Graphene Synthesis by Chemical Vapour Deposition (CVD): A Review on Growth Mechanism and Techniques

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Abstract- This review article deals with the growth mechanism and techniques of graphene synthesis using chemical vapour deposition (CVD). Different aspects of graphene synthesis and growth mechanism are reviewed based on current researches in the field of catalysis. Materials aspects such as the roles of hydrocarbon, gas, solid and liquid are discussed. Effect of experimental parameters on growth-control such as temperature, vapour pressure, gas flow rate, annealing time and scalability on graphene diameter and distribution are explained. The advantages of growing graphene directly on dielectric substrates were also discussed. Finally, recommendation on where the future holds were postulated.

Keywords: Chemical vapour deposition (CVD), graphene, growth mechanism, substrates and synthesis.

1.0 INTRODUCTION

The amount of literature on graphene will continue to be on the rise due to its immense importance in today’s technological advanced world. This makes it a real struggle to keep up with the developments. Newcomers are left without a broad perspective and are largely unaware of previous arguments and solved problems, whereas the scientific community’s notables already show signs of forgetting their earlier papers (Geim, 2009). To alleviate this short coming, many reviews and books on graphene are in the making.

Neto et al. (2009), extensively enumerated and discussed broadly the electronic properties of graphene. Due to huge amount of literature available, graphene research has now reached the stage where a strategic update is needed to cover the latest progress, emerging trends and opening opportunities. This paper is intended to serve this purpose without repeating, whenever possible, the information available in the earlier reviews.

Graphene is a single atomic plane of graphite, isolated from its environment and considered free-standing. The basic reason for this is that nature strictly forbids the growth of low-dimensional (D) crystals (Geim, 2009; Neto et al., 2009). Crystal growth requires high temperatures thus, thermal fluctuations that are detrimental for the stability of macroscopic 1D and 2D objects are eminent. Flat molecules and nm-sized crystallites can be grown, but as their lateral size increases, the phonon density integrated over the 3D thermal vibrations rapidly grows, diverging on a macroscopic scale. However, 2D crystals can be grown artificially despite its difficulty naturally. A monolayer can be grown inside or on top of another crystal and then remove the bulk at sufficiently low temperature such that thermal fluctuations are unable to break atomic bonds even in macroscopic 2D crystals and mold them into 3D shapes (Geim, 2009).

To create 2D crystals, mechanically splitting of a strong layered materials such as graphite into individual atomic planes is needed (Fig. 1A). This is how graphene was first isolated and studied. Although delicate and time consuming, the handcraft provides crystals of high structural and electronic quality, which can currently reach sizes of a couple of mm.

Instead of cleaving graphite manually, it is also possible to automate the process by employing, for example, ultrasonic cleavage (Hernandez et al., 2008). This leads to stable suspensions of submicron graphene crystallites (Fig. 1B), which can then be used to make polycrystalline films and composite materials (Hernandez et al., 2008; Darkin et al., 2007). The ultrasonic cleavage of chemically “loosened” graphite, in which atomic planes are partially detached first by intercalation, making the sonification more efficient (Darkin et al., 2007).

An alternative route is to start with graphitic layers grown epitaxially on top of other crystals (Oshima and Nagashima, 1997) (Fig. 1C). This is the 3D growth during which epitaxial layers remain bound to the underlying substrate and the bond-breaking fluctuations suppressed. After the epitaxial structure is cooled down, one can remove the substrate by chemical etching. The isolation of epitaxial monolayers and their transfer onto weakly binding substrates may now seem obvious but it was realized only recently (Reina et al., 2007; Kim et al., 2008). When a tungsten (011) wafer is epitaxially grown on a thin Ni (111) film, it is followed by chemical vapour deposition of a carbon monolayer (the growth of graphene on Ni can be self-terminating with little lattice mismatch) (Oshima and
Nagashima, 1997; Grüneis & Vyalikh, 2008. In this manner, wafer-scale single crystals of graphene (chemically bound to Ni) have been grown. However, wafers of continuous few-layer graphene have already been grown on polycrystalline Ni films and transferred onto plastic and Si wafers (Kim et al., 2008).

These films exhibit carrier mobility $\mu$ of up to 4,000 cm$^2$/Vs close to that of cleaved graphene, even before the substrate material, growth and transfer procedures have been optimized.

The extraordinary properties and potential applications of graphene have motivated the development of large-scale, synthetic graphene grown by various methods, such as graphitization of SiC surfaces (Emteev et al., 2009) and chemical vapour deposition (CVD) on transition metals such as Ni and Cu (Li et al., 2009). In particular, it has been shown that large and predominantly monolayer graphene of excellent quality can be synthesized by CVD on polycrystalline Cu foils (Li et al., 2009). This relatively simple and low-cost method has been used to produce graphene that can reach impressive sizes and can be easily transferred to other substrates (Cao et al., 2010). However, the large-scale synthetic graphene films produced so far are typically polycrystalline (Li et al., 2010) consisting of many single-crystalline grains separated by grain boundaries. In the growth of such polycrystalline graphene, graphene grains nucleate from random and uncontrolled locations. As the growth of such grains proceeds, they coalesce and eventually form an interconnected polycrystalline film. The grain boundaries are expected to degrade the electrical and mechanical properties of the resulting films (Huang et al., 2011). It is a fact that the availability of high quality, large single-crystal Si wafers is foundational to the present Si-based electronics (Yazeyv & Louie, 2010; Wu et al., 2010). In order for graphene to become the potential in “carbon-based” electronics, it is necessary to synthesize high-quality single-crystalline graphene films, and to achieve better control over the nucleation of individual graphene grains thereby avoiding the grain boundaries in fabricated graphene devices.

2.0 CHEMICAL VAPOUR DEPOSITION (CVD)

In the recent, CVD is the most popular method of producing CNT and graphene. In this process, thermal decomposition of a hydrocarbon vapour is achieved in the presence of a metal catalyst. Hence, it is also known as thermal CVD or catalytic CVD (to distinguish it from many other kinds of CVD used for various purposes) (Kumar & Ando, 2010). By mid-twentieth century, CVD was an established method for producing carbon microfibers utilizing thermal decomposition of hydrocarbons in the presence of metal catalysts. In 1952 Radushkevich and Lukyanovich published a range of electron micrographs clearly exhibiting tubular carbon filaments of 50–100 nm diameter grown from thermal decomposition of carbon monoxide on iron catalyst at 600 °C (Mahdizadeh Moghaddam & Fanaei Sheikhhoeslami, 2015). They observed iron carbides encapsulated in the filament tips; accordingly, they proposed that, at first, carbon dissolution in iron resulted in the formation of iron carbide, and then, subsequent carbon deposition over iron carbide led to the formation of graphene layers. Tesner and Echeistova, (1952) also reported similar carbon threads on lampblack particles exposed to methane, benzene or cyclohexane atmospheres at temperatures above 977 °C.

Davis et al. (1953) published detailed electron micrographs and XRD spectra of carbon nanofibers grown from the reaction of CO and Fe$_2$O$_3$ at 450 °C in blast furnace
brickworks. They postulated that the catalyst for the reaction, either iron or iron carbide, formed on the surface of the iron oxide as a speck which in turn gave rise to a thread of carbon. They suggested that, at the time of carbon deposition, the catalyst particles were located on the growing ends of the threads. The threads were described as layered carbon, varying in thickness from 10 to 200 nm. Similar findings were reported by Hofer et al. (1955), Walker (1959), and Baird et al. (1971) as cited in (Rostrup-Nielsen, 1984). In the 1970s extensive works were carried out independently by Baker and Endo to synthesize and understand tubular nanofibers of multi-layered carbon (Oberlin et al., 1976).

2. ADVANTAGES OF CVD

Compared to arc-discharge and laser-ablation methods, CVD is a simple and economic technique for synthesizing CNTs and graphene at low temperature and ambient pressure. In crystallinity, arc-discharge and laser-grown CNTs are superior to the CVD-grown ones. However, CVD-grown MWCNTs possess inferior crystallinity, the crystallinity of SWCNTs grown by CVD is close to that grown by arc discharge or laser ablation methods. In the contrary, in yield and purity, the CVD is much better than the arc discharge and laser ablation methods. In addition, CVD is versatile in the sense that it offers large scale production of hydrocarbons in any state (solid, liquid or gas), it also enables the growth of graphene on various substrates in different forms and sizes, such as powder, thin or thick films, aligned or entangled, straight or coiled, or a desired architecture on predefined sites of a patterned substrate. It also offers better control on the growth parameters.

3.0 GRAPHENE SYNTHESIS

Mattevi et al. (2011), grew single-layer graphene films on copper foils by chemical vapour deposition (CVD) using three different growth recipes, which they referred to as growth methods A, B and C. They reported that all data were taken on graphene grown with method A, which was similar to the recipe reported in (Li et al., 2010). Methods B and C are of slight variations, whereby B uses ultrapure copper foils of 99.999% purity and C uses a rapid thermal processor furnace. In their work, graphene films were transferred onto copper foil transmission electron microscopy (TEM) grids using two different techniques. One key innovation over previous graphene TEM sample fabrication was the gentle transfer of the graphene onto a TEM grid using a minimum of polymer support and baking the samples in air to remove the polymer without liquid solvents (Regan et al., 2010). This technique produces large arrays of free-standing graphene sheets covering up to 90% of the TEM grid holes. They used aberration-corrected annular dark-field scanning transmission electron microscopy (ADF-STEM) to characterize the membranes at atomic scale. Graphene damage threshold was necessary to limit beam-induced damage when the electron beam voltage was kept below 100 keV. Along with TEM, it has been possible study the lattice and atomic defects of graphene and boron nitrene (Hashimoto et al., 2004; Meyer et al., 2008; Krivanek et al., 2004). Figure 2a shows a large array of the suspended, single-layer graphene membranes used in the study carried out by (Huang et al., 2011). Figure 2b shows an ADF-STEM image of the crystal lattice within a single graphene grain. Away from the grain boundaries, such regions are defect free.

![Fig. 2: Atomic-resolution ADF-STEM images of graphene crystals (Huang et al., 2011)](image-url)
In Figure 2c, two graphene grains meet with a relative disorientation of 27°, forming a tilt boundary. As highlighted in Figure 2d, the two crystals are stitched together by a series of pentagons, heptagons and distorted hexagons. The grain boundary is not straight, and the defects along the boundary are not periodic. Although the boundary dislocation resembles structures proposed theoretically. Additionally, shown in Figure 3(a-c) are three composite DF-TEM images of graphene grown using methods A, B and C. The slight differences between growth methods effected significant changes in the grain size, shape and crystallographic orientation of the CVD graphene. Their result showed that for method C the grains averaged 1-4 mm in diameter (Fig. 3c), this value is larger in magnitude compared to the grains grown using method A. It can be suggested that DF-TEM methods is a powerful characterization tool for understanding and controlling grain growth, which would be right for graphene study and applications. The ability to image the grain structure in graphene monolayers easily opens the door to the systematic exploration of the effects of grain structure on the physical, chemical, optical and electronic properties of graphene membranes. They concluded that graphene studies are further facilitated because grain boundaries are visible in scanning electron microscopy and atomic force microscopy (AFM) phase imaging owing to preferential decoration of the grain boundaries with surface contamination (Huang et al., 2011).

Fig. 3: Grain structure and mobility’s for three growth conditions (Huang et al., 2011).

Zhang et al. (2013) reported a low cost and scalable technique to fabricate large area films of single- to few-layer graphene and to transfer the films to nonspecific substrates via ambient pressure chemical vapour deposition (CVD) on polycrystalline Ni films. These films consist of regions of 1 to 12 graphene layers where a single- or bilayer regions can be up to 20 μm in lateral size. The films are continuous over the entire area and can be patterned lithographically or by pre-patterning the underlying Ni film. In their work, they used ambient-pressure CVD to synthesize single- to few layer graphene films on evaporated polycrystalline Ni. The use of ambient pressure and Ni films, makes the process inexpensive with high yield growth of graphene over large areas with properties closer to those found by microcleaving HOPG. Furthermore their method allows the flexibility of transferring the produced film to alternative substrates by wet-etching the Ni film. This will enable the graphene films to be utilized without further treatment and exhibiting high optical transparency and electrical conductivity. The graphene film produced in this method can be patterned by standard lithographic processes. Alternatively, the catalytic Ni surface can be pre-patterned in order to produce graphene patterns of desired geometries at controlled locations. The growth of graphene monolayers on single crystalline transition metals such as Co, Pt, Ir, Ru and Ni has been reported (Goodman and yates, 1983). The nucleation and growth of graphene usually occurs by exposure of the transition metal surface to a hydrocarbon gas under low pressure or UHV conditions.

Reina et al. (2008) reported exposing polycrystalline Ni film at 900-1000 °C to a highly diluted hydrocarbon flow under ambient pressure. This gives rise to an ultrathin graphene film (1 to 10 layers) over the Ni surface. The Ni films were e-beam evaporated onto SiO2/Si substrates and thermally annealed before the CVD synthesis. Thermal annealing before the CVD process generates a Ni film microstructure with single-crystalline grains of sizes between 1 μm to 20 μm. The surfaces of these grains have atomically flat terraces and steps, similar to the surface of single crystal substrates used for epitaxial UHV graphene growth (Sutter et al., 2008; Reina et al., 2008). Through this method, the growth of graphene on the surface of individual Ni grains is similar to the growth of graphene on the surface of a single crystal substrate. The growth of graphene can be attributed to the precipitation of graphite from carbon species within the Ni film as observed for other transition metals, such as Ru. During the exposure of the Ni surface to a H2 and CH4 gas mixture in atmospheric conditions, the Ni film and the carbon atoms provided by this CVD process form a solid solution. Since the solubility of carbon in Ni is temperature-dependent, carbon atoms precipitate as a graphene layer on the Ni surface upon cooling of the sample. Due to the
formation of grain boundaries, the top surface of the Ni film becomes discontinuous after thermal annealing. However, in their work, they found that single and a few layer graphene bridges cross these gaps, thus forming a continuous film over the entire Ni area as shown in Fig. 4b.

The ability to grow single and few-layer graphene with CVD has numerous advantages over techniques. Analogous to the case of carbon nanotube growth, this technique can potentially enable the simple growth of graphene at particular locations and with desired geometries by controlling the catalyst morphology and position (Hayamizu et al., 2008). Figure 5 shows results from the direct CVD growth of graphene pattern using a pre-patterned Ni structure (Figure 5a). After CVD, the graphene is transferred to a SiO\textsubscript{2}/Si substrate (Figure 5b). This is a significant addition to the capabilities of graphene device fabrication and integration. For example, in the case of O\textsubscript{2} plasma-sensitive substrates or substrates which cannot withstand the lithographic processes, graphene devices can be patterned through this approach.

Graphene ribbons were produced using selective graphene growth on metal-sidewall by chemical vapour deposition (An et al., 2012). Their process started by depositing a 300 nm-thick SiO\textsubscript{2} on a Si substrate. Then a 300 nm-Ni and a 300 nm-SiO\textsubscript{2} were sequentially deposited by sputtering and CVD, respectively. The Ni film acts as a catalyst for graphene growth, and the top 300 nm-SiO\textsubscript{2} acts as a blocking layer to protect graphene synthesis on the top surface of Ni catalyst. A photoresist (PR) was spin-coated and patterned by photo lithography as shown in Figure 6a. The exposed SiO\textsubscript{2}/Ni stack layer was dry-etched by reactive ion etcher (RIE) or wet-etched by buffered oxide etchant (BOE) and nitric acid-based etchant for SiO\textsubscript{2} and Ni, respectively. Next, the PR was removed by acetone. This will allow, only sidewall of the Ni catalyst been exposed, upon which graphene film would be selectively grown by CVD as shown in Figure 6b. Samples (1-2 cm\textsuperscript{2} in size) were loaded into a CVD quartz reactor with a halogen lamp heating system.
The chamber was vacuumed under 1 m Torr by a mechanical pump, and purged at argon (Ar) ambient (99.99% purity). Then hydrogen (H$_2$, 99.99% purity) gas was allowed to flow into a reactor to prevent the oxidation of catalyst Ni metal while increasing the temperature. Samples were pre-annealed under Ar and H$_2$ gas ambient at 900-950°C, and the growth was performed at 600-900°C as shown in Figure 6c. After synthesis, shown in Figure 6d is a PMMA coated and etched back carefully to expose only the top oxide upon Ni layer. By doing this, the top SiO$_2$ layer could be selectively etched without damaging the bottom SiO$_2$ on Si substrate.

![Fig. 6: Three dimensional schematic process flow for synthesizing graphene ribbons on the sidewall of Ni catalyst (An et al., 2012)](image_url)

The top oxide and the PMMA were removed sequentially by RIE and acetone, respectively as shown in Figure 6e. Next, spin on glass (SOG) film as a supporting film for the extremely thin vertical graphene film was coated and etched back, (Figure 6f) carefully to expose only the top surface of Ni layer. After the coat and etch-back process, the SOG film surrounds the Ni catalyst. Graphene channel was patterned by lithograph and then the exposed Ni was removed using FeCl$_3$-based Ni etchant, resulting in two parallel graphene ribbons shown in Figure 6g. In order to see top gate modulation behaviour of the resultant graphene ribbons, SOG as a top gate dielectric was coated and Al as a top metal electrode was patterned (Figure 6h). They concluded that compared to the conventional CVD process for graphene ribbon transistors their method do not need the graphene transfer process since the sidewall-graphene is used.

4.0 EFFECT OF EXPERIMENTAL PARAMETERS

Graphene synthesis involves many parameters such as hydrocarbon, catalyst, temperature, pressure, gas-flow rate, deposition time, reactor geometry. However, to keep our discussion compact, this review will try to delve into the fundamental factors that could have great influence on high quality synthesis of monolayer, bilayer or few-layer graphene films. The correct synthesis parameters should be selected to achieve high quality graphene.

4.1 Types of Precursor Materials

Gas, liquid and solid precursors were used for graphene synthesis using mainly hydrocarbons and polymers (C and H based compounds). The critical parameter in graphene synthesis is the energy needed to perform the whole process depending on the type of precursor (Zhang et al., 2011). One way to reduce the energy demand is by using low C-H bond energy precursors. In low C-H bond precursors the process is highly endothermic in gas phase however on the metal surfaces, there is a significant reduction of the energy required, owing to the presence of strong M–CH$_x$-1 and M–H interactions (Chen et al., 2013).

Zhang et al. (2011) reported that the dehydrogenation in gas phase can be performed by high temperature or plasma assisted processes. Whereas when the species are adsorbed the decomposition is a catalytic process. In typical reactions in horizontal CVD quartz hot-reactors gas phase decomposition is always performed before adsorption. Sometime as in the case of CH$_4$, graphene synthesis, the effect of the thermal heating of the gas is negligible, so thermo-catalytic decomposition on metal surface is crucial. Therefore, there are two possible routes in synthesis: gas pre-activation-dissociation before reaching the substrate or only thermo-catalytic decomposition.
4.1.1 Hydrocarbons (Gases)
Methane (CH₄), ethylene (CH₂=CH₂) and acetylene (C₂H₂) being the dehydrogenation energies having values of 410 kJ/mol = 98.4 Kcal/mol, 443 kJ/mol = 106.32 Kcal/mol and 506 kJ/mol = 121.44 Kcal/mol for the methane, ethylene and acetylene respectively were used as typical gaseous carbon precursors (Lou, 2007). Methane is the most used and highly stable saturated molecule so the dehydrogenation in the gas phase of CH₄ to CH₂⁺ is highly endothermic. On the metal surfaces, there is a significant reduction in these values and theoretical calculations explained that over some transition metals even exothermic dehydrogenation processes could take place.

Hydrogen (H₂), were widely used in the cleaning and crystallization of the metallic substrates (annealing step), via oxygen reduction. Molecular Hydrogen (H₂), used as diluent gas of the carbon precursor (typically CH₄, various ratios of CH₄:H₂ had a significant role in graphene CVD growth (Vlassiouk et al., 2011). Hydrogen interaction with substrate could affect the subsequent CH₄ chemisorption kinetics (Losurdo et al., 2011). The role of hydrogen in determining the graphene growth kinetics and in limiting the graphene thickness comes from numerous observations such as that when fraction of CH₄ with respect to H₂ is increased, the graphene growth on Cu is no longer self-limiting (Gao et al., 2010). However, a contrary results had been obtained depending on the synthesis and conditions used (Li et al., 2011).

4.1.2 Liquids
Zhang et al. (2012) reported the use of toluene and LPCVD to grow continuous monolayer graphene films at 500°C to 600°C on flat electro-polished Cu foils (after 980°C annealing). In this work, they considered toluene because it is less toxic than benzene and others.

4.1.3 Solids
Solid precursors have been reported in many researches involving graphene synthesis (Muñoz, & Gómez-Aleixandre, 2013). In their work, it was demonstrated that large area, high quality graphene can be grown from solids. Among the solid precursors used are, polymer films, small molecules, evaporated solids. In addition, materials like food, insects, and waste were used as solid carbon source to generate high-quality monolayer graphene.

4.2 Substrates
It has been reported in different literatures the key role metal plays as catalyst in the formation of graphene layers Thus it is important to look at the critical issues concerning substrate material revolving around chemical and physical properties, crystallography and morphology of the substrates. The differences due to metallic or dielectric character of the substrates is reviewed.

Transition metals
The formation of few layered graphene resulting from industrial heterogeneous catalysis on transition metal surfaces has been known for years. The catalytic power of transition metals and some of their compounds is well known and arises from their partially filled d-orbitals or from de formation of intermediate compounds that favours the reactivity of the precursor gases (Muñoz, R., & Gómez-Aleixandre, 2013). Thus, catalysis by metals results from their ability to provide low activation energy pathways for reactions either by the facile change of oxidation states or formation of intermediate compounds. The CVD method on transition metals such as Ni, Pd, Ru, Ir and Cu foils or evaporated films, revealed that the properties of the as-grown graphene films such as quality, continuity, and layer number distribution are dependent on the catalyst used. It has been reported that the different catalytic activity and solubility leads to different growth mechanisms (Esconjauregui et al., 2009). Controlling both the methane concentration and the substrate cooling rate during growth can significantly improve the thickness uniformity (Kim et al., 2009).

Metal Alloys
Recently, more experimental efforts were made with the intention of controlling the number of layers of nucleated graphene films. Thin Ni films and fast-cooling processes were used to hinder carbon precipitation leading to the formation un-uniform graphene but poly-graphene with only monolayer regions and a wide range of thicknesses was grown by these methods. It is observed that monolayer graphene grows on the flat dimension boundaries of the metal grains while multilayer graphene (n >3) preferentially forms at the metal grain boundaries. This lack of control was the main reason to study the growth of graphene on metal alloys.

Dielectric substrates
It is of immense importance to directly grow graphene films on dielectric substrates such as BN, Si, SiO₂, Al₂O₃, GaN, MgO, Si₃N₄. Researchers have tried growing directly graphene films on these substrates [43], however, highly conductive films were very difficult to synthesize. Important applications were reported for the replacement of conventional transparent conductive films (TCFs), including InO₂:Sn (ITO), SnO₂:F (FTO) and so on for graphene films (Jeng et al., 2011). However, the highest efficiency achieved in solar cells was only 41.7% which can still not compete with conventional solar cells. Example on the synthesis of graphene over dielectric substrates are highlighted below.

Bi et al. (2012), reported the direct growth of graphene films on dielectric substrates by ambient pressure CVD (APCVD) at 1100–1200°C using a gas mixture of methane (CH₄), hydrogen (H₂) and argon (Ar). Observation showed that at 1200 °C, graphene grown on BN, Si, SiO₂ and AlN substrates, not only monolayer were produced but also few layer of graphene growth were reported. Other singular approach was the direct chemical vapour deposition of a single or few-layer graphene film on dielectric surfaces via a sacrificial copper film (Ismach et al., 2010). They grew graphene on micrometer-thick copper foils using the CVD technique, and result showed that, a significant amount of the copper evaporates and deposits at the edges of the fused silica tube used in the CVD.
5.0 GRAPHENE GROWTH CONTROL

Pressure and temperature have been mentioned as the key factors during graphene growth. Other dynamic factors, such as gas flow and gas residence time inside the processing chamber, also play important roles that will be reviewed in this section. This review will concentrate more on the pressure and temperature parameters.

5.1 Pressure

It very important that prior to synthesis, the vacuum level be minimized in order to get high purity layers. The lower the base pressure of the reactor, the higher the probability of less density of impurities and residual oxygen. Often, recipes with diluents (H₂) of the precursor gases have been proposed for reducing residual oxygen during annealing and growing stages of the synthesis. Researcher had been done at variety of pressure range, HV (High Vacuum, \(10^{-1}-10^{-6}\) Torr), LP (Low Pressure 0.1-1 Torr) and AP (Atmospheric Pressure). It was possible to grow graphene with acceptable quality in all ranges, but great differences in graphene domain size and morphology were observed. In LP CVD flower-like to six lobed structures were commonly grown. In contrast, in APCVD, hexagonal structures of graphene were synthesized (Bhaviripudi et al., 2010). Concerning the domain size, both cases offer graphene flakes near millimetre size and continuous monolayer films when using Cu catalyst. They also used total pressure on Cu. Their results revealed that even though the thermodynamics of the system remains the same, whether the process was performed at AP or LP or under UHV conditions, the kinetics of the growth phenomenon was different. To better support the discussion of the formation of multi-layer graphene at an early stage and the limited further growth of the top layers Wu et al. (2012), developed a two-step ambient pressure CVD process with similar to earlier reserachers. Their result showed that, as continuous graphene film is formed on the catalytic Cu surface, growth of extra graphene layer was inhibited because of the absence of Cu to catalytically decompose the carbon precursor gas. Another significant factor related to the experimental pressure is the sublimation-evaporation during the process due to the vapour pressure. The vapour pressure of the substrate was demonstrated to have a strong influence on the growth rate and orientation of the graphene grains (Joseph et al., 2010).

Studies on graphene growth optimization indicated that hydrocarbon pressure is one of the major factors affecting the graphene growth (Wu et al., 2010). A minimum partial pressure of hydrocarbon is required in most of the experiments for graphene to cover the Cu surface during growth. The pressure of the hydrocarbon determines the concentration of the carbon species on the Cu surface during graphene growth. It is thus suggested that a relatively low precursor with partial pressure is highly recommended in all pressure ranges. The synthesis of high quality graphene using very low total pressure with almost only carbon precursors and low quantity of H₂ was reported (Li et al., 2011). Zhang et al. (2011) investigated the correlation between the grain morphology and the total pressure and methane to hydrogen ratio in LP. With methane-to-hydrogen ratio of 1:12.5 and at different total pressures, the graphene grains changed from irregular small flakes to mostly four-lobe grains and finally to mostly six-lobe flower. When increasing the total pressure to 300 mTorr, the six-lobe graphene flowers turned to irregular shape. Interestingly, similar results were obtained when keeping the total pressure at 150 mTorr and gradually increasing the methane to hydrogen ratio from 1:30 to 1:2. All these observations indicated that increasing the total pressure of the CVD system had a similar effect on the morphology of graphene grains as increasing the methane-to-hydrogen ratio. Gao et al. (2012), observed that the graphene edges become regular and straighter, because edges with a low stability were selectively etched away by an active atomic H when the CH₄/H₂ ratio is low. Wang et al. (2012) in their work, observed that when only the CH₄ supply was cut off and the sample was cooled, after the growth stage, in a high concentration H₂ atmosphere, the graphene domains would appear to be etched into rectangular openings. In the work carried out by Zhang et al. (2011), they proposed that low concentration H₂ could reduce the etch rate considerably and result in no significant etching damage.

5.2 Temperature

The temperature gradient inside the reactor is one factor that can readily cause inhomogeneous growth of graphene during synthesis. In catalysis, it reported that enhanced dissociation of carbon precursors at high temperature and also surface smoothing via metal grain growth is the basic step in graphene synthesis over metal foils (Bae et al., 2010). Depending on the catalytic activity of the metal, the process temperatures can vary between 800-1100ºC. Ni is intensively studied because the phase diagram of Ni and C reveals that at high temperature solid solution is formed (above 800ºC) and that the metastable formation of Ni₃C phase promotes the precipitation of carbon out of Ni. Co and Fe show also carbon solubility at 850ºC-1000ºC although graphite precipitation from Fe can be obtained only under very specific conditions. It was demonstrated that high T (>1035 °C) yields a low density of graphene nuclei when growing leading to large domain size. In addition, at higher temperatures, more metal were observed to evaporate from surfaces which might be due to pressure conditions resulting to promotion of surface roughness.

A “hot-wall” reactor consisting a quartz tube located inside a furnace is the most used configuration in graphene synthesis so far (Park et al., 2010). In this reactor, the reaction is heterogeneous, there will be no need in heating the gas to high temperature before reaching the surface. In the cold wall technique, the gas phase reactions resulting in no particulate contamination is reduced completely. Synthesis of high quality graphene films on a Ni foils using a cold-wall reactor with a rapid thermal processing (RTP) heater was reported (Huang et al., 2012). The reported results differed from previous observations in the growth of graphene on Ni substrates by CVD due to the rapid process, opening new grounds on growth kinetics. These results suggested that two different growth mechanisms could exist in the case of Ni. To verify the direct
growth mechanism of CVD process very short growth time (10 s) and different \( \text{H}_2 \) gas flow rates during the growth stage were investigated. Result showed that defect density decreased with decreasing \( \text{H}_2 \) flow rate. It is suggested that hydrogen is not necessary to synthesize high-quality graphene by RTP direct growth mechanism using a Ni catalyst, consistent with the study of CVD growth of graphene on Cu foils (Gao et al., 2010). Geng et al. (2012) demonstrated in AP that the use of liquid Cu (T>1084ºC Cu) can be particularly effective for controlling the nucleation process in graphene CVD systems. It was observed that the grain boundaries were eliminated and the results showed the production of uniform, self-aligned, large-sized, single-domain, hexagonal graphene flakes (HGF) and continuous monolayer films. This new route involved the formation of liquid Cu phase on quartz and W substrates at growth temperature above Cu melting point. Liquid Cu surface could be involved in the translation or rotation of HGFs, while minimization of surface energy may be responsible for the alignment. The average size of individual HGFs determined by both nucleation density and growth rate was about 20–30 μm. Increasing growth temperature led to increase HGFs with average sizes of about 50 μm; and lowering \( \text{CH}_4 \) flow rate led to approximately 120 μm. The average growth rate of HGFs was estimated to be 10–50 μm/min on flat Cu/W, which is much higher than the rate of 0.1–0.2 μm/min observed for the case of HGFs grown on a Cu solid surface (Wu et al., 2011).

Low temperature processes for graphene synthesis are highly recommended for industrial applications. The need to develop methods and techniques for low temperature synthesis of high quality graphene is of immense importance as regards potential applications. The development of graphene growth on arbitrary surfaces at low temperatures (for example, by means of plasma assisted deposition) with a minimal number of defects (Novoselov et al., 2012). Different works using surface wave plasma (SWP)-CVD and remote plasma assisted CVD exhibited a capacity to synthesize graphene at lower temperatures and over substrates other than used in standard processes (Al foil) (Kim et al., 2011). In the former method no monolayer graphene was deposited but few layer, graphene was synthesized at a relatively higher temperature of 650ºC in the latter method. In another approach Kim et al. (2011), synthesized graphene films on polycrystalline nickel foil using a cold-wall type microwave MPECVD system with a heating stage. A substrate temperature of 450 to 750ºC and a total pressure of 20 Torr under various mixing ratios of \( \text{H}_2 \) and \( \text{CH}_4 \) were used. The dependence of monolayer graphene synthesis on temperature was investigated and it was clearly shown that the higher the temperature the higher quality graphene was grown so far. Teresawa et al. (2012) investigated multilayer graphene grown on Cu foils by radio frequency (RF) plasma enhanced chemical vapour deposition (PE-CVD). The growth of graphene was investigated at various conditions, changing the plasma power, gas pressures, and the substrate temperature. Result showed that at high substrate temperatures, the growth of the first layer of graphene was affected by the catalytic action of Cu, while the growth, at low temperature, of multilayer graphene was dominated mostly by radicals generated in the plasma. Significant difference was noticed for the different temperatures used in reference to the grain size, number of layers and growth rates on few layer graphene. It was also observed that the grain size of graphene decreases with the thickness. The growth rate of the subsequent layers in multilayer graphene was measured approximately five times slower than that of the first layer graphene. In thermal CVD, the difference in the growth rate between the first layer and the second layer was more than 10 (Li et al., 2009). In contrast to thermal CVD, the activated carbon fragment such as \( \text{C}_2 \) radical is formed in PE-CVD and the graphene growth occurs even at 500 ºC. Rapid synthesis radio-frequency plasma-enhanced chemical vapour deposition (RF-PECVD) revealed as a very powerful technique for the synthesis of large-scale graphene at relatively low temperature in a short time (Qi et al., 2012). Large-area single graphene of high quality was synthesized on Ni films deposited on a thermally oxidized Si, at a relatively low temperature (650°C). In the deposition process, trace amount of \( \text{CH}_4 \) was introduced into the PECVD chamber and only a short deposition time (30-60 s) was used. Single or multilayer graphene were obtained due to carbon atoms discharge which diffuse into the Ni film and then segregate out at its surface. Increasing number of graphene layers were obtained with longer deposition times using larger \( \text{CH}_4 \) flows at a cooling rate of about 10ºC/s.

5.3 Gas Flow Rate
Experiments have revealed that gas flow rate is an important factor to be considered during graphene synthesis. Report showed that the density of graphene nuclei decreased as temperature increased or as methane flow \( \text{JMe} \) (sccm) and methane partial pressure \( \text{PMMe} \) (mTorr) decreased (Li et al., 2010). It then suffice to say that, high temperature and low \( \text{JMe} \) and \( \text{PMMe} \) produces a low density of graphene nuclei and thus large domain size. Li et al. (2011), demonstrated the CVD growth of graphene single crystals up to 0.5 mm in size in quasi-static flow regime, using a copper enclosure in LP. Subsequent experiments in quasi-static flow achieved the growth of large-grain, single-crystalline six-lobe graphene...
flowers with grain size up to 100 μm (Zhang et al., 2012). Result showed that, graphene grown on a Cu foil placed outside the small vapour trapping tube did not show any “flower” shape, but continuous graphene film with slight etching. This result indicated that the vapour trapping tube changed the local environment inside the tube, especially in reducing the carbon supply and creating a quasi-static reactant gas distribution that resulted in large flower shaped graphene grains.

In line with the experiments, it is concluded that when methane flow rate decreased (from 300 sccm to 180 sccm) using Fe foils while keeping the other parameters unchanged bilayer graphene instead of multilayer was obtained (Xue et al., 2011).

5.4 Annealing Time
Researches has shown that the presence of impurities and defects on the surface of a substrate affects the nucleation behaviour considerably. Gao et al. (2012), demonstrated that the graphene nucleation rate near a step edge may be 104–107 times greater than that on a terrace due to a significantly lower nucleation barrier. As known, high temperature treatments of the substrate revealed to be helpful for the reduction of volatile impurities, contaminants, and defects on a copper surface, thus leading to the hindering of graphene nucleation. Wang et al. (2012), used 3 hours of annealing time to reduce the nucleation density on copper foils resulting in large hexagonal domains. The effects of total annealing time and temperature on the orientation and size of grains within Cu foils and Cu–Ni alloy foils were also studied (Robinson et al., 2012). The annealing process could be summarized in two stages. During the grain growth, the first step is to incorporate and order atoms from the disordered regions, resulting in some ordered regions. The second step is the growth of large grains at the expense of 24 smaller ones. As the temperature increases to a value close to the melting point of the metal, the diffusion coefficient of the atoms within the foil becomes very large, resulting in the growth of grains with macroscopic dimensions. Concerning the effect of H2 during the annealing treatment, it is suggested that H2 can eliminate certain impurities such as sulphur (S) and phosphorus (P) that may cause local variations in the carbon dissolvability in the metal substrates (Angermann & Hörz, 1993). Therefore, it seems clear that long annealing times at low pressure of reducing gases combined with high temperature, yielded low nucleation density and subsequent large domains. This route is highly desirable in high quality graphene synthesis.

5.5 Scalability
One of the advantages of graphene synthesis using the CVD is the ability to maximize the scale without losing the homogeneity of large area films (Bae et al. 2010). In their work, they used an 8-inch-wide double tubular quartz reactor which allows for a monolayer graphene film to be synthesized on a roll of copper foil with dimensions as large as 30 inches in the diagonal direction. Optical properties of different layers of these films were measured such as bilayer, tri-layer and four-layer graphene.

Roll-to-roll microwave plasma (CVD) was also used for the continuous deposition of graphene films in industrial mass production (Takatoshi et al., 2012). Few layer graphene films, which consist of flakes with a nano-meter size, were deposited onto a Cu foil, although it was expected that graphene films can be obtained on other substrates by optimizing the deposition conditions.

6.0 FUTURE DIRECTIONS
Researchers have succeeded in growing graphene from almost all metals and substrates. However, an indebt analysis into the growth of graphene on dielectric substrates have not been fully exploited. The full exploitation of graphene grown on dielectric substrates will allow researchers understand how dielectric substrates affect the physical, chemical, electronic and optical and magnetic properties of as-grown graphene.

7.0 CONCLUSION
An in-depth review on the synthesis of graphene by CVD techniques is presented, reviewing meaningful results obtained by different researchers around the world. The preparation of graphene deposits necessarily requires to follow some definite steps, such as slow enough supply of carbon species to the growing surface that allows surface diffusion of carbon atoms over the substrate. Different precursors may be used as carbon atoms source for the preparation of graphene. Among them, a mixture hydrocarbon-hydrogen and particularly methane-hydrogen is most widely used. We also showed that pressure and temperature are also decisive parameters for the successful growth of CVD few-layer graphene from hydrocarbon/hydrogen gas mixtures. Low pressure (LP) CVD regimes enhance evaporation of catalyst and etched domains, although the control of the number of layers seems to be more precise. Also highlighted is the importance of long annealing periods of metal substrate/catalyst at low pressure in a reducing gas combined with high temperature which leads to a low nucleation density and afterwards large domains, which is good for high quality graphene synthesis.

In addition, low temperature processes for graphene synthesis are being developed by using plasma assisted processes. This will be an extensive area of research in the near future with the intention to synthesize controllable number of graphene layers on arbitrary substrates with a reliable and reproducible method. However, physical, optical and electronic properties of these graphene grown films grown on dielectric substrates needs to be extensively studied.

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