Graphene is a promising electrode material not only due to its intrinsic properties like good electrical conductivity, high mechanical strength and high chemical stability, but also because of its high theoretical surface area. In this report, the effect of CVD parameters to the growth of high quality graphene on metal substrates by using plasma enhanced chemical vapor deposition (PECVD) was extensively studied. Interestingly, synthesizing high quality graphene by PECVD technique is not only depending on the CVD parameters, but also depending on the catalysts and its plasma sources. It was found that Ni and Cu are the most favored metal catalysts for PECVD graphene growth. With high solubility of carbon (> 0.1 at. %), Ni effectively promote the growth of multilayer graphene by PECVD. However, large-area synthesis has made relatively inexpensive Cu as one of the most attractive substrates for monolayer graphene growth. Further details on the potential use of different transition metal catalysts in synthesizing graphene and consequently the synthesis and usage of graphene based devices are discussed in this report.

Graphene is a defect-free flat carbon monolayer that made up all carbon materials. Graphene was officially named after graphite with the suffix –ene which is used for fused polycyclic aromatic hydrocarbons. The first attempt to study the theoretical electronic properties and structure of graphene in 2D (known as graphene in 1994) was by Phillip Russell Wallace in 1947. It was then studied by D. F. Johnston, J. W. McClure, and M. Yamazaki in 3 dimensions around 1955–1957. Graphene however, was just an “academic materials” by then since it was not possible to exist in free state by that time. Graphene physically existed in free state in 2004 by Konstantin Novoselov and Andre Geim using a simple method known as Scotch-tape method. These two scientists had managed to produce, isolate, identify, and characterize the graphene and won a Nobel Prize in Physics in 2010. There was a speculation whether or not graphene might be used in most applications based on its excellent properties. This new discovery has created a ‘graphene gold rush’ where every effort and funding are tunnels into graphene’s experiments to understand more and prove the ability of this material.

The basic structure of carbonaceous materials consists of one carbon atom with 4 valence electrons. The unique properties of graphene come from the arrangement of 3 electrons in each carbon atom in a π-bonds with the nearest neighbor of another carbon atom by chemical bonding, and hence leaving one of electron that delocalized on the graphene layer (π orbital). Due to the existence of π orbital in graphene, it tends to agglomerate or restacking, and hence will reduce the surface area of graphene. Nonetheless, the 4th electron of carbon that delocalized around the graphene layer has its own advantage. The massless electron that travels along the sheet of graphene helps to conduct electricity with high mobility and hence its application is widely studied in electrochemical energy storage devices (EESDs).

2D structure of graphene has been massively studied since it was first explored and tests. Monolayer and bilayer graphene are readily open to dope with other foreign materials which makes it easily activated (extrinsic graphene). In contrast, synthesized graphene sheets normally altered by reduction or addition of carbon atoms in graphene’s chemical composition (intrinsic graphene).

Another structure of graphene sheet recently made was crumpled graphene which exist in 3D structure (Table I). It is different from other 3D structure of graphene that combined with other carbonaceous materials to form 3D structure as it is graphene sheets alone. Crumpled graphene is basically graphene sheet that is crumpled by means of bending and folding resulting in high pore volume and high surface area. It is also shown almost no loss of pore volume under compression. Crumpled graphene can undergo lots of processes such as solvent dispersion and molding, without affecting its properties. This altered graphene sheet has high potential in polymer composites field, catalytic support, and energy storage devices.

Graphene has been known to have outstanding properties since it was theoretically discovered until recently proven (Table II). It is the thinnest materials with a thickness of one carbon atom, ~ 0.35 Å. Graphene has the highest specific surface area (SSA) ever recorded among carbon materials. This high SSA gives a promising fact that graphene is able to store more energy than other carbonaceous materials. In addition, the delocalized electrons in graphene sheets that travel in high speed with intrinsic mobility of ~2–2.5 × 10^5 cm^2/vs, help to transport current efficiently. Apart from the properties mentioned in Table II, the transparency of graphene will find use in flexible electronics for example in smart watch and RFID-tags application.

Recent advancement of graphene is in biomedical application. It is amazingly biocompatible in tissue engineering due to its extraordinary property in mechanical strength. For example, it could be incorporated into the scaffold materials used for tissue engineering to improve their strength and elasticity as well as potentially to modulate their biological performance in areas such as proliferation, differentiation and cell adhesion. However, further study is critical for the particular form of graphene before it can fulfill the technical requirements of biomedical application.

It was found that the structure of graphene and the presence of defects have a great impact on its properties. An example of highly defective form of graphene with a disrupted sp^2-bonding network is graphene oxide (GO). Hence, by determining the properties of synthesized graphene with defects, it is possible to control its final properties.
graphene, the process of synthesizing graphene is important to modify its structure that favors a specific application.

