and engineering world. However, the meteoric flux of graphene research [3] sparked by the Geim’s group stemmed from a humble beginning some 70 years prior. Two dimensional carbon sheets were first incepted by Wallace in 1947 while developing tight binding models for graphite [4]. Whether or not two dimensional crystal structures could exist was a topic of debate at the time, and it was though that two dimensional structures where thermodynamically unstable[5]. As a consequence early mono atomic films were grown from three dimensional substrates. From the 1960’s on, synthesis of graphitic layers on transitional metals was studied, using both chemical vapour deposition (CVD) and segregation of carbon from metal substrates to the surface [6–8]. However it was the simple (yet very refined) method of mechanical exfoliation with adhesive tape that has produced the first true freestanding graphene crystal, for which the 2010 Nobel Prize in physics was awarded.

With contemporary research on graphene still in its infancy, it is difficult to predict with confidence graphene’s dominant role of as an engineering material. With extremely high mobility many believe that commercial use of graphene will be first realized in high-electron-mobility transistors, or as robust conductive coating for flexible touch screen applications [9]. In the context of transistor fabrication graphene research is carried out as a means to augment and improve existing technologies as is done with high k dielectrics, FinFET’s and strained materials.

A pivotal factor in the growth of graphene as a new engineering material is the production of large area, high quality crystal. This thesis will explore the various methods of modern graphene production and the results and findings of our own large area synthesis of graphitic films formed through the segregation of carbon through nickel films from a silicon carbide carbon source.
2. Graphene Background

Graphene is a monoatomic sheet of carbon atoms. Carbon consists of 6 electrons, the first 2 electrons existing in the 1s orbital and are strongly bound to the atomic nucleus and therefore do not participate in chemical bonding and will have little influence on the physical properties of graphene other than dielectric screening. In the second energy shell, hybridization between the s and p orbital’s give rise to \( sp^2 \) hybrid covalent C-C bonds called (\( \sigma \) bond) that make up graphene’s honeycomb lattice. Currently, \( sp^2 \) are the strongest bonds found in nature [10]. The remaining half filled 2p states will form the valance band localized perpendicular to the honeycomb lattice and give rise to the graphene’s peculiar electronic properties.

![Figure 1: A)sp2 bonding configuration B) Real space representation of \( \pi \) and \( \sigma \) bonds [11]](image)

2.1 Lattice Structure

The graphene lattice has a two atom basis (A and B in Figure 2). Primitive translation vectors \( a_1 \) and \( a_2 \) are given in Equation 1, while the next nearest neighbours \( \delta_1, \delta_2, \delta_3 \) are given in Equation 2, where ‘a’ is the carbon-carbon distance and is approximately 1.42Å. Reciprocal lattice vectors are \( b_1 \) and \( b_2 \) are given in Equation 3.

\[
a_1 = \frac{a}{2} (3, \sqrt{3}), a_2 = \frac{a}{2} (3, -\sqrt{3}) \quad \text{(Equation 1)}
\]

\[
\delta_1 = \frac{a}{2} (1, \sqrt{3}), \delta_2 = \frac{a}{2} (1, -\sqrt{3}), \delta_3 = -a(1,0) \quad \text{(Equation 2)}
\]

\[
b_1 = \frac{2\pi}{3a} (1, \sqrt{3}), b_2 = \frac{2\pi}{3a} (1, -\sqrt{3}) \quad \text{(Equation 3)}
\]
2.2 Band Structure

While graphene’s mechanical strength is in part due to $\sigma$ bonds that make up its honeycomb structure, the perpendicular $\pi$ bonds are responsible for its peculiar band structure. As seen in Figure 3 the conduction and valence bands come into sharp contact at 6 points within the Brillouin zone, at these 6 points the low energy dispersion relations are nearly linear and have zero effective mass. Electrons in these low energy regions mimic relativistic quasi-particles, or ‘Dirac fermions’ that are governed by the Dirac equation [13], and as such the K and K’ points where the bands touch are known as Dirac points.

From the cut away in Figure 3, the valance and conduction bands do meet at each K point leaving no bandgap making graphene a semi-metal, this naturally puts some limits in using graphene as channel material in logic circuits. At present much research is being directed into opening bandgaps in graphene
and such methods include, asymmetric stretching of graphene, applying voltages to bilayer graphene, and forming graphene into nanoribbons [14].

2.3 Physical Properties
A property of principal concern in electronics is mobility and in this regard graphene has the largest mobility of any known material. Suspended graphene field effect transistors (FETs) have exhibited mobility’s of 200000 cm²/V s and full ballistic transport throughout the 1.2 μm channel [15]. However, impurity scattering will significantly reduce mobility when graphene is transferred to SiO₂ substrates or grown epitaxially [16]. As mentioned previously the σ bonds in graphene are the strongest in nature and give graphene and ultimate breaking strength of 42 N/m and a Young’s modulus of 1.0 TPa [10]. Graphene also exhibits a superb thermal conductivity ranging from 4.84 - 5.30 kW/mK, making it a topic of study in thermal interfacial materials [17].

A word of caution must be given when reading into many of the high figures of merit that graphene is known for, as these figures are mostly obtained from pristine lab conditions and experimental devices. When dealing with real world applications and real world devices it must be stressed that graphene’s many figures of merit will not be representative of the nominal operation in real world devices.
3. Production Methods

The methods of large area graphene synthesis are numerous and all have their advantages and drawbacks. As this thesis is based on catalytic growth from a SiC carbon source we will discuss several related methods production, notably: Annealing of SiC, CVD growth on nickel and copper, and carbon segregation through nickel catalysts. One must keep in mind that the various methods discussed are by no means exhaustive, and are only to serve as a guide to some relevant synthesis processes.

3.1 Sublimation of SiC Wafers

The underlying method in synthesizing graphene from SiC wafers is to sublime silicon from the wafer surface whereby the remaining carbon will reform into a graphene sheet. The annealing of SiC comes with some simplicity as it avoids the use of metal catalysts and as such is favourable in traditional CMOS processing. However the price of this simplicity is paid by the use of high annealing temperatures (upwards of 1300°C) and ultra high vacuum needed to achieve silicon sublimation. In addition the surface topography of SiC will limit the area of graphene growth as graphene is limited to the horizontal terraces with little growth occurring on vertical edges.

Epitaxial graphene synthesis from SiC was first carried by Von Bommel et al. in 1974[18], this process was carried out in UHV and at temperatures above 800°C. From these experiments it was found that the orientation of the crystal plays a principal role in graphene growth, with carbon terminated faces having higher rates of graphene growth then silicon terminated sides.

After Geim’s discovery in 2004, Berger et al. were the first to fabricate graphene devices on Si-terminated 6H-SiC wafers. In this work synthesis occurred in UHV conditions and at temperatures ranging from 1250-1450°C. These conditions produced “ultrathin epitaxial graphite”, possibly to say that the films produced were multilayer graphite. Afterwards traditional lithography techniques were applied in patterning devices in which moderate field effect was seen, and thus served as an inspiring proof of concept into a new breed of graphene SiC devices. Studies into graphene synthesis on SiC by Emtsev et al.[19] go on to show that graphene defects in sublimed SiC are caused by high silicon sublimation rates seen in UHV synthesis, and that sublimation can better be controlled by utilizing argon at atmospheric pressures. In this way, true monolayer graphene can be synthesized on SiC terraces. The downside of atmospheric annealing in argon is naturally the higher temperatures required (1600°C) in order to initiate sublimation in ambient pressure argon.

Following in the success approach to controlling silicon sublimation, de Heer et al [20] have recently published a refined synthesis method referred to as confinement controlled sublimation (CCS). In this method SiC wafers are confined in a non reactive graphite chamber with a small leakage aperture which maintains a higher silicon vapour pressure and thus limits the sublimation rate. The CCS method has been used with both UHV and argon atmospheres and can effectively grow graphene on both the silicon and carbon terminated faces of SiC by tuning both the temperature and size of the leak aperture.

3.2 SiC on Si

There are several other divisions in the methods of graphene synthesis from SiC, one of which consists of growing SiC films on silicon via gas source molecular beam epitaxy, followed by an in-situ UHV anneal
This method reports marginally lower annealing temperatures in UHV (1200°C) in comparison to Berger’s annealing temperatures that range from 1250-1450°C, however this demonstrates the utility of SiC synthesis method without relying on expensive SiC wafers.

3.3 Etching SiC on Si
All the methods discussed thus far rely on physical sublimation of silicon from the SiC surface, another possibility exists by inducing a chemical reaction that will consume silicon in favour of carbon and thus induce graphene synthesis. This method was first exploited by Moon et al. [22] in which a SiC film is first grown on a silicon substrate with mono methyl saline, subsequently the SiC film is exposed to a halogen gas which leads to the de-adsorption of silicon and formation of graphene. The most impressive aspect of this research is that this process is carried out in chemical vapour deposition (CVD) reactor with synthesis temperatures of 850°C. Further research in this method may show promise as a low temperature solution to synthesising graphene on silicon substrates.

3.4 Chemical Vapour Deposition
Nickel has been one of the best working catalysts in the prior synthesis of carbon nanotubes and these methods have been adapted in the production of graphene through the use of CVD[23]. Nickel provides a very soluble media in which carbon can diffuse into while at high temperature. Upon cooling the carbon solubility will start to decrease causing the dissolved carbon to escape from the nickel film, ultimately segregating on the surface to form graphite and graphene. While nominal CVD reactions do not involve chemical diffusion, it is believed that diffusion is responsible for CVD graphene synthesis using methane as a source gas[23]. The formation of graphene even in CVD methods is determined by the thermal history of the nickel film, and CVD process using methane at temperatures of 1000-900°C will yield 1-10 layers of graphene. During the above process, the evaporated nickel film will undergo recrystallization, forming grains of 20μm, sheets of continuous graphene are ultimately limited to the size of these nickel grains, however by carefully dosing and cooling of samples can produce larger areas of single and few layers of graphene up 85% surface coverage[24].

Transferring graphene films from nickel is carried out be first applying poly methyl methacrylate (PMMA) over the graphene, followed by selectively etching the underlying nickel with hydrochloric acid. After etching, the PMMA/graphene film can be transferred onto an arbitrary substrate and the PMMA can be subsequently removed with acetone.

Similar CVD methods using copper as catalytic film have also been established [25]. As copper has a limited solubility for carbon, CVD synthesis utilizing methane as a carbon source have been found to be self limiting, with most of the synthesis area containing single layer graphene. Unlike nickel, CVD growth on copper is found to be non temporal and authors report that the synthesis mechanism is a truly catalytic surface reaction unlike the segregation that takes place in nickel. The Exacting details of the copper – carbon reaction mechanism are still unknown. At present CVD on copper provides the largest possible area of synthesized graphene with a graphene yield of 95% and continuous growth over copper grain boundaries.
3.5 Solid Source Segregation

The study of carbon segregation and monolayer carbon growth was first carried out by Eizenberg and Blakely in the late 1970’s [8]. In this work Ni (111) was doped with carbon and then gradually annealed in UHV, while in situ Auger electron spectroscopy measured the both nickel and carbon signals on the film surface.

Numerous trials were carried out each with different concentrations of doping concentrations of carbon. Samples were gradually heated or cooled as to best allow the system to remain in equilibrium for a given temperature. Three distinct segregation regimes were seen in this experiment, with results being identical for both heating and cooling conditions.

![Figure 4: Schematic graph describing carbon Auger signals while annealing carbon doped Ni (111).][8]

Figure 4 shows a pictorial rendition of carbon Auger signals from the film surface during the cooling/heating process. As can be seen there are low carbon signals at high range temperatures where the carbon solubility would be highest. Temperature $T_s$ marks the beginning of Eiezenburg terms segregation, upon which the carbon signal remains constant for $>100^\circ \text{K}$. At temperature $T_p$ the carbon signal begins to increase once more to the point where it attenuates Auger electrons coming from the nickel.

The most striking fact from this experiment is that carbon signals coming from the intermediate “surface monolayer phase” are the same regardless of the prior carbon doping concentration. Based on the inelastic mean free path of the carbon signals from this phase, Eizenburg estimates that 4Å of carbon would cause such a signal and thus deduces the intermediate phase consists of monolayer carbon. Both temperatures $T_s$ and $T_p$ vary according the carbon doping concentration but roughly remain 100°K apart. It is important to mention that nickel films are specifically (111) and that doping was carried out by annealing the nickel surface in graphite powder over the course of several weeks. Such an annealing method my help preserve the original crystal structure of the nickel, however this is not specifically mentioned by the authors.
The temperature-solubility relation comes in the form of an Arrhenius expression as seen in Equation 4, where \( S_0 \) is an entropic pre-factor related to the density of sites where solute atoms are positioned, \( H \) is activation enthalpy, and \( k \) is Boltzmann’s constant.

\[
S = S_0 e^{\frac{H}{kT}} \quad \text{(Equation 4)}
\]

The temperature-solubility relation for Eizenburg’s three different phase regimes can be seen in Figure 5. Entropic pre-factors and precipitation enthalpies used in this plot are taken from experimental values found by Lander et al. [27]. The enthalpy used to plot the thick black line that marks the beginning of segregation is found from Eizenburg’s work.

Subsequent research carried out by Baraton et al. [26] investigates carbon segregation with carbon doped nickel, and attempts to limit carbon diffusion to the “nickel and graphene” region seen in Figure 5. By limiting the carbon implantation to elementary doses based on the surface density of graphene it was reasoned that further annealing could produce single layer graphene. Ultimately annealing of the carbon implanted nickel only produced nano-crystalline graphene, tunnelling electron microscopy (TEM) provide further insight as to carbon segregation from the nickel film.
TEM observation as seen in Figure 6 seem to indicate that graphite flakes first start to develop along nickel grain boundaries that are known to be preferential precipitation sites for carbon. Baraton deduces that carbon segregation takes place in a two step process first consisting of local migration of carbon to nickel grain boundaries, upon reaching a critical mass of carbon the grain boundary will serve as a nucleation site for graphene and graphite growth. Once nucleation occurs, graphene layers will grow latterly across the nickel surface and possibly cover nickel grain boundaries that are un active due to lack of lack of surface curvature. Ultimately Baraton’s experiment yielded nanocrystaline graphene films, such results are probably due to very fast surface diffusion from grain boundaries during quenching and over saturation of carbon even when only using a carbon dose equivalent to the surface density of 2 graphene layers.

3.6 Silicon Carbide – Nickel System

In the segregation methods previously discussed carbon is first introduced into the nickel film by doping and energetic implantation, however our study will use SiC is used as a carbon source. In using nickel films on SiC we are ultimately presented with a Si-C-Ni, ternary system. In such a system nickel silicide formation at the SiC-Ni interface plays a crucial role in the thermal evolution of the SiC-Ni system. With species diffusing in multiple directions, and formation of multiple silicide types, the overall thermal evolution of the SiC-Ni system is somewhat difficult to model, although theoretical isothermal phase diagrams for the Si-C-Ni system do exist [28]. Experimental studies based on Rutherford back scattering (RBS) and X-ray analysis have examined silicide formation in the SiC-Ni systems for various temperatures [29], and while these studies do not specifically examine higher temperature processes, they do serve as a rough guide as to the various silicide species that come about with annealing.
As can be seen in Figure 7, annealing temperatures of 450°C will first start carbon diffusion into the nickel ultimately leading to graphitisation of the nickel surface, with first formation of silicide starting after and additional 30min of annealing. Ni<sub>31</sub>Si<sub>12</sub> formation can be seen at 500°C, this formation eventually gets consumed by Ni<sub>2</sub>Si which is the dominate silicide type at higher temperatures. Again it must be stressed that the findings presented in Figure 7 are to just simply serve as rough guide as to some of the silicide formations that occur while annealing. In reality the annealing regimes that produce segregated graphene usually only involve brief heating followed by quenching, unlike the 30min anneals seen in the previously mentioned study.

### 3.7 Motivating Papers

The underlying motivation for annealing a Si/SiC/Ni system comes from two papers which successfully report graphene synthesis using such methods [30], [31], the methods and processing details of this research will be discussed in further detail.
Research carried out by Juang et al. [30] synthesis graphene through nickel segregation on both 6H-SiC wafers and 3C-SiC/Si. Processing begins with the evaporation of 200nm nickel films on each substrate, followed by vacuum annealing at $10^{-7}$ Torr to temperatures of 700°C and 750°C. Upon reaching the desired target temperature samples are quenched at controlled cooling rates of 10-20°C/sec by simply turning off the heater. In have a very quick thermal treatment it is speculated that unwanted silicide formation will be limited while carbon successful diffuses thru the nickel to form graphene. Graphene was successfully synthesized using these methods, notably it was found that both 6H-SiC and 3C-SiC produced graphene of comparable quality. Additional trials were also carried out utilizing a 1nm nickel film which resulted in no traces of graphene growth. Principal conclusions of this study find that rapid heating of SiC/Ni systems are a viable approach for graphene growth and that with this method, SiC morphology does not impact the quality of graphene. Rapid annealing is a major theme in the work carried out by Juang and this cannot be understated as prolonged annealing will result in unwanted silicide formation from both the SiC and Si substrate, and ultimately unwanted graphite precipitation.

Alternative approaches carried out in research done by Hofrichter [31] try in part to mitigate some of these unfavourable reactions. Hofrichter’s experiment utilizes the following system: Ni(500nm) / a-SiC(50nm) / SiO2(300nm) / c-Si. The principle difference in layer structures used in this experiment and Juang’s is the 300nm thermal oxide that serves as a chemically stable buffer effectively preventing silicon diffusion from the crystalline substrate into the nickel. Carbon segregation is induced with a 30s annealing at 1100°C in a ambient pressure nitrogen atmosphere. With this experimental setup, multilayered graphene sheets were grown with some single layer areas being clearly evident. Another theme in Hofrichter’s work is using much thicker nickel films with respect to the SiC, in this way only sub-stoichiometric amounts of silicide are formed while annealing. Negligible silicide growth is seen in this study and as such, graphene can be transferred to the underlying oxide layer by simple etching the nickel with nitric acid and hydrogen peroxide.

In summation, we find considerable evidence in the viability of the SiC/Ni system to produce graphene with quick thermal annealing. Major hurdles in both of the studies examined above suggest that unwanted silicide growth is an innate problem with this system, and that short anneal times and thicker nickel films can help in limiting silicide growth close to the SiC/Ni interface and away from graphene that has segregated on the nickel surface.
4. Characterization Techniques

With graphene being a monoatomic structure and difficult to quantify, characterization tools such as Raman play a large role in future discussions and thus will discussed in full before exploring the various methods of graphene synthesis. There are many characterization tools that exist to examine the quality of graphene crystals, some of these include: X-ray diffraction, transmission electron microscopy, low energy electron diffraction, Raman spectroscopy, and scanning electron microscopy (SEM). Of these methods Raman spectroscopy is the principal tool used by many groups as it time efficient, non destructive and does not require vacuum.

4.1 Raman Spectroscopy

Raman spectroscopy is based upon the inelastic scattering of light, commonly known as Raman scattering, named after its founder: Sir Chandrasekhara Venkata Raman. The premise of Raman spectroscopy is to measure the phase difference between monochromatic incoming light and reflected light that is inelastically scattered upon hitting the specimen. Raman spectroscopy offers a quick and easy method of characterization of materials however, this ease of use comes the expense of interpreting the Raman spectra which can be problematic.

Raman scattering of light is caused by electron-phonon reactions. In this process the electric field of an excited electron promoted to the conduction perturbs the molecules ionic core forming a dipole oscillation creating a phonon in the crystal lattice. These phonons create an unstable ‘virtual’ energy state, in carbon based systems this virtual state is usually of lower energy then the conduction band for a given value of k in reciprocal space. Raman scattering occurs when an electrons in the conduction band emit phonons into the lattice, thus bringing them into said virtual state of lower energy, from which they will drop back to the conduction band releasing a photon of lower energy, this type of Raman scattering is known as Stokes scattering. There is also the possibility of the a virtual state being higher than the natural electronic state, in which case a phonon from the crystal lattice is annihilated and relaxation of the electron will create a photon of higher energy, this called an anti-Stokes shift and is generally a less favourable event.

Raman spectroscopy will measure the energy shift between the incoming monochromatic light and the returning scattered which will be of a different wavelength do to phonon creation. Knowing the phonon dispersion relations of a molecule we can predict the allowed Raman scattering events and thus the Raman spectra. From both theoretical and empirically found Raman spectra’s of known graphene systems, one can make inferences as to the structure of an experimental sample from its Raman spectra.

4.2 Graphene Raman Spectra

The peculiar dispersion relation of carbon’s π electrons is responsible for high resonance in virtual states [32], making Raman spectroscopy a tool of big importance in the characterization of any carbon based system and research in the use of Raman on carbon systems was well established before the discovery of graphene. In the following discussion we will go over the nominal Raman spectra’s of graphene and various graphitic allotropes.
The most prominent features of the pristine graphene Raman spectra are the G and 2D peaks located at wavenumbers 1582 cm$^{-1}$ and 2700 cm$^{-1}$ respectively. These two peaks can be seen in the lower spectra of Figure 8. As the uniformity of the graphene crystal degrades additional phonon scattering will occur, giving rise to the D at 1350 cm$^{-1}$ seen in Figure 9.

### 4.2.1 Graphene G Peak
In carbon allotropes the G peak is the telltale of sp$^2$ bonding and is caused by the vibration of sp$^2$ bonds. The sp$^2$ bonds that give rise to the G are not necessarily bounded in 6 fold rings as it is in graphene, single chains of sp$^2$ bonds will also produce this resonance [1]. The G peak is the result of a double degenerate phonon mode near the centre of the first Brillouin zone. In graphene systems the G peak is the only first order Raman process (see Figure 10), meaning that only one phonon participates in scattering [34]. Generally speaking the order of a Raman process is given by number of participating phonons, what complicates this nomenclature is that some phonons in higher order processes will involve elastic phonons that will not lead to a increase or decrease the energy of the electron.
In general the G peak intensity will increase linearly with increasing graphene thickness [35], by and large this can be understood as more carbon rings in multi layer graphene being excited, and hence the intensity of the G peak can help determine the amount of graphene layers present. The evolution of the G peak from mono layer graphene to multi layer graphene is seen in Figure 11. The linearity of the G peak intensity with increasing graphene layers can be seen in Figure 12, notice that this relationship only holds for multi layer graphene up 15 layers.

![Figure 11: Evolution of Raman spectra with increasing graphene thickness on various substrates. (C) and (D) show enlarged 2D band regions with fitted curves (in black) representing 2D sub-bands. [36]](image1)

![Figure 12: G peak intensity of multiple layer graphene. The “a-h” region consists of more then 10 layers of graphene with a thickness of 5nm to 10nm. The dotted red line is a visual queue to guide the eye[35]](image2)

### 4.2.2 Graphene D Peak

As seen in Figure 9, the D peak is located at approximately 1350 cm\(^{-1}\). This peak is indicative of defect sites in a graphene system and as such, pristine graphene will have no D peak. Pristine graphene will actually consist of two sub peaks, in the presence of additional graphene layers these peaks will merge to form a single Lorentzian curve. Looking at Figure 10 we can there are four steps in this scattering mechanism. 1) Laser induced electron is excitation. 2) A defect in the crystal elastically scatters the electron to a K’, where K’ is related to K by time reversal symmetry. 3) The electron is scattered back to the K point by an inelastic event. 4) Finally electron hole recombination and photon emission. Notice in Figure 10 that all elastic events are represented by horizontal lines, and inelastic events will have a component in the vertical direction.

When dealing with pristine graphene crystal, the D peak will increase with increasing defects in the crystal. In the case of vary pristine the \(I_D/I_G\) roughly proportional to the length between defects.
However, at large defect concentrations the length between defects will begin to decrease, at which point the D peak will be at maximum intensity. Now additional defects will serve to lower the D peak intensity and phonon dispersion will be dominated by bulk structural disorder in the graphene crystal (see local activation model)[37].

4.2.3 Graphene 2D Peak
The second most prominent feature of the graphene Raman spectra is the 2D peak at 2700 cm\(^{-1}\), and in pristine graphene has in intensity roughly 4 times greater than the G peak as can be seen in Figure 9. Historically this was called the G' peak as it was the second most established peak in a graphitic system, and because it occurs at roughly twice the wavenumber of the D peak some authors call it the 2D peak [34]. In this paper we will refer the 2700 cm\(^{-1}\) the 2D as merely coincide with authors at KTH.

Indeed the most striking feature of the graphene Raman spectra is the rather large intensity of the 2D peak, this normally explained by second order process involving two phonons at the K' and hence is called an ‘intervalley’ process. However, in the case of mono layer graphene with its nearly symmetrical valance and conduction bands, holes can also be scattered to neighbouring K' points. An additional mechanism whereby both electrons and holes scattered at K’ recombine resonantly is known as a triple resonance condition and might explain why the 2D peak intensity is so high in the case of mono-layer graphene [34]. At present the main argument as to why a strong 2D peak is very indicative of quality graphene is because the needed symmetry required to have both resonant hole and electron scattering that takes place in triple resonance. Many authors write that the particulars of electron-phonon, and hole-phonon processes that take place in the 2D peak is poorly understood and further theoretical and experimental research is need in this area [34], [37].

An important point to note when interpreting Raman spectra of graphene is that the 2D peak will form a Lorentzian curve in mono-layer graphene. Graphene samples consisting of more than one layer will have a muted intensity and larger full-width-half-maximum (FWHM) as the 2D will be the superposition of additional resonances that occur from additional graphene layers.

4.2.4 Bilayer Graphene 2D Peak
Bi-layer graphene stacked in a Bernal configuration will have a more complex electronic structure allowing for additional Raman resonances in the 2D band. In this system there are two allowed translational phonon modes to the K’ and two possibilities for electron-hole creation, thus giving 4 resonances, which form a convoluted 2D band over each individual sub band, this can be seen in Figure 13.
The biggest difference in the evolution of the 2D peak will be from mono bi-layer graphene, where four additional scattering modes will be incorporated into 2700 cm$^{-1}$ region, along with a marked increase in the 2D FWHM. As the amount of graphene layers is increased the shape of the 2D peak will morph as different sub peaks become more resonant and have higher intensities as seen in Figure 14. Overall it is possible to distinguish up to 4 or 5 layers of graphene, with the Raman spectra of 5 or more layers being indistinguishable from that of bulk graphite [33].

An important fact to mention when interpreting the Raman spectra of few layer graphene is that the 4 sub peaks in the 2D are only present with proper Bernal stacking of the layers, turibostatic graphite which does not have proper Bernal stacking will only exhibit 2D peak in the form of a single Lorentzian peak, which will be up-shifted by 20 cm$^{-1}$ and with a FWHM of approximately 50 cm$^{-1}$ (double that of graphene) [33].

In principle, pristine graphene should have an $I_D/I_G$ ratio of 4, and the number of graphene layers could be inferred by degradation of this ratio. However, this ratio is sensitive to doping, disorder, and as such these factors should be controlled for or externally validated in order to clearly delineate their effects when using Raman as means of layer numeration [37].

4.3 Raman Spectra of Disorder and Amorphous Carbon systems

Thus far in our discussions we have only talked about the Raman spectra of graphene and few layer graphene. In this section we will be discussing bulk carbon systems and how they morph from bulk sp$^2$. 
bonded graphic stages to nano-crystalline graphite and finally, amorphous sp\(^2\) to amorphous sp\(^3\) (defected diamond).

As mentioned before the D peak phonon mode is not allowed in pristine graphene crystals, and in the case of graphene an increasing D peak intensity is the result of increasing disorder. An important underlying element in this analysis is there first must be an established 6-fold aromatic ring structure in the carbon lattice in order for elastic scattering of defects to occur which give rise to the D peak [1]. Secondly we reiterate the dependence of the G peak on the presence of σ bonds either in a honeycomb lattice or dangling chains and will be located in wavenumbers 1500-1630 cm\(^{-1}\) [1].

The pioneering work of Tuinstra and Koenig first made the relationship between ID/IG and disorder in graphitic sp\(^2\) structures [39]. Tunistra’s work demonstrates the inverse relation between ID/IG and defect length and is shown in Equation 4, where C(λ) is the laser wavelength used in the Raman system and \(L_A\) is the length between defects, which some authors call activated areas.

\[
\frac{I_D}{I_G} = \frac{C(\lambda)}{L_A} \quad \text{(Equation 4)}
\]

Tunistra’s relation does however not hold when disorder in the system becomes so great that σ bonds start to morph into their sp\(^3\) form, and this model breaks down when defects become more predominate and exhibit smaller defect lengths. Studies carried out by Ferrari et al. have built on this model of increasing disorder in graphite systems [1]. In the Ferrari’s Raman study of disordered graphitic systems he outlines a three stage disorder model starting from well ordered graphite and increasing disorder till all bonds are of sp\(^3\) character:

1) graphite -> nanocrystalline graphite (nc-G)
2) nanocrystalline graphite to - -> amorphous carbon (a-C)
3) amorphous carbon-> 100 sp\(^3\) (defected diamond)

Stage 1: As mentioned before the D peak intensity will increase with defect intensity, and the G peak intensity will remain stable and thus Tunistra’s inverse relation is obeyed. The D’ peak (second order K’ phonon mode) will be established which will skew the G peak, up-shifting its wavenumber. As disorder manifests regions of ordered graphite will start to cluster, and when these smaller clustered regions start to lose their order the D peak will decrease as the amount of 6 fold rings needed for phonon resonance is lost. The point where ID/IG ratio begins to decline marks the end of nanocrystalline phase and Tunistra inverse relation.

Stage 2: Again degradation of the system continues the D peak will lose intensity. As mentioned previously, the D phonon modes require the presence of a 6 fold carbon ring, and thus in this stage the D peak intensity is proportional to finding a six fold ring in a graphitic cluster, which is proportional to the cluster size. Thus in stage 2, the D peak is a sign of order, as opposed disorder. As disorder continues in the system, the G peak will start to disperse and D (no proportional to number of graphite clusters) will start to decrease. Eventually the \(I_D/I_G\) ratio will decrease to 0, at which point the second
stage will end. The $I_D/I_G$ ratios and G peak locations throughout the first two disorder stages can be seen in Figure 16.

![Figure 15: $I_D/I_G$ ratio vs. Defect length. Stage 1 is seen on the right side, with stage two being on the left side. [1]](image1)

![Figure 16: $I_D/I_G$ and G position over all three stages of disorder. [1]](image2)

### 4.3 Substrate Effects on Raman Spectra

In previous conversations we neglected any mention of the substrates on which the graphene is mounted and how these substrates affect Raman spectra. A very popular and desirable substrate for characterizing graphene is 300nm SiO$_2$. This surface provides the best contrast in characterizing graphene flakes under an optical microscope [40], and naturally provides an insulating surface on which to further construct devices. Strong Raman signatures seen on 300nm SiO$_2$ substrates are generally attributed to favourable interference enhancement between the graphene and SiO$_2$ substrate [35]. Empirical studies of exfoliated graphene on various substrates have demonstrated that weak interaction between graphene sheets and various substrates have a negligible on Raman spectra [36].

### 4.4 Epitaxial Raman Spectra

When characterizing epitaxial graphene grown on SiC there are several complications that are not seen with transferred graphene. Unlike polymorphous metals, SiC crystals will exhibit a strong Raman spectra that will dwarf the characteristic graphene spectra, thus one it may be required to subtract the characteristic SiC spectra from the epitaxial graphene spectra in order obtain nominal graphene peaks [41]. While baseline subtraction is a common practice in graphene characterization [42], the situation with epitaxial graphene on SiC is further complicated as the graphene Raman spectra will nominally will be ten times lower in intensity then freestanding transferred graphene [43], this decrease in intensity is generally attributed to lack of favourable substrate interference. Furthermore, graphene grown on SiC will exhibit significantly up-shifted G and 2D peaks, which can be attributed to inherent compression of
the graphene from the substrate [43]. As the characterization of SiC epitaxial graphene is somewhat more complicated when compared to freestanding transferred graphene, a small survey of various Raman acquisition routines can be seen in Table 1.

Table 1: Raman Configurations for SiC epitaxial graphene

<table>
<thead>
<tr>
<th>Paper</th>
<th>Substrate</th>
<th>Raman λ (nm)</th>
<th>Raman Power (mW)</th>
<th>Acquisition time (min)</th>
<th>Spot diameter (nm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni – 2008 [42]</td>
<td>6H SiC (both Si and C faces)</td>
<td>532</td>
<td>0.1</td>
<td></td>
<td>500</td>
<td>Smaller SiC spectra is seen, baseline subtraction not required</td>
</tr>
<tr>
<td>Röhrl – 2008 [43]</td>
<td>6H SiC (0001)</td>
<td>532</td>
<td>?</td>
<td>?</td>
<td>2000</td>
<td>Baseline subtraction of Nominal SiC spectra required</td>
</tr>
<tr>
<td>Su Lee - 2008 [44]</td>
<td>4H SiC and 6H SiC</td>
<td>488</td>
<td>12</td>
<td>30</td>
<td>1000</td>
<td>Baseline subtraction of Nominal SiC spectra required</td>
</tr>
<tr>
<td>Miyamoto – 2008 [45]</td>
<td>3C SiC on Si</td>
<td>541</td>
<td>?</td>
<td>?</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>
6. Experiment
Through the course of this study, the annealing of various different structures was examined, these include: SiC/Si, Ni/SiC/Si, and Cu/SiC/Si. For the sake of clarity, experimental procedure, results and preliminary discussions for each structure will be individually presented. Comparative discussions will follow in the next section.

6.1 SiC/Si
All experimental trials were carried out with epitaxially grown SiC films on Si (111) substrates. SiC films of 10 and 100nm were fabricated and serve as a carbon sources for all the experiments carried out in this study. In annealing the SiC/Si without any metal film we explore the possibility of favourable silicon sublimation and or diffusion. Experiments were carried out 900°C and 10⁻⁶Torr, these being the maximum steady state temperature and pressure of the furnace.

6.1.2 SiC/Si Vacuum Anneal Procedure
1. Anneal for 1 hour 30 minutes, followed by quenching in load lock under vacuum
2. Potential graphene growth was characterized via Raman spectroscopy with a 514nm 20mW excitation source, with acquisition times of several minutes.

6.1.3 SiC/Si Vacuum Anneal Results

![Raman spectra for SiC/Si samples annealed at 900°C for 1 hour, 30min at 10⁻⁷Torr.](image)

Figure 17: Raman spectra for SiC/Si samples annealed at 900°C for 1 hour, 30min at 10⁻⁷Torr.

The absence any definitive 2D(2700cm⁻¹) what so ever in the Raman spectra shown in Figure 17 rules out any presence of graphene, however peaks at 1605cm⁻¹ and 1420cm⁻¹ in the 100nm SiC plot can be seen
that are reminiscent of D(1350 cm\(^{-1}\)) and G(1582 cm\(^{-1}\)) peaks in and graphite. Two factors must be considered when interpreting the spectrum presented in Figure 17.

The absence of a 2D peak and presence of a very large intensity D peak could be interpreted as a nanocrystalline graphite – amorphous graphite system. In the nanocrystalline graphite – amorphous graphite regime, where G peak blue shifts of 20 cm\(^{-1}\) can be expected. The G peak in Figure 17 is blue shifted by 23 cm\(^{-1}\) from the nominal G peak value, however with a I\(_D\)/I\(_G\) ratio of approximately 1 the data does not neatly fit into the graphitization regime outline by Ferrari (seen in Figure 16).

Secondly, we expect that graphene grown on SiC will be epitaxially strained, which in turn blue-shifts G peaks by roughly 20 cm\(^{-1}\)(on 3C-SiC [44]), with little affect seen on the D peak. The tentative D peak in Figure 17 is blue shifted by 91 cm\(^{-1}\), which further does not follow data seen in literature. Ultimately, reconciling the effects of both the graphite disorder and substrate effects into the Raman spectra seen in Figure 17 is somewhat unwise if not impossible.

6.2 Ni/SiC/Si

As discussed in section 2, the favourable solubility of carbon in nickel films provides a catalytic effect allowing graphene synthesis to occur at lower temperature in both CVD and solid source methods. The following experiments utilize the following structure: Ni(200nm)/SiC(10-100nm)/Si, which consists of the same SiC/Si wafers with a 200nm evaporated nickel film. The thickness of the film was chosen primarily as it is used in work carried out by Juang [30] as well as others [8], [26]. Parallel experiments were carried out using both vacuum annealing and rapid thermal annealing (RTA) and with similar temperatures.

Much of the literature that documents nickel segregation methods emphasize that graphene synthesis occurs very fast and with this knowledge, annealing was first carried out times of 30 and 60s. At the time of the experiment Raman characterization with a less preferential 633nm excitation source and 1mm spot size was available for use, and with subsequent characterization did not reveal any graphene or graphitic growth with 30 and 60s annealing times. In light of these findings a second trial was conducted with much longer 15 and 30min using the same temperatures in order to better initiate carbon segregation. Only the findings of the subsequent long anneals will be discussed as suitable characterization with a 514nm Raman excitation was properly carried out.

6.2.1 Ni/SiC/Si Vacuum Anneal – Procedure

1. All samples were treated according to the experimental conditions listed in Table 2. The pressure for all trials was kept constant at 10\(^{-7}\) Torr.
2. After annealing samples were quenched in the furnace load lock while under vacuum.
3. Potential graphene growth was characterized via Raman spectroscopy with a 514nm 12mW excitation source, with acquisition times of 8 seconds.
### Table 2: Ni/SiC/Si vacuum anneal experimental matrix

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>SiC thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>15/30</td>
<td>10/100</td>
</tr>
<tr>
<td>775</td>
<td>15/30</td>
<td>10/100</td>
</tr>
<tr>
<td>800</td>
<td>15/30</td>
<td>10/100</td>
</tr>
<tr>
<td>825</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

#### 6.2.2 Ni/SiC/Si Vacuum Anneal – Results

Preliminary Raman spectra seen in Figure 18 clearly show distinguishable D,G and 2D peaks at nominal wavenumbers, all spectra are vertically offset from one another for clarity. Striking features seen in the spectra include the high D peak and low 2D peak intensities when compared to that of the G peak. Such spectra are indicative of a graphitic film, with closer inspection of the 2D wavenumbers showing fairly symmetrical peaks with no clearly evident modulations one might expect in few layer graphene. Such symmetrical, low intensity 2D peaks suggest that any hexagonal carbon structures are turbostratic and not Bernal stacked.

In several of the G peaks, a small modulations can be seen to the left of the peak apex, this is most likely caused by G peak merging with the D' peak, which is a less predominate defect scattering Raman mode. Nominal NiSi peaks can be seen the lower most wavenumbers of the spectra along with much lower intensity NiSi₂ peaks at 300 cm⁻¹ these peaks correspond with Raman silicide studies performed by Zhao [45].
While qualitative inspections indicate the presence of graphitic growth, it is ultimately the $I_D/I_G$ and $I_{2D}/I_G$ ratio that will best indicate the level of graphite and graphene disorder respectively.

Figures 19 and 20 plot the evolution of both $I_D/I_G$ and $I_{2D}/I_G$ ratios over the span of annealing temperatures used in the experiment. In order to obtain a more representative view of the entire graphene sample, additional Raman characterization was carried at random spots on each sample. All Raman spectra were then semi-automatically fitted with Lorentzian curves using the “Multiple Peak Fit” tool in Origin 8.5, and then subsequently plotted.

In Figure 19 it can be seen that the $I_D/I_G$ ratios for both the 10 and 100nm SiC samples do not correlate with annealing time. No definite correlation between $I_D/I_G$ and annealing temperature can be seen with the 10nm SiC samples, while the 100nm SiC samples have a constant with a ratio of approximately 1.2 for all temperatures. With $I_D/I_G$ ratios between 0.6 and 2.2 and all peaks located at nominal wavenumbers, the Raman spectra do fit within Ferrari’s definition of a nanocrystalline graphitic system as discussed in Section 4.

Figure 18: Raman spectra of samples vacuum annealed at $10^{-7}$Torr at various times and temperatures. All spectral baselines are offset for clarity.
Given the random and limited data of Figure 20 little if any correlations can be made, although the 100nm SiC samples do seem to have somewhat more consistent values throughout the different temperatures. With $I_{2D}/I_G$ ratios ranging from 0.6 – 1.4, and $I_D/I_G$ ratios of 0.6 – 2.2, a nanocrystalline graphitic system is the best possible description given the data. SEM micrographs taken before and after annealing are shown in Figures 21-25. They support the conclusions drawn from Raman data that any growth formed after annealing is disordered and not graphene.
6.2.3 Ni/SiC/Si Vacuum Anneal RBS

With contact between nickel and SiC, we can expect silicidation given the annealing temperatures used in this experiment. With Raman spectra showing some nickel mono silicide we can assume that there is at least some silicidation has occurred. In order to best characterize the amount of silicide formation during annealing we utilize Rutherford backscattering (RBS) analysis to examine the various elemental composition throughout the entire sample thickness.

RBS spectra were obtained using 2000keV helium ions with a spot size of approximately 1mm. All data was collected at Uppsala University RBS facilities. Figures 26 and 27 show the resultant RBS spectra for both 10 and 100nm SiC samples vacuum annealed at 750 and 775°C.
Figure 26: 10nm SiC RBS spectra

Figure 27: 100nm SiC RBS spectra
The blue plots in Figures 26 and 27 show the un-annealed RBS spectra in which, clear step edges for Ni and Si can be clearly identified. The SiC step can only be seen in the 100nm sample and not the 10nm, given that carbon is a lighter element and very little is present in the 10nm sample we can surmise that our particular experimental setup was not able to clearly distinguish the SiC edge in the thinner film.

Upon annealing we see that for both samples that counts of nickel step decrease by half probably due in to migrating silicon making its way to the nickel surface. Having silicides on the surface would coincide with Raman spectra that reviled that at least some NiSi exists on the nickel surface. With each annealed sample we can see that silicon step is shifted roughly by 100 channels indicating mix of the SiC and nickel films. Throughout the channels between the silicon – nickel step we see varying intensities that indicate that there are various species of silicide throughout the nickel region. Given the amplitudes of the channels in this region we suspect that multiple species of nickel silicide exist in this region, namely NiSi and NiSi₂.

Notably it can be seen in the 100nm plot that there is no SiC step edge in the annealed samples, this leads us to believe that all of SiC is consumed in during the annealing process. With a similar experimental Ni/SiC system it was also found that all the SiC decomposed during annealing [31].

6.2.4 Ni/SiC/Si Rapid Thermal Anneal Procedure
1. All samples were annealed at various temperatures for 30s under an ambient nitrogen atmosphere, with an addition long anneal of 5min. The experimental matrix can be seen in Table 3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>SiC thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>30</td>
<td>10/100</td>
</tr>
<tr>
<td>800</td>
<td>30</td>
<td>10/100</td>
</tr>
<tr>
<td>900</td>
<td>30</td>
<td>10/100</td>
</tr>
<tr>
<td>1100</td>
<td>30</td>
<td>10/100</td>
</tr>
<tr>
<td>1100</td>
<td>350</td>
<td>100</td>
</tr>
</tbody>
</table>

2. Potential graphene growth was characterized via Raman spectroscopy with a 514nm 10mW excitation source, with acquisition times of 8s.
6.2.5 Ni/SiC/Si Rapid Thermal Anneal Results

The very first observation we make on these samples is their very discoloured and charred appearance, not seen in any of the vacuum anneals carried out previously.

From Figure 28 it is evident that there is no sign of graphite or graphene growth, as no G or 2D peaks can be found. All the samples annealed show NiSi and NiSi$_2$ peaks that correspond to previous Raman silicide studies performed by Zhao [45]. The Raman intensity of both species of silicide are seen to increase with annealing temperature, with negligible differences seen between the two SiC thicknesses. According to Zhao, NiSi$_2$ will exhibit a smaller Raman signature than NiSi, this is illustrated in Figure 28 where only a small NiSi$_2$ peaks can be seen at 300cm$^{-1}$.

Interestingly, the silicon peak at 520cm$^{-1}$ can only be seen at annealing temperatures of 700°C and the long 350s anneal at 1100°C, at present there is no explanation as to this phenomena. Two other peculiarities seen in Figure 26 are large peaks at 1000cm$^{-1}$ and 2800cm$^{-1}$ in (1100°C-3500s) and (700°C 100nm) SiC samples. These anomalies could be due to heavy charring defects mentioned before.
6.3 Cu/SiC/Si
At present, the use of catalytic copper films produce the largest most coherent graphene crystals due to the self-limiting nature of the catalytic reaction. As graphene growth is surface based surface growth CVD methods are primarily used when synthesising graphene on copper, in this study we examine any possible graphitic growth that may occur at the SiC/Cu interface.

6.3.1 Cu/SiC/Si Vacuum Anneal Procedure
1. Like previous experiments, both 10nm and 100nm SiC/Si chips were used as carbon sources. Copper films of various thicknesses were sputtered on the SiC/Si chips.
2. All samples were according experimental conditions listed in Table 4, the pressure for all trials was kept constant at 10⁻₇ Torr.
3. Potential graphene growth was characterized via Raman spectroscopy with a 514nm 20mW excitation source, with acquisition times of 10 seconds.

<table>
<thead>
<tr>
<th>Copper Thickness (nm)</th>
<th>SiC Thickness (nm)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10/100</td>
<td>900</td>
<td>25</td>
</tr>
<tr>
<td>200</td>
<td>10/100</td>
<td>900</td>
<td>25</td>
</tr>
<tr>
<td>500</td>
<td>10/100</td>
<td>900</td>
<td>25</td>
</tr>
</tbody>
</table>
6.3.2 Cu/SiC/Si Vacuum Anneal Results

Most of the spectra seen on Figure 29 are quite indistinguishable from their respective baselines with the exception of the Cu(10nm) / SiC(10nm) / Si plot which does seem to show D and G peaks at 1342 cm$^{-1}$ and 1600 cm$^{-1}$. With such prominent and well placed peaks an argument could be made that graphite was forming at the Cu – SiC interface, but without any trace of 2D peak we can undoubtedly say that no graphene has been synthesized. Granting that the peaks that we see in Figure 29 are true D and G peaks presents many interesting questions, mainly as to where the growth is taking place and if subsequent etching of the copper film could allow for electrical characterization. Similar synthesis research using copper along with solid source carbon has been carried out with negative results for graphene growth [46], however Raman spectra for their copper anneals were not published and a comparison of results cannot be made. As the catalytic effect of copper is known to be self-limiting, most of the present literature focuses on surface reactions involving CVD and MBE methods. Thus, there is little to no reference information to be found about an approach as presented in this thesis.
7. Summary and Conclusions
Of all the experiments carried out in this study straight SiC annealing offers the most promise as an industrial graphene solution. With this being said, the straight anneal of SiC was the most advantageous growth experiment given our annealing process was carried out at somewhat lower temperatures and pressures than indicated in supporting literature. In the context of this study the SiC thin film anneal was the simplest experiment to carry out as it didn’t not require addition metal deposition, however the characterization of subsequent results proved to be the most complex. Of all the experiments preformed the SiC anneals presented the only Raman spectra for which there would be considerable substrate effects. Given that these experiments were the simplest and therefore the first to be carried out, little was known as to the most adequate Raman acquisition routines needed to best interpret then given data. At present we cannot strictly rule out the presence of any graphitization that may have occurred given the processing conditions. With the knowledge acquired throughout the course of this study a revisiting of this investigation would be prudent; first with a detailed Raman study of the given SiC thin films followed by further analysis of annealed samples.

Overall, the Ni/SiC/Si system provided the best results in terms of graphitization. Raman spectra with nominal wavenumbers for each peak were seen in most results, and while no graphene could be seen we can make firm arguments for the presence of graphite. From the SEM micrographs seen in Figures 22-25 it can be seen that surface graphitization is extremely disordered and rough, this must be considered when quantifying data obtained from Raman characterization. In performing Raman on multiple spots on each sample, we best try to obtain a better picture of overall graphitization throughout the samples surface.

From multiple spot Raman characterization presented in Figures Figure 19 and Figure 20 we can see that the $I_D/I_G$ and $I_{2D}/I_G$ ratios are fairly random with higher, and somewhat more consistent $I_{2D}/I_G$ ratios seen in the 100nm SiC samples. The higher $I_{2D}/I_G$ ratio in the 100nm SiC could be due in part to greater graphitization caused by the larger amounts of carbon in the system. With absolutely no correlation seen with annealing time for any of the trials in this experiment we may further assume that graphite growth occurred at a time lesser then the minimum annealing time of 15min, and that subsequent data is imparted by only temperature, pressure and SiC thickness. In the motivating literature it was noted that carbon segregation from through the nickel grain boundaries occurs very quickly, that being said preliminary proof of concept experiments using anneal times of 30-60s failed to produce any graphitization thus longer anneals were preformed. Unfortunately the longer annealing times used appear to drastically overshoot the graphitization event. These long anneal times also resulted in significant nickel silicide growth of which nominal Raman peaks can be seen in all samples. Attempts to separate the graphite from the substrate were unsuccessful; this is likely due to a large part of the nickel film being converted into silicide. Given that the graphitization would appear to happen very quickly a, temporal study using fixed temperatures and may prove successful in catching the graphitization event. Parallel Ni/SiC/Si experiments carried out using the RTA furnace had less favourable outcomes then experiments carried out in vacuum. It is difficult speculate as to what exactly happened during annealing, with samples coming out of the oven appearing very charred and discoloured it may be
reasonable to assume that an unfavourable surface reaction (possibly oxidization) occurred before any graphitization occurred.

Ultimately, annealing of the Ni/SiC/Si system successfully produced amorphous graphitic films, but failed to produce graphene. For this particular system, the SiC thickness was seen to have the greatest impact on resulting graphitic films with higher \( I_{2D}/I_G \) seen with greater SiC thickness. No correlation with time was seen in any of these trials which suggest that graphitization occurred prior to experiment being ceased. Future experiments utilizing quicker annealing times along with controlled cooling rates are seen as the best option for obtaining true graphene films in subsequent follow up experiments.

Graphite was also produced in the final experiment utilizing copper thin films. From literature we know that graphene films will synthesis only at the copper interface as copper has a lower solubility for carbon. Figure 29 shows a spectrum with well defined Raman D and G Raman peaks, thus there is good evidence that graphite was grown from underneath the copper film. Only the thinnest copper film of 10nm produced discernible Raman spectra. This begs the question of the possibility of graphite existing under the thicker copper that may have possibly drown out any graphitic Raman signal, regrettfully this was not thought of at the time of the experiment. Revisiting may likely prove beneficial in finding further graphitic growth by subsequently etching away copper thin films.
10. References


