Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 05, May-2019

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

Abubakar Yakubu
Department of Physics,
Kebbi University of Science and Technology,
Aliero, Nigeria

Sani Garba Danjumma
Faculty of Science, Polytechnic,
Dakingari, Nigeria

Zulkifli Abbas
Physics Department
University Putra Malaysia

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 comings, 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 μ 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.

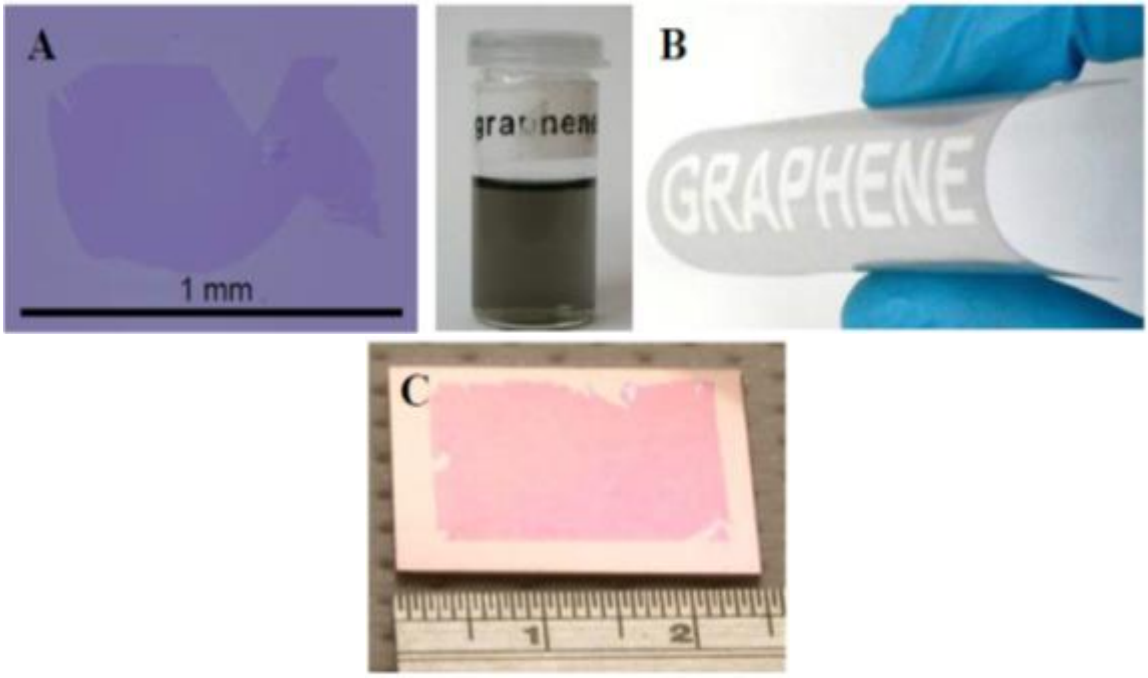

Fig. 1: (A) Large graphene crystal prepared on an oxidized Si wafer (B) Suspension of microcrystals obtained by ultrasound cleavage of graphite (C) First graphene wafers (Geim, 2009).

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 (Yazyev & 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 ^{0}C (Mahdizadeh Moghaddam & Fanaei Sheikhoeslami, 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 ^{0}C.

Davis *et al.* (1953) published detailed electron micrographs and XRD spectra of carbon nanofibers grown from the reaction of CO and Fe_2O_4 at 450 ^{0}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 ei 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.

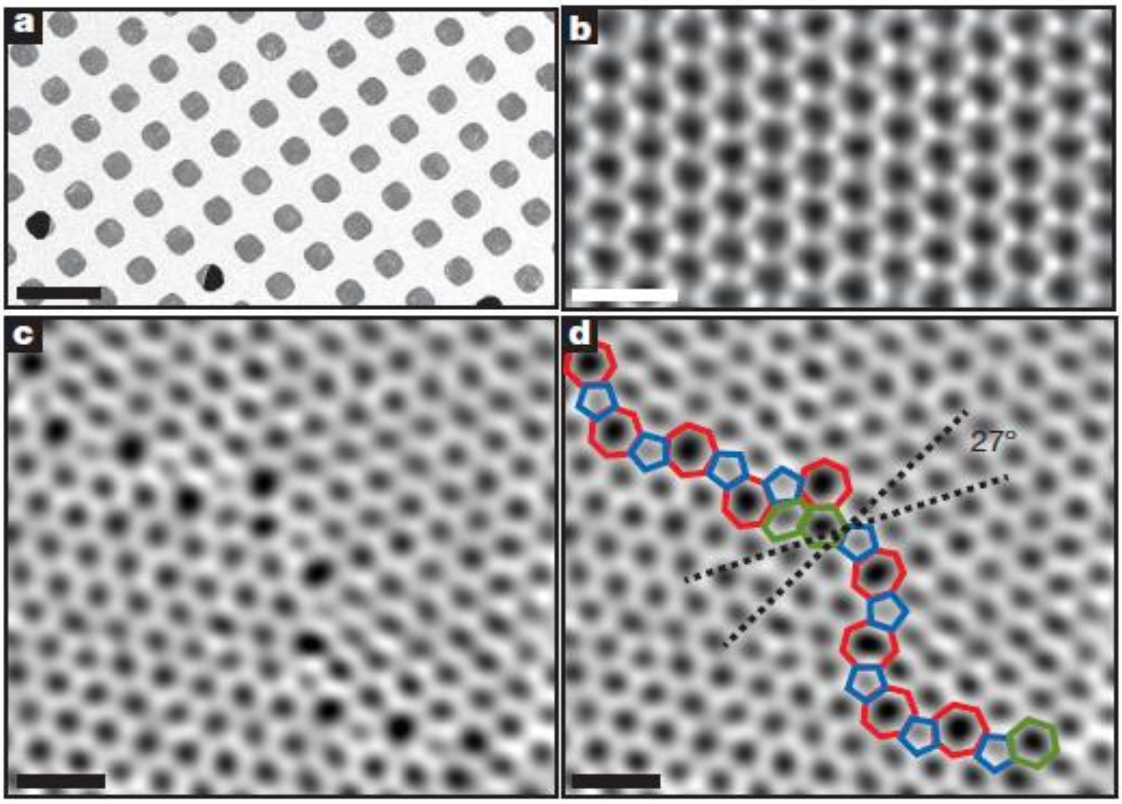

Fig. 2: Atomic-resolution ADF-STEM images of graphene crystals (Huang *et al.*, 2011)

In Figure 2c, two graphene grains meet with a relative disorientation of 27^0, 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).

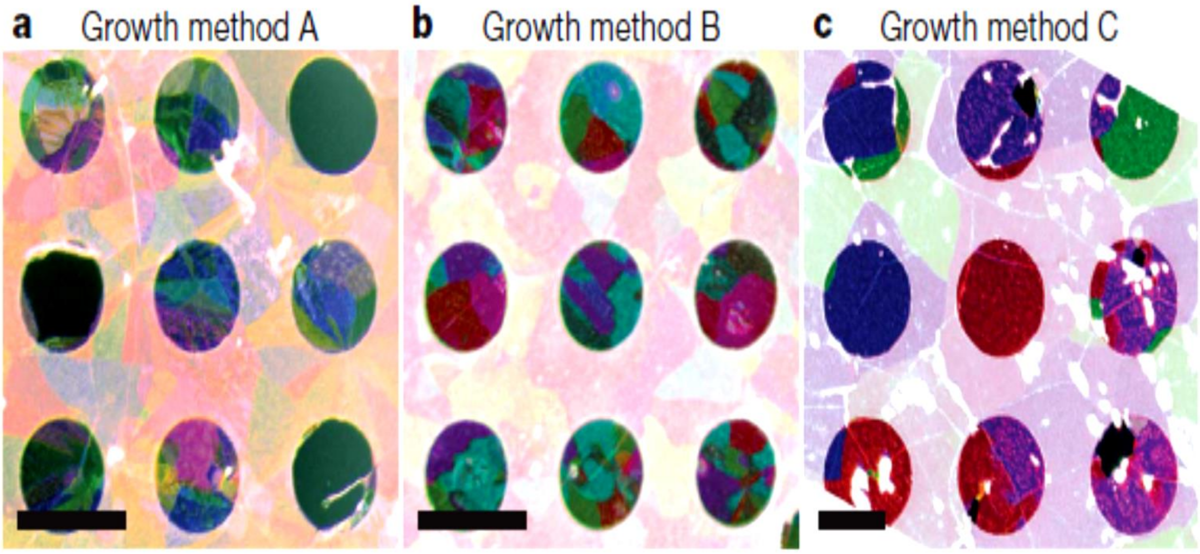

Fig. 3: Grain structure and mobility’s for three growth conditions (Huang *et al.*, 2011).

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 micro-cleaving 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 SiO_2/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), (Fig. 4a). 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 H_2 and CH_4 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.

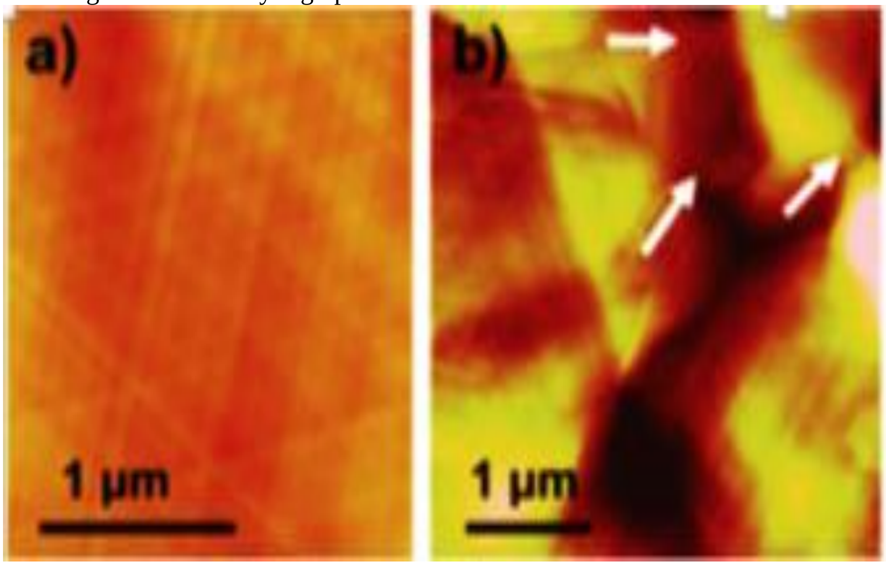

Fig. 4: Graphene films grown by CVD on Ni. (a) AFM image of the surface of a Ni grain, (b) AFM image of a graphene film on polycrystalline Ni (Reina *et al.*, 2008)

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_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_2 plasma-sensitive substrates or substrates which cannot withstand the lithographic processes, graphene devices can be patterned through this approach.

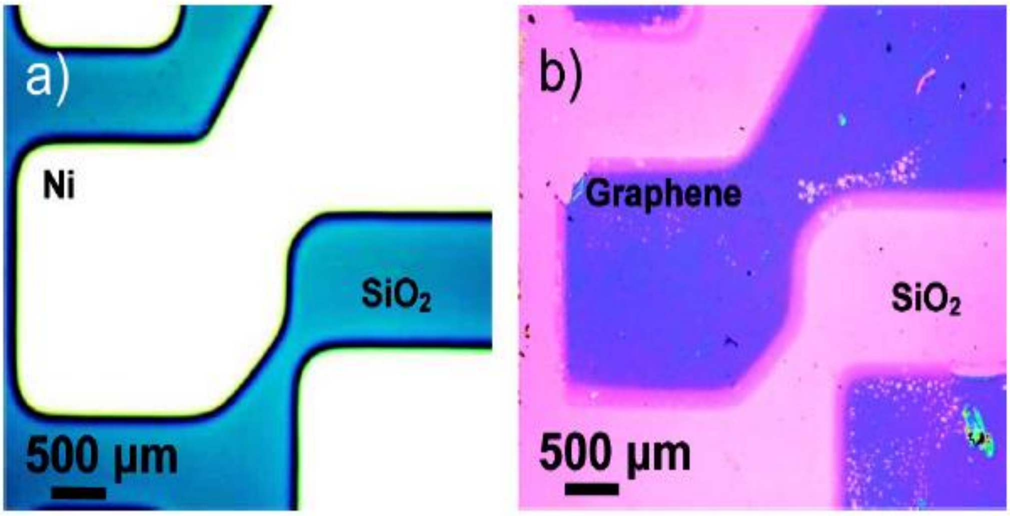

Fig. 5: Direct growth of graphene patterns from pre-patterned Ni structures (Hayamizu *et al.*, 2008)

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_2 on a Si substrate. Then a 300 nm-Ni and a 300 nm-SiO_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_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_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_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^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 ^{0}C, and the growth was performed at 600-900 ^{0}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.

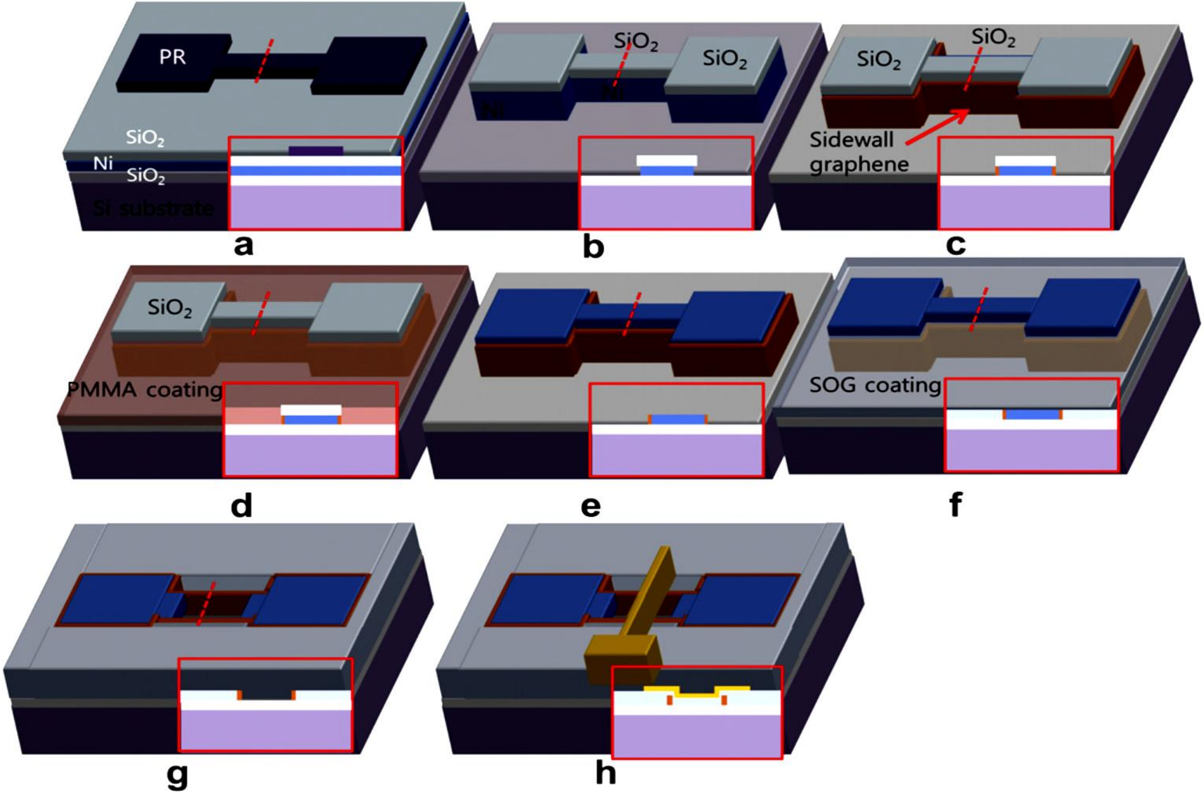

Fig. 6: Three dimensional schematic process flow for synthesizing graphene ribbons on the sidewall of Ni catalyst (An *et al.*, 2012)

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 (CH_4), ethylene (CH_2=CH_2) and acetylene (C_2H_2) 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 CH_x to CH_{x-1} 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 (H_2), were widely used in the cleaning and crystallization of the metallic substrates (annealing step), via oxygen reduction. Molecular Hydrogen (H_2), used as diluent gas of the carbon precursor (typically CH_4, various ratios of CH_4–H_2 had a significant role in graphene CVD growth Vlassiouk *et al.*, 2011). Hydrogen interaction with substrate could affect the subsequent CH_4 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 CH_4 with respect to H_2 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 500ºC to 600ºC on flat electro-polished Cu foils (after 980ºC 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, SiO_2, Al_2O_3, GaN, MgO, Si_3N_4. 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 In_2O_3:Sn (ITO), SnO_2:F (FTO) and so on for graphene films (Jerng *et al.*, 2011). However, the highest efficiency achieved in solar cells was only 4.17% 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 1100–1200ºC using a gas mixture of methane (CH_4), hydrogen (H_2) and argon (Ar). Observation showed that at 1200 ºC, graphene grown on BN, Si, SiO_2 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 has 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 (H_2) 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^{-4}-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-four 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 reseraches. 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 H_2 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 CH_4/H_2 ratio is low. Wang *et al.* (2012) in their work, observed that when only the CH_4 supply was cut off and the sample was cooled, after the growth stage, in a high concentration H_2 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 H_2 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 Ni_3C 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 ºC) 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). If 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 H_2 gas flow rates during the growth stage were investigated. Result showed that defect density decreased with decreasing 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 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 synthesis 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 MPCVD system with a heating stage. A substrate temperature of 450 to 750ºC and a total pressure of 20 Torr under various mixing ratios of H_2 and 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 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 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 CH_4 flows at a cooling rate of about 10°C/s.

SudanáKayastha, (2012), reported direct synthesis of nano-graphene films on silicon (n-Si) and glass (SiO_2) substrates by microwave assisted surface wave plasma (MW-SWP) CVD at 400-560ºC. Result showed that directly grown deposit consisted of triangular shaped nano-graphene domains with sizes of 80–100 nm in lengths that interconnect to form a continuous film. For the deposition process, a gas mixture of C_2H_2 and Ar at a pressure of 45 Pa was used. Kumar et al. (2012), reported a unique process for rapid synthesis (100 s duration) of few-layer graphene films on Cu foil by microwave plasma chemical vapour deposition (MPCVD). The process can produce films of controllable quality from amorphous to highly crystalline by adjusting plasma conditions during growth and with no supplemental substrate heating. The hydrogen plasma was also used to remove the native oxide layer enabling graphene growth on metal Cu. It was suggested that the same process could be used for rapid synthesis of primarily single-layer graphene.

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 JMe (sccm) and methane partial pressure PMe (mTorr) decreased (Li *et al.*, 2010). It then suffice to say that, high temperature and low JMe and PMe 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 H_2 during the annealing treatment, it is suggested that H_2 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.

REFERENCE

[1] An, H., Lee, W. G., & Jung, J. (2012). Synthesis of graphene ribbons using selective chemical vapor deposition. *Current Applied Physics*, *12*(4), 1113-1117.

[2] Angermann, H. H., & Hörz, G. (1993). Influence of sulfur on surface carbon monolayer formation and graphite growth on nickel. *Applied surface science*, *70*, 163-168.

[3] Bacon, R. (1960). Growth, structure, and properties of graphite whiskers. *Journal of Applied Physics*, *31*(2), 283-290.

[4] Bae, S., Kim, H., Lee, Y., Xu, X., Park, J. S., Zheng, Y., ... & Iijima, S. (2010). Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature nanotechnology*, *5*(8), 574-578.

[5] Berger, C. Song, Z. M. Li, X. B. Wu, X. S. Brown, N. Naud, C. Mayo, D. Li, T. B. Hass, J. Marchenkov, A. N. Conrad, E. H. First, P. N. de Heer, W. A. (2006). Electronic confinement and coherence in patterned epitaxial graphene. *Science, 312* (5777), 1191–1196.

[6] Bhaviripudi, S., Jia, X., Dresselhaus, M. S., & Kong, J. (2010). Role of kinetic factors in chemical vapor deposition synthesis of uniform large area graphene using copper catalyst. *Nano letters*, *10*(10), 4128-4133.

[7] Bi, H., Sun, S., Huang, F., Xie, X., & Jiang, M. (2012). Direct growth of few-layer graphene films on SiO_2 substrates and their photovoltaic applications. *Journal of Materials Chemistry*, *22*(2), 411-416.

[8] Cao, H., Yu, Q., Jauregui, L. A., Tian, J., Wu, W., Liu, Z., & Chen, Y. P. (2010). Electronic transport in chemical vapour deposited graphene synthesized on Cu: Quantum Hall effect and weak localization. *Applied Physics Letters*, *96*(12), 122106-122106.

[9] Chen, W. F., Wang, C. H., Sasaki, K., Marinkovic, N., Xu, W., Muckerman, J. T., ... & Adzic, R. R. (2013). Highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production. *Energy & Environmental Science*, *6*(3), 943-951.

[10] Darkin, D. A. Stankovich, S. Zimney, E. J. Piner, R. D Dommett, G. H. Evmenenko, G. (2007). Preparation and characterization of graphene oxide paper. *Nature*, 448 (7152), pp. 457–460

[11] Davis, W. R., Slawson, R. J., & Rigby, G. R. (1953). An unusual form of carbon.

[12] Emtsev, K. V., Bostwick, A., Horn, K., Jobst, J., Kellogg, G. L., Ley, L., & Seyller, T. (2009). Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature materials*, *8*(3), 203-207.

[13] Esconjauregui, S., Whelan, C. M., & Maex, K. (2009). The reasons why metals catalyze the nucleation and growth of carbon nanotubes and other carbon nanomorphologies. *Carbon*, *47*(3), 659-669.

[14] Gao, J., Zhao, J., & Ding, F. (2012). Transition metal surface passivation induced graphene edge reconstruction. *Journal of the American Chemical Society*, *134*(14), 6204-6209.

[15] Gao, L., Ren, W., Xu, H., Jin, L., Wang, Z., Ma, T., ..& Cheng, H. M. (2012). Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum. *Nature communications*, *3*, 699.

[16] Gao, L., Ren, W., Zhao, J., Ma, L. P., Chen, Z., & Cheng, H. M. (2010). Efficient growth of high-quality graphene films on Cu foils by ambient pressure chemical vapour deposition. *Applied Physics Letters*, *97*(18), 183109.

[17] Geim, A. K. (2009). Graphene: Status and Prospects. *Science*, *324*(5934), 1530-1534.

[18] Geng, D., Wu, B., Guo, Y., Huang, L., Xue, Y., Chen, J., ... & Liu, Y. (2012). Uniform hexagonal graphene flakes and films grown on liquid copper surface. *Proceedings of the National Academy of Sciences*, *109*(21), 7992-7996.

[19] Goodman, D. W. Yates, J. T. (1983). CO isotopic mixing measurements on nickel: Evidence for irreversibility of CO dissociation. *J. Catal. 82* (2), 255–260.

[20] Grüneis, A., & Vyalikh, D. V. (2008). Tunable hybridization between electronic states of graphene and a metal surface. *Physical Review B*, *77*(19), 193401.

[21] Hashimoto, A., Suenaga, K., Gloter, A., Urita, K., & Iijima, S. (2004). Direct evidence for atomic defects in graphene layers. *Nature*, *430*(7002), 870-873.

[22] Hayamizu, Y. Yamada, T. Mizuno, K. Davis, R. C. Futaba, D. N. Yumura, M. Hata, K. (2008). Integrated three-dimensional microelectromechanical devices from processable carbon nanotube wafers. *Nat. Nanotechnol. 3* (5), 289–294.

[23] Hernandez, Y., Nicolosi, V., Lotya, M., Blighe, F. M., Sun, Z., De, S., & Coleman, J. N. (2008). High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, *3*(9), 563-568.

[24] Huang, L., Chang, Q. H., Guo, G. L., Liu, Y., Xie, Y. Q., Wang, T., ... & Yang, H. F. (2012). Synthesis of high-quality graphene films on nickel foils by rapid thermal chemical vapor deposition. *Carbon*, *50*(2), 551-556.

[25] Huang, P. Y., Ruiz-Vargas, C. S., van der Zande, A. M., Whitney, W. S., Levendorf, M. P., Kevek, J. W., & Muller, D. A. (2011). Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature*, *469*(7330), 389-392.

[26] Ismach, A., Druzgalski, C., Penwell, S., Schwartzberg, A., Zheng, M., Javey, A., ... & Zhang, Y. (2010). Direct chemical vapor deposition of graphene on dielectric surfaces. *Nano letters*, *10*(5), 1542-1548.

[27] Jerng, S. K., Yu, D. S., Kim, Y. S., Ryou, J., Hong, S., Kim, C., ... & Chun, S. H. (2011). Nanocrystalline graphite growth on sapphire by carbon molecular beam epitaxy. *The Journal of Physical Chemistry C*, *115*(11), 4491-4494.

[28] Joseph M. Wofford, Shu Nie, Kevin F. McCarty, Norman C. Bartelt and Oscar D. Dubon Graphene Islands on Cu Foils: The Interplay between Shape, Orientation, and Defects. *Nano Lett.* 2010, 10, 4890-4896

[29] Kim, J., Ishihara, M., Koga, Y., Tsugawa, K., Hasegawa, M., & Iijima, S. (2011). Low-temperature synthesis of large-area graphene-based transparent conductive films using surface wave plasma chemical vapor deposition.*Applied physics letters*, *98*(9), 091502.

[30] Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J. M., Kim, K. S., & Hong, B. H. (2009). Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, *457*(7230), 706-710.

[31] Kim, Y., Song, W., Lee, S. Y., Jeon, C., Jung, W., Kim, M., & Park, C. Y. (2011). Low-temperature synthesis of graphene on nickel foil by microwave plasma chemical vapor deposition. *Applied physics letters*, *98*(26), 263106.

[32] Krivanek, O. L., Chisholm, M. F., Nicolosi, V., Pennycook, T. J., Corbin, G. J., Dellby, N., & Pennycook, S. J. (2010). Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy. *Nature*, *464*(7288), 571-574.

[33] Kumar, A., Voevodin, A. A., Zemlyanov, D., Zakharov, D. N., & Fisher, T. S. (2012). Rapid synthesis of few-layer graphene over Cu foil. *Carbon*, *50*(4), 1546-1553.

[34] Kumar, M., & Ando, Y. (2010). Chemical vapour deposition of carbon nanotubes: a review on growth mechanism and mass production. *Journal of nanoscience and nanotechnology*, *10*(6), 3739-3758.

[35] Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., & Ruoff, R. S. (2009). Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, *324*(5932), 1312-1314.

[36] Li, X., Cai, W., Colombo, L., & Ruoff, R. S. (2009). Evolution of graphene growth on Ni and Cu by carbon isotope labeling. *Nano letters*, *9*(12), 4268-4272.

[37] Li, X., Magnuson, C. W., Venugopal, A., An, J., Suk, J. W., Han, B., & Ruoff, R. S. (2010). Graphene films with large domain size by a two-step chemical vapour deposition process. *Nano letters*, *10*(11), 4328-4334.

[38] Li, X., Magnuson, C. W., Venugopal, A., Tromp, R. M., Hannon, J. B., Vogel, E. M., ... & Ruoff, R. S. (2011). Large-area graphene single crystals grown by low-pressure chemical vapor deposition of methane on copper. *Journal of the American Chemical Society*, *133*(9), 2816-2819.

[39] Losurdo, M., Giangregorio, M. M., Capezzuto, P., & Bruno, G. (2011). Graphene CVD growth on copper and nickel: role of hydrogen in kinetics and structure. *Physical Chemistry Chemical Physics*, *13*(46), 20836-20843.

[40] Luo, Y. R. (2007). *Comprehensive handbook of chemical bond energies*. CRC press.

[41] Madden, H. H. Kuppers, J. Ertl, G. (1973). Interaction of carbon monoxide with (110) nickel surfaces. *J. Chem. Phys. 58* (8), 3401–3410.

[42] Mattevi, C., Kim, H., & Chhowalla, M. (2011). A review of chemical vapour deposition of graphene on copper. *Journal of Materials Chemistry*, *21*(10), 3324-3334.

[43] Meyer, J. C., Kisielowski, C., Erni, R., Rossell, M. D., Crommie, M. F., & Zettl, A. (2008). Direct imaging of lattice atoms and topological defects in graphene membranes. *Nano letters*, *8*(11), 3582-3586.

[44] Muñoz, R., & Gómez-Aleixandre, C. (2013). Review of CVD synthesis of graphene. *Chemical Vapor Deposition*, *19*(10-11-12), 297-322.

[45] Neto, A. C., Guinea, F., Peres, N. M. R., Novoselov, K. S., & Geim, A. K. (2009). The electronic properties of graphene. *Reviews of modern physics*, *81*(1), 109.

[46] Novoselov, K. S., Fal, V. I., Colombo, L., Gellert, P. R., Schwab, M. G., & Kim, K. (2012). A roadmap for graphene. *Nature*, *490*(7419), 192-200.

[47] Oberlin, A., Endo, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. *Journal of Crystal Growth*, *32*(3), 335-349.

[48] Oshima, C and Nagashima, A. (1997). Ultra-thin epitaxial films of graphite and hexagonal boron nitride on solid surfaces, *J. Phys.: Condens. Matter* **9** 1 doi:10.1088/0953-8984/9/1/004

[49] Park, H. J., Meyer, J., Roth, S., & Skákalová, V. (2010). Growth and properties of few-layer graphene prepared by chemical vapor deposition. *Carbon*, *48*(4), 1088-1094.

[50] Qi, J., Zhang, L., Cao, J., Zheng, W., Wang, X., & Feng, J. (2012). Synthesis of graphene on a Ni film by radio-frequency plasma-enhanced chemical vapor deposition. *Chinese Science Bulletin*, *57*(23), 3040-3044.

[51] Regan, W., Alem, N., Alemán, B., Geng, B., Girit, Ç., Maserati, L., & Zettl, A. (2010). A direct transfer of layer-area graphene. *Applied Physics Letters*, *96*(11), 113102.

[52] Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V.,, & Kong, J. (2008). Large area, few-layer graphene films on arbitrary substrates by chemical vapour deposition. *Nano letters*, *9*(1), 30-35.

[53] Robinson, Z. R., Tyagi, P., Murray, T. M., Ventrice Jr, C. A., Chen, S., Munson, A., ... & Ruoff, R. S. (2012). Substrate grain size and orientation of Cu and Cu–Ni foils used for the growth of graphene films. *Journal of Vacuum Science & Technology A*, *30*(1), 011401.

[54] Rostrup-Nielsen, J. R. (1984). *Catalytic steam reforming* (pp. 1-117). Springer Berlin Heidelberg.

[55] Schultzenberger, P., & Schultzenberger, L. (1890). Sur quelques faits relatifs a l'histoire du carbon. *CR Acad Sci Paris*, *111*, 774.

[56] Sheikhoeslami, T. F., & Moghaddam, A. H. M. Transport Phenomena in Nano and Micro Scales.

[57] SudanáKayastha, M. (2012). Direct growth of nanographene films by surface wave plasma chemical vapor deposition and their application in photovoltaic devices. *RSC Advances*, *2*(8), 3225-3230.

[58] Sutter, E. P. S. (2006). Au-Induced Encapsulation of Ge Nanowires in Protective C Shells. *AdV. Mater. 18* (19), 2583–2588.

[59] Sutter, P. W. Flege, J. I. Sutter, E. A. (2008). Epitaxial graphene on ruthenium. *Nat. Mater. 7* (5), 406–411.

[60] Takatoshi, Y, Masatou, I., Jaeho, K., Masataka, H., Sumio, I. (2012). A roll-to-roll microwave plasma chemical vapour deposition process for the production of 294mm width graphene films at low temperature. *CARBON*, 50, 2615-2619

[61] Terasawa, T. O., & Saiki, K. (2012). Growth of graphene on Cu by plasma enhanced chemical vapor deposition. *Carbon*, *50*(3), 869-874.

[62] Vlassiouk, I., Regmi, M., Fulvio, P., Dai, S., Datskos, P., Eres, G., & Smirnov, S. (2011). Role of hydrogen in chemical vapor deposition growth of large single-crystal graphene. *Acs Nano*, *5*(7), 6069-6076.

[63] Wang, H., Wang, G., Bao, P., Yang, S., Zhu, W., Xie, X., & Zhang, W. J. (2012). Controllable synthesis of submillimeter single-crystal monolayer graphene domains on copper foils by suppressing nucleation. *Journal of the American Chemical Society*, *134*(8), 3627-3630.

[64] Wu, B., Geng, D., Guo, Y., Huang, L., Xue, Y., Zheng, J., ... & Hu, W. (2011). Equiangular Hexagon-Shape-Controlled Synthesis of Graphene on Copper Surface. *Advanced Materials*, *23*(31), 3522-3525.

[65] Wu, W., Liu, Z., Jauregui, L. A., Yu, Q., Pillai, R., Cao, H., & Pei, S. S. (2010). Wafer-scale synthesis of graphene by chemical vapour deposition and its application in hydrogen sensing. *Sensors and Actuators B: Chemical*, *150*(1), 296-300.

[66] Wu, W., Yu, Q., Peng, P., Liu, Z., Bao, J., & Pei, S. S. (2012). Control of thickness uniformity and grain size in graphene films for transparent conductive electrodes. *Nanotechnology*, *23*(3), 035603.

[67] Xue, Y., Wu, B., Guo, Y., Huang, L., Jiang, L., Chen, J., ... & Yu, G. (2011). Synthesis of large-area, few-layer graphene on iron foil by chemical vapour deposition. *Nano Research*, *4*(12), 1208-1214.

[68] Yazyev, O. V., & Louie, S. G. (2010). Electronic transport in polycrystalline graphene. *Nature materials*, *9*(10), 806-809.

[69] Zhang, B., Lee, W. H., Piner, R., Kholmanov, I., Wu, Y., Li, H., ... & Ruoff, R. S. (2012). Low-temperature chemical vapor deposition growth of graphene from toluene on electropolished copper foils. *ACS nano*, *6*(3), 2471-2476.

[70] Zhang, W., Wu, P., Li, Z., & Yang, J. (2011). First-principles thermodynamics of graphene growth on Cu surfaces. *The Journal of Physical Chemistry C*, *115*(36), 17782-17787.

[71] Zhang, Y. I., Zhang, L., & Zhou, C. (2013). Review of chemical vapor deposition of graphene and related applications. *Accounts of chemical research*, *46*(10), 2329-2339.

[72] Zhang, Y., Li, Z., Kim, P., Zhang, L., & Zhou, C. (2011). Anisotropic hydrogen etching of chemical vapour deposited graphene. *ACS nano*, *6*(1), 126-132.

[73] Zhang, Y., Zhang, L., Kim, P., Ge, M., Li, Z., & Zhou, C. (2012). Vapor trapping growth of single-crystalline graphene flowers: synthesis, morphology, and electronic properties. *Nano letters*, *12*(6), 2810-2816.