**Graphene Growth**

**Graphene growth/synthesis techniques.**—There are six most common graphene production techniques that are crucial in determining the properties of the product: 1) bottom-up synthesis, 2) mechanical exfoliation, 3) synthesis on SiC, 4) reduction of graphene oxide, 5) liquid-phase exfoliation and 6) chemical vapor deposition (CVD).\(^{11-13}\) The restricted utilize of graphene on basic research and its utilization for commercial applications such as high-frequency transistors and touch screens is due to high production costs and finite scalability of methods such as mechanical exfoliation\(^{14,15}\) synthesis on SiC\(^{12,15}\) and bottom-up synthesis from organic precursors.\(^{13,15}\)

Similarly, CVD of hydrocarbons\(^{11}\) for mass-production of graphene for energy storage seems generally unsuitable due to moderate product purity, high cost and rather low yield.\(^{15}\) Production of vertical graphene nanosheet electrodes\(^{17}\) is efficient by CVD technique even though it is known that the packing density of the as-obtained graphene is very low.\(^{16}\) Other than those techniques, two techniques are widely employed for the bulk production of graphene: 1) liquid-phase exfoliation, and 2) reduction of graphene oxide.

Thermal expansion of graphite intercalation compounds or also known as ‘expandable graphite’ to obtain pristine or expanded graphene is very low.\(^{16}\) Other than those techniques, two techniques are widely employed for the bulk production of graphene: 1) liquid-phase exfoliation, and 2) reduction of graphene oxide.

**Thermal expansion of graphite intercalation compounds** or also known as ‘expandable graphite’ to obtain pristine or expanded graphene is very low.\(^{16}\) Other than those techniques, two techniques are widely employed for the bulk production of graphene: 1) liquid-phase exfoliation, and 2) reduction of graphene oxide.

Highly defective form of graphene with a disrupted sp2-bonding network which is called Graphite oxide (GO) is produced by strong oxidation of pristine graphite\(^{25,26}\) followed by stirring or ultrasound in liquid media.\(^{24}\) In order to restore the π network, GO must be reduced.\(^{25}\) The production of reduced graphene oxide (RGO) is commonly involved chemical, thermal and electrochemical processes.\(^{15,25,26}\) The production of bulk quantities with high yield and low-cost is achievable despite the low-to-medium quality of the obtained material due to the presence of both extrinsic defects; O- and H-containing groups, and intrinsic defects; edges and deformations. Alternative techniques are available for producing commercially available graphene for EESDs such as carbon nanotube unzipping\(^{27}\) or direct arc-discharge\(^{28}\) rather than using liquid-phase exfoliation and reduction of GO.

Despite the unsuitability of CVD for mass-production, it is a rather easy approach to obtain graphene with the desired features as compared to other techniques. CVD is widely known to involve the decomposition of a carbon feedstock, with the aid of heat and metal catalysts. Various metals, such as Cu, Ni, Pt, Ru, and Ir, have been proven to catalyze the growth of graphene. The number of graphene layers can be controlled by the type, thickness and crystal orientation of the catalyst used, whereas the size area of the graphene corresponds to the size of the catalyst. According to Azam et al., 2013, there are five types of CVD; 1) water-assisted CVD(WACVD), 2) alcohol catalytic CVD (ACCVD), 3) thermal CVD(TCVD), 4) floating catalyst CVD (FCCVD) and 5) plasma-enhanced CVD (PECVD).\(^{29}\) However, the most common CVD used for carbon nanotube (CNT) or graphene growth is ACCVD, TCVD and PECVD.

ACCVD is a technique that involves pyrolytic decomposition of hydrocarbon gases; commonly benzene, ethanol, acetylene, ethylene, etc., with the presence of metal catalysts at elevated temperatures in the range of 600–1,200°C.\(^{30}\) It is a simple technique due to the need of simple equipment; an oven, a tubular reactor, and a set of mass flow controllers to feed the gas.\(^{31}\) The main parameters to be carefully handle that control the graphene structures are catalyst, carbon feedstock, flow rate, time, pressure, temperature, and gas flow rate.

Plasma-enhanced CVD (PECVD) is well-known as a main technique for graphene synthesis. Even though thermal CVD (T-CVD) is a good potential, PECVD is more popular because its merits in lower substrate temperature, higher growth selectivity, and better control.
in nanostructure ordering/patterning due to the presence of energetic electrons, excited molecules and atoms, free radicals, photons, and other active species in the plasma region. Compared with T-CVD, PECVD growth is more complex.

Plasma-enhanced chemical vapor deposition.—Similar to other techniques, PECVD also uses gas sources. The main difference is that to activate the gas, thermal energy will be used, whereas the electron impact will activate molecules in the main chamber. The gas activation takes place in a non-equilibrium plasma, generally referred to as a glow discharge. To grow graphene, feedstock gas, catalyst nature, and substrate temperature are among parameters that require consideration. The schematic of PECVD set-up is shown in Figure 1.

Plasma sources.—There are several different modes of PECVD technique. Three major modes to generate the plasmas at RF domain frequency are evanescent electromagnetic (H) mode, propagating wave (W) mode, and electrostatic (E) mode. The basic principle in H-Mode inductively coupled plasma (ICP) is that the energy from RF power is coupled by an inductive circuit element. The inductive coil stimulates the magnetic field in ICP discharges. It is able to provide breakdown and sustain the inductively coupled discharge when there is high-frequency vortex electric field in the system.

A connection of one electrode to the power supply while another one electrode is grounded producing a pair of parallel plane electrodes separated by a small distance is called E-Mode capacitively coupled plasma ( CCP). Parallel-plane geometry of CCP has simpler setup and separation by a small distance is called E-Mode capacitively coupled plasma. The basic principle in E-Mode is that the energy from RF power is coupled by a circuit element. The inductive coil stimulates the electric field in CCP discharges. It is able to provide breakdown and sustain the inductively coupled discharge when there is high-frequency vortex electric field in the system.

Along cathode to anode, there are eight major regions categorized in a basic parallel-plane dc glow discharge: Aston dark space, cathode glow, cathode dark space (cathode sheath), negative glow, Faraday space, positive column, anode glow, and anode dark space. Both the growth rate and the alignment of graphene sheets are affected by the electric field and high ion flux during growth. For parallel-plane dc glow PECVD graphene growth systems, the typical voltage and power were -50 to -250 V and 3 kW, respectively, and the inter-electrode gap was usually several centimeters.

Microwave (MW) plasma is a type of electroless plasma system with electromagnetic radiation in GHz range. The interaction between the field and the plasma is quasi-optical due to the wavelength of MW is in the centimeter range, which is comparable with the discharge system size. Two different modes for MW confined by a reflective boundary are transverse electric mode (electric field perpendicular to wave travel direction) and transverse magnetic mode (magnetic field perpendicular to wave travel direction).

Various metal catalysts.—Various metals such as ruthenium (Ru), iridium (Ir), nickel (Ni), and copper (Cu) have been used as substrate materials for graphene synthesis. Other than metals, semiconductors and insulators also frequently used for the synthesis such as Si, carbon particle, crystal, GaAs, quartz, SiO2, and Al2O3 (sapphire). Comparatively, CVD is a rather easy approach to obtain graphene with the desired features. CVD is widely known to involve the decomposition of a carbon feedstock, either hydrocarbons or polymers, with the aid of heat and metal catalysts. As mentioned earlier, the number of graphene layers can be controlled by the type and thickness of the catalyst used, whereas the size area of the graphene corresponds to the size of the catalyst. Due to their non-filled d-shells, these transition metals are able to absorb and interact with the hydrocarbons that are used as the carbon sources.

Similarly, graphene growth requires the same transition metal group as CNT synthesis. It is means that any studies related on parameters for CNT growth could be useful for graphene growth. Fe, Co and Ni are the most common transition metals for the synthesis of CNTs. Different metals each have their own unique mechanism for growing graphene. The ability of the transition metal to facilitate hydrocarbon dehydrogenation and carbon segregation will affect the quality of the graphene growth. The as-grown graphene and different type of substrates would have different interaction strengths and growth mechanisms. There are 11 different transition metals that possess different interaction properties with graphene summarized by Batzill.

In order for researchers to predict the overall outcome of graphene growth, the study of the phase diagrams of the transition metals to carbon enables very useful. These metals are commonly having relatively high carbon solubility. From the phase diagram in Figure 2, the solubility of carbon can reach a maximum of 4.1 at.% and 2.7 at.% for Co and Ni, respectively. Fe is estimated to have the carbon solubility of >25 at.% Ni and Co would form metastable carbide at high temperature and the maximum is at ~1600 K. For most of the CVD process, the temperature is operated at around 1000°C. According to the phase diagrams, the solubility of carbon is ~0.6 at.% and ~9.9 at.% for Ni and Co, respectively. During the cooling stage, the carbon solubility decreases and the carbon precipitation gives the formation of graphene.

Large-area growth of graphene films using plasma-assisted CVD on Cu has been established recently. Generally, annealing temperature is ranging from 450 to 1000°C. The former study most comparable to the current work is that of Kim et al., who employed a custom-designed, multi-slot microwave antenna system to prompt plasma over a large-area surface. In producing high quality graphene on a large scale, it was proved that CVD of hydrocarbons onto relatively inexpensive polycrystalline Ni and Cu substrates is a highly promising approach. Since the wet etching of Ni and Cu is feasible and straightforward, the transfer of graphene grown on Ni and Cu onto arbitrary substrates is readily achievable.

Commonly, in previous research, multilayered graphene is found to be grown on high solubility of carbon (>0.1 at.%). Ni substrate by CVD technique. Even though Reina et al. recently did show that their Raman spectrum was similar to that of ideal single layer graphene (SLG) and provided the fact that SLG could be synthesized on Ni substrates, the thickness control of large area uniform graphene growth still remains a challenge. The growth of multilayer graphene on Ni has been ascribed to the growth mechanism, which is suggested to proceed via a combination of CVD surface growth at the growth temperature, and precipitation of carbon from bulk to the surface of Ni upon cooling after CVD growth. Cu is one of the most attractive substrates for graphene growth due to its inexpensive large-area synthesis. For better understanding in mechanism underlying thermal CVD of graphene on Cu, some
studies reported that before introducing hydrocarbon gas mixtures, the substrates are typically preheated to approximately 900–1000°C.95–97 As the demand for graphene is increased, CVD is a very helpful technique in rapid graphene growth at reduced substrate temperatures. As reported using various methods of plasma excitations, to activate graphene growth at reduced substrate temperatures, plasma energy is very helpful in the detachment process of hydrocarbons.79–82,98–100 These approaches resulted in producing graphene flakes and vertically standing graphene sheets.

Hydrocarbon gases can break down on transition metals that have low carbon solubility during this technique.101 A fraction of the carbon atoms in a metal at elevated temperatures (900–1100°C), are known to precipitate as a graphite film upon cooling. In producing high-quality graphene films with >95% as monolayer on Cu, this method has been practiced.102,103 The growth of graphene is limited to the surface of Cu as the growth mechanism of SLG has been attributed primarily to the low solubility of C in Cu (≈0.001 at.%). It is proved by Bae et al. that have been obtained SLG films up to 30 in grown on Cu by using low pressure CVD.102 The transferred films show a sheet resistance of ~30 Ω/sq with ~90% optical transmittance for a doped four-layer graphene film (layer-by-layer transfer) and mobilities up to 7350 cm² V⁻¹ s⁻¹ at low temperature. It is well known that CVD growth of graphene on Cu substrates is considered to be self-limiting and somewhat surface mediated, leading to the growth of predominantly single-layer films due to the extremely low carbon solubility in Cu.84,97 Certain CVD conditions such as high growth pressure and large amount of carbon precursor has been reported for such self-limiting growth to be occurred, where massive non-uniform multi-layer graphene films are grown.104,105 For a better controlling of thickness and uniformity of CVD graphene films grown on Cu, a detailed understanding of the formation of the multi-layer feature is strongly required. Consisting of numerous grain boundaries, large scale CVD graphene films produced so far are found to be polycrystalline.106,107

**Effect of substrates on graphene growth.**—There are several important parameters involved in the graphene growth by PECVD such as type of precursors, growth pressure, substrate temperatures, flow rate and gas ratio. While the overall growth reaction is a relatively simple which breaking methane gas into solid carbon (C) and hydrogen gas (H₂), much is still left to learn about the exact mechanisms of graphene growth. Multiple growth mechanism has been suggested by various authors.

**Different metal substrates.**—For differing metal substrates of varying carbon solubility, it is generally agreed there are 2 possible ways...
for graphene to grow. Through isotopic labelling of the methane, switching from $^{12}$CH$_4$ to $^{13}$CH$_4$ midway of a CVD reaction for a Cu substrate as well as a Ni substrate, different graphene growth mechanism was observed. One is the purely surface based reaction for low carbon solubility metals such as Cu. In such reaction, hydrocarbon is adsorbed onto the surface, decomposed by the Cu substrate to form the graphene. Alternatively, metals with high carbon solubility would have the carbon atoms diffuse into the substrate bulk till it reaches critical super-saturation from which it will then start to precipitate to the surface forming graphene thus creating a multi-layered graphene. These two mechanisms are illustrated in the following Figure 3. High carbon solubility metals such as Ni would diffuse both $^{12}$C and $^{13}$C into the metal bulk before forming graphene that is comprised of randomly mixed with $^{12}$C and $^{13}$C. This is in contrast to the low carbon solubility Cu substrate where the resulting graphene has a center comprised of Ref. $^{111}$C and outer ring of Ref. $^{110}$C proving the growth is only surface mediated.

Substrates morphology.—Besides, substrates morphology also played an important role to grow high quality graphene. Han et al. reported that the formation of nucleation sites and size of graphene domains was strongly influenced by substrates morphology. The comparison was done between polished and unpolished Cu and it was found that a lot of nucleation sites existed after 3 s on the unpolished Cu with average domain size of about 30 μm$^2$ compared to the polished Cu with average domain size of about 140 μm$^2$. These nucleation sites coalesced together to form a continuous monolayer graphene with increasing growth time. After 5 and 10 min growth, there was formation of stripe-like multilayer graphene islands on the unpolished sample and no transformation of the monolayer graphene was found on the polished sample. Figure 4 shows the optical micrographs of the graphene grown on the polished and unpolished Cu.

Substrate surface orientation.—Surface orientation also affects the quality of the graphene produced. Ishihara et al. had grown graphene on a polycrystalline Cu with several surface orientations of (111), (101) and (100) as verified by electron backscattered diffraction (EBSD) shown in Figure 5b. Analysis of I$_{2D}$/I$_G$ ratio from Raman spectra as shown in Figure 5d reveals that single-layer graphene (SLG) or few-layer graphene (FLG) were preferentially formed on the Cu(111) surface than on Cu(100) surface. Higher I$_{2D}$/I$_G$ ratio indicated smaller thickness of the graphene layer produced. There were no graphitic peaks recorded on the Cu(101) surface. Wood et al. also reported that Cu(111) surface contributed to accelerated formation of high quality, monolayer graphene growth with higher coverage compared with other orientations due to higher carbon diffusion rate. It is commonly well known that in graphene, the carbon bonds with each other to form hexagons in a honeycomb lattice with a two-atom basis. Couple this with the fact that FCC-structured metals with (111) surface termination also have the hexagonal structure for its interstitial sites which matched with the structure of the graphene may explain the preferential growth of graphene on certain orientations. The other surface terminations like (100) and (110) tend to have square-shaped and rectangular-shaped of the interstitial sites. This observation further strengthens the fact that the most suitable substrates to grow

![Figure 3. Schematic diagram of the possible distribution of C isotopes in graphene films based on different growth mechanisms for sequential input of C isotopes. (a) Surface segregation and/or precipitation. (b) Surface adsorption](Reproduced with permission from Ref. 108).

![Figure 4. Optical micrographs of the graphene grown on (a) polished Cu and (b) unpolished Cu (Reproduced with permission from Ref. 109).](207.241.231.81)
high quality graphene is FCC-structured metals with the (111) surface orientation.

**Underlying mechanism of graphene growth.**—Current CVD mostly produces graphene with a polycrystalline structure. This type of graphene contains many defects causing a decrement of several of its superlative characteristics. In crystal materials, polycrystalline can be defined as the combination of single-crystalline domains that consist of different lattice orientations with grain boundaries separating each one of them. Mattevi, Kim and Chhowalla had illustrated the growth process of typical CVD done on copper substrate as in Figure 6. First, the oxide layer on the Cu substrate was reduced in hydrogen atmosphere which also leads to annealing process of Cu. At this stage, crystal grain growth and removal of crystal defects occurs. Then, there will be formation of many nucleation sites on the Cu surface and all of these sites will grow until all of them merge together and form a graphene film on the surface of the metals. Each nucleation site will form a domain with different lattice orientation and these differences will lead to the formation of grain boundaries on the graphene. Grain boundaries (GB) can be considered as surface defect as it will disrupt the characteristics of graphene especially the electrical and thermal conductivity. Due to that, recently much attention was given to grow graphene on single-crystal metal substrates in an attempt to reduce lattice orientation mismatch. Despite this, the formation of mismatched graphene domains still remains unresolved. Gao et al. suggested that any interaction between graphene and substrate can contribute to the formation of domains on the graphene. Graphene has a lattice parameter of 2.46 Å, while Cu(111) has 2.56 Å. Due to this small lattice different, there was formation of multiple Moiré patterns which indicate the weak interaction between graphene and Cu(111). Additionally, this also proves that grown graphene has preferred orientations which cause the formation of graphene domains. Contradictory to this, Ogawa et al. reported that Cu(111) surface had a single orientation of graphene while other Cu orientation such as (100) formed multi-domain structure with two preferential orientation. By this, the advantages of using single-crystal metal substrates still remain unclear.

Yet, a lot of researches need to be done to explore the mechanism of graphene growth on metal substrates. Clear understanding on the effect of metals surface orientation toward the formation of graphene might contribute to the formation of high quality graphene for commercial used. To produce a high quality graphene, the relationship between types of substrates, growth mechanism, surface morphology and orientation and lattice characteristic need to be fully understand.

Reaction temperature has been one of the most important factors to produce high quality graphene. In Ni substrate itself, varying temperatures would induce different graphene growth mechanisms. Ultrahigh vacuum graphene growth on single crystal nickel (111) from 10^{-5} Torr ethylene was observed by LEED and Auger electron spectroscopy for surface carbide and graphene. At temperatures from 460°C to 650°C, the mechanism of graphene growth is similar to that of other transition metal. However, at temperatures lower than 460°C, graphene formation is from the carbide surface that created upon exposure to hydrocarbons. Through DFT modelling, it was shown that graphene growth occurs by carbon segregation from bulk to the graphene-carbide interface.

Various observations on the effect of the methane partial pressure on the graphene growth was studied. In the case of Cu-Ni alloy, at lower methane partial pressure (>0.003 mbar) only the growth of monolayer graphene was possible. However, bilayer and tri-layer graphene forms when the partial pressure is increased to 0.5 mbar. Additionally, several groups have noted that the increase in partial pressure of methane also increases the nucleation density of graphene in
the substrate. In order to achieve single crystal graphene, this presents a problem as an increased nucleation causes the formation of multiple graphene domains namely polycrystalline graphene.

Therefore, in one of the attempt to selectively grow single crystal graphene, a repeated etching and re-growing CVD technique was developed,\textsuperscript{119} resulting in single crystal graphene of up to \( \sim 3 \) mm in size with electron mobility of \( 13000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) grown on Pt substrate. Through the application of hydrogen etching and regrowing cycle, unnecessary nucleation sites are removed thus reducing the nucleation sites as shown in Figure 7. The remaining nucleation site will then regrow forming large area single crystals as the cycle repeats. This was also reported to also have the additional benefit of healing any structural defect occurring during the growth.

Other concerns are on the surface modification of the substrate in which graphene is grown by themselves. Mechanically exfoliated graphene grown on hydrogen terminated (110) germanium was shown to be a monolayer single crystal graphene that is wrinkle free.\textsuperscript{120} This etch-free dry transfer was repeated for 5 times using the same substrate each time resulting in the same graphene quality showing the reusability of the H-terminated single crystal Ge/Si substrate.

The substrate single crystal (110) germanium was grown epitaxially on Si(110) wafer and then graphene was grown by low pressure CVD. H-terminated surface allows the formation of freestanding graphene islands meaning that when multiple graphene nucleation sites coalesce it happens without any grain boundary defects. Combining this with the minimal thermal expansion coefficient between the materials, wrinkle free growth is also made possible. Furthermore, the weak adhesion of graphene to the substrate allows next to no damage to the graphene and also the substrate without the need for hazardous and destructive etching process. Using the Drude model, the carrier mobility was determined to be \( 7250 \pm 1390 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) (SD) with a maximum of \( 10620 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \).

The positive effect of hydrogen has been noted by various authors such as Memon et al.\textsuperscript{121} and Vlassiouk et al.\textsuperscript{122} For a copper substrate, the removal of the oxide surface is vital for graphene growth. The presence of hydrogen during the reaction itself is reported to assist in the formation of carbon active species, CH\textsubscript{4} and also in removing unwanted C-C bonds through etching as was mentioned in the etching and regrowing method above. Vlassiouk et al.\textsuperscript{122} also notes that the resulting shapes of graphene differ greatly according to the pyrolysis pressure. Higher pressure causes the preferential growth of hexagonal graphene instead of irregular shaped ones albeit at the reduction in the maximum domain sizes grown.

The parameters mentioned above, while not comprehensive, cover the main parameters that greatly affect graphene growth and its resulting quality. It has been shown that carbon solubility of the metallic substrate results thickness of the graphene grown such as the monolayer graphene on Cu and the multilayered graphene in Ni metal. For Cu substrate, a smoother surface allows the development of bigger domains which is a priority in producing high quality domain. Furthermore, certain crystal orientation of the surface was also shown to facilitate graphene growth better than others as seen by the preferential growth of graphene on Cu(111) rather than other surface orientation. Apart from affecting the growth mechanism and decomposition of hydrocarbons, temperature control is vital for the graphene domains itself by changing the carbon solubility of the metals. In the case of methane based CVD, its partial pressure also has the ability of causing the growth of multi layered graphene when it is too high as well as the formation of multiple nucleation sites which leads to undesirable multi-domain polycrystalline graphene. This was successfully overcome by developing a grow, etch and re-grow procedure where excess nucleation sites are removed allowing only select sites to develop into bigger domains.

Finally, hydrogen gas is found to be vital in many ways. Initially, it prevents the formation of surface oxides on the metallic substrate. During the reaction, hydrogen terminated substrate surface allows a wrinkle free graphene growth without any grain boundary. The hydrogen terminated surface was also shown to facilitate the facile recovery of graphene film even by mechanical exfoliation from the substrate. All in all, understanding the growth mechanism is the key in producing large area high quality graphene especially for a single crystal graphene. It could be clearly seen that changes in each of the reaction parameters brings a big change on how the reaction mechanism itself proceeds and much is yet still to be understood.

**Applications of Graphene**

There is a research interest of graphene in various fields such as in physics, chemistry, and materials science. Graphene is a promising electrode material due to its high theoretical surface area of 2630 m\textsuperscript{2}g\textsuperscript{−1} and a very high intrinsic electrical conductivity in plane as well as high mechanical strength and chemical stability.\textsuperscript{123} There have been several reports on the graphene-based electrodes for various applications such as in solar cell,\textsuperscript{124} thermoelectric devices,\textsuperscript{125} fuel cells,\textsuperscript{126} ultraviolet light sensor,\textsuperscript{127} ultrathin organic photodetectors,\textsuperscript{128} liquid crystal device,\textsuperscript{129} and so on. In this section, only a limited number of works involving energy conversion (field effect transistors and field emission displays) and storage devices (supercapacitors and Li-ion batteries) due to graphene becoming more interesting materials to be studied for the rapid growth in commercialization.

**Electronic devices utilizing graphene synthesized from PECVD.**—Due to unique band structures, the carriers in graphene are bipolar, with electrons and holes that can be continuously tuned by a gate electrical field.\textsuperscript{130} Majority in the experimental values of the field effect mobility of graphene showed one order of magnitude higher than Si. Graphene grown on Cu films has been widely employed as a method to produce large scale transistor arrays with uniform electrical properties.\textsuperscript{131} One of the most potential applications of graphene is in field effect transistors (FETs). Basically, graphene should be in the form of quasi one dimensional structure as per requirement to be used in FET applications.\textsuperscript{132} Wei et al.\textsuperscript{133} reported the routes to modulate the electronic characteristic of graphene by nitrogen doping using critical PECVD (Figure 8). This metal free growth of high quality hexagonal nitrogen doped graphene crystals or continuous nitrogen doped graphene films with atomically clean surfaces directly on SiO\textsubscript{2}/Si, Al\textsubscript{2}O\textsubscript{3}, hexagonal boron nitride(h-BN), mica, highly oriented pyrolytic graphite substrates at 435 C. The FET mobility of nitrogen doped graphene resulted in the range of 100 to 400 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1}. This study reveal that by doping the nitrogen with graphene can effectively produce high quality of material without metal catalyst. Also, it is atomically clean surface, as well as enhances the performance of electrical device and overcome the conventional post growth process. This value may be further improved by using boron nitride, other modified surfaces,\textsuperscript{134} or metals\textsuperscript{135} to improve the carrier injection from the electrodes and to reduce amount of charged impurities trapped in the SiO\textsubscript{2} surface.

Herein, Wei et al.\textsuperscript{136} described the production of graphene crystal growth by using critical PECVD. During the growth process, H\textsubscript{2} plasma was introduced to etch the graphene from the edges.\textsuperscript{137} The results were fabricated by using hexagonal graphene crystals. The results showed a symmetrical linear output curves which display the good ohmic contacts between electrode and hexagonal graphene crystals. The value for FET mobility was in the range of
550–1600 cm$^2$ V$^{-1}$ s$^{-1}$ with the dirac point at a positive gate voltage around 10 to 30 V. Also, the comparable mobility of the hexagonal graphene crystals with graphene materials prepared by Cu-CVD and peel-off graphene materials indicates their high electrical quality for device applications with the FET mobilities were 600–1500 cm$^2$ V$^{-1}$ s$^{-1}$ and 850–2200 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The results are higher than those amorphous carbon nitrogen films (10 cm$^2$ V$^{-1}$ s$^{-1}$) produced by metal free PECVD and to those of nitrogen doped graphene (200 to 450 cm$^2$ V$^{-1}$ s$^{-1}$).

Moreover, microwave plasma CVD (MPCVD) was employed by Kim et al. to synthesize high quality monolayer graphene film.$^{138}$ Various synthesis temperatures in the range of 450 to 750 °C were used to investigate the sheet resistance. From the findings, the high transmittance of graphene films was ~89% at 450 °C with good sheet resistances of 1855 Ω/sq. Meanwhile, the best sheet resistance of graphene film was at 750 °C with sheet resistance of 590 Ω/sq. This high quality graphene production is potentially useful for manufacturing future large-area electronic devices using microwave plasma CVD at significantly lower temperatures than that in conventional thermal CVD processes.

In addition, Kim et al.$^{139}$ successfully demonstrated one-step approach to fabricate patterning graphene on SiO$_2$ substrate without using catalysts or lithography. A shadow mask composed of stainless steel is placed on the top of the SiO$_2$ (300 nm)/n-Si wafer substrate. The graphene growth was performed by using PECVD. O$_2$ gas was purged into the chamber prior the graphene growth to remove any organic material on the top surface of substrate. The flow rate and RF power employed was 40 sccm and 50 W, respectively. The CVD and RF plasma parameter during graphene growth was 10 mTorr, 2 sccm, and 20 sccm for pressure, hydrogen and methane flow rates, respectively. After finishing the graphene growth, the sample was cooled immediately by turning off the heating power with the cooling rate of 3 °C s$^{-1}$. This is a simple graphene method compared to other graphene growth processes such as graphene transfer, catalyst-etching, lithography, and metal catalysts which can be prepared in several hours by using different shapes of samples. From Hall bar measurements show lower mobility 105 cm$^2$ V$^{-1}$ s$^{-1}$ but higher compared with catalyst-free nanocrystalline graphene (1–40 cm$^2$ V$^{-1}$ s$^{-1}$) and chemically reduced graphene oxide films (~1 cm$^2$ V$^{-1}$ s$^{-1}$). Further growth optimization is required to improve the high quality of graphene production for future graphene applications.

To achieve high field enhancement, graphene sheets either as single or few layers need to be erected on the substrates.$^{132}$ Among the graphene growth techniques, PECVD showed the most promising process for field emission applications compared with other graphene growth techniques which resulted in flat graphene layers on substrates.$^{140}$ Jiang et al. have recently reported the preparation of vertically standing graphene (VSG) films on Cu foil by using a MPCVD.$^{141}$ The result obtained show an excellent properties with atomically thin edges of graphene sheets and homogenous surface morphology.$^{142}$ may be attributed by many factors such as VSG film possess plenty of atomic-thick graphene edges, and the unique formation of VSG film growth with good interfacial contact$^{145}$ as well as low resistance between films and substrates. Moreover, the as-prepared VSG films demonstrated large field-enhancement factor, low threshold field and low turn-on electric field of 1.1 × 10$^4$, 3.0 V μm$^{-1}$, and 1.3 V μm$^{-1}$, respectively.

Wu et al. successfully demonstrated a fabrication of sensitive and large scale manufacturing of selective FET biosensor by using PECVD technique to directly grown vertically-oriented graphene sheets on gold electrodes.$^{144}$ The direct growth of vertically-oriented graphene sheets on gold electrodes showed the turn-on electric field of 2.3 V mm$^{-1}$ and the threshold field of 5.2 V mm$^{-1}$ at 10 mA cm$^{-2}$ substantially lower than those of the graphene-powder coating with the turn-on electric field of 5.2 V mm$^{-1}$ and the threshold field of 9.6 V mm$^{-1}$.

Chockalingam et al.$^{145}$ demonstrated that at 1 mA cm$^{-2}$ current density the MWCNT-graphene-like nanocarbon hybrid film exhibit

Figure 8. Schematic illustrations of (a) the PECVD system used for growth of nitrogen doped graphene and (b) the growth procedure (Reproduced with permission from Ref. 133).
the minimum threshold field of 3.6 V mm\(^{-1}\) accompanied with field enhancement factor (β) is 3164 at 20 Torr. Meanwhile, the maximum current density and β at 5 Torr were found to be 0.12 mA cm\(^{-2}\) with field enhancement factor of 3356. The good adhesion between MWCNT and Ni substrate show high density of material which produces good contact and lower the electrical resistance. Alternatively, multilayer graphene (MLG) on chemically prepared silicon nanowire (SiNW) were successfully fabricated by Deng et al.\(^{146}\) using microwave PCVD. From the field emission study indicates that hybrid MLG–SiNW display remarkable and excellent properties of field emission performance compared with SiNWs. They have a low turn-on electric field of 2.42 V mm\(^{-1}\), large current density of 3.49 mA cm\(^{-2}\) and excellent field emission stability. Both materials possess remarkable properties which can contribute to an excellent field emission material in potential applications for vacuum electron sources.

To summarize this section, hexagonal graphene crystals with graphene materials prepared by Cu-CVD and peel-off graphene materials indicates their high electrical quality with the FET mobilities 600 to 1500 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 850 to 2200 cm\(^2\) V\(^{-1}\) s\(^{-1}\) compared with the amorphous carbon nitorgen films produced by metal free PECVD (10 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and nitrogen doped graphene (200 to 450 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). Also, the graphene pattern on SiO\(_2\) show lower mobility 105 (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) but higher compared with catalyst-free nanocrystalline graphene (1–40 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and chemically reduced graphene oxide films (\~{}1 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). The direct growth of vertically-oriented graphene sheets on gold electrodes showed the turn-on electric field of 2.3 V \(\mu\)m\(^{-1}\) at 10 mA cm\(^{-2}\) and the threshold field of 5.2 V \(\mu\)m\(^{-1}\) at 10 mA cm\(^{-2}\) substantially lower than those of the graphene-powder coating with the turn-on electric field of 5.2 V \(\mu\)m\(^{-1}\) and the threshold field of 9.6 V mm\(^{-1}\). These vertically-oriented graphene sheets showed higher threshold field compared with other material such as hybrid multilayer graphene–silicon nanowire (2.42 V \(\mu\)m\(^{-1}\)), MWCNT-graphene (3.6 V mm\(^{-1}\)), and vertically standing graphene (3.0 V \(\mu\)m\(^{-1}\)). The above results suggest that single-layer graphene have a great potential as high-performance field emitters.

**PECVD-graphene based supercapacitors and li-ion batteries.**— Over the past decade, there is a high demand for advanced renewable electrodes for energy-storage applications.\(^{147}\) Among various energy storage devices, supercapacitor has been extensively studied to be utilized as power sources because of high power density, long cycle life, high stability, and rapid charging/discharging rate.\(^{148–151}\) The superb characteristic are widely used in energy management, memory back-up systems, consumer electronics, and industrial power.\(^{149,152,153}\) The combination of high energy density fuel cells or batteries and high power density of supercapacitors to be used in various applications such as starters, generators, and electric braking assistance.\(^{154}\)

The 3D graphene and vertically oriented few-layer graphene (VFG) nanocup (3D VFG) was successfully demonstrated by Qi et al.\(^{155}\) using PECVD. This as-fabricated 3D VFG was grown on alveolate Pt film display large specific area and good specific capacitance for high performance supercapacitor. From electrochemical measurements indicated as-fabricated 3D VFG display higher specific capacitance of 1052 mF cm\(^{-2}\) compared to VFG-plane 337 mF cm\(^{-2}\) and excellent cycling stability of 93% capacitance retention after 3000 cycles which suggested that great opportunities in supercapacitor application (Figure 9). This excellent electrochemical performance of electrode material may be attributed from the 3D VFG-nanocup hybrid structured characteristic such as high specific surface area for ion transmission and storage.

The critical issue of contact resistance in a supercapacitor has been solved by Bo et al.\(^{156}\) by building bridges of vertical graphene (VG) nanosheets between the current collector and active materials. The “bridges” was constructed by directly grown VG nanosheets on the

Figure 9. (a) CV curves of the Pt film, VFG-nanocup and VFG-plane in 6 M KOH; (b) specific capacitances of the VFG-nanocup and VFG-plane supercapacitors; (c) charge/discharge curves of the VFG nanocup at 0.1 mA cm\(^{-2}\); (d) cyclic stability of the VFG-nanocup supercapacitor at 0.1 mA cm\(^{-2}\) over 3000 cycles (Reproduced with permission from Ref. 155).
surface of nickel foam current collector by PECVD process. The constructed VG-bridged supercapacitor show superb rate performance proved from cyclic voltammetry measurement at scan rate from 20 to 1000 mV s\(^{-1}\) and galvanostatic charge/discharge measurement at 1 to 100 A g\(^{-1}\) with capacitance retention of \(\sim 90\%\). In addition, this VG bridged graphene-film also display power capability of 112.6 kW kg\(^{-1}\) at high current density of 600 A g\(^{-1}\). By employing VG nanosheets will enhance supercapacitor performance due to their superior characteristic such as high chemical tolerance, excellent electrical conductivity, high chemical tolerance as well as unique growth orientation. Also, VG nanosheets can build up a short-cut and high speed bridge between the current collector and active materials to facilitate electron transport during the charge/discharge processes. They were expected that this work will open up new opportunities in advanced application.

Also, Bo et al. has reported on a one-step binder-free fabrication method for supercapacitor electrodes consisting of vertically-oriented graphene (VG) uniformly grown on a metallic current collector by PECVD. The as-prepared vertically-oriented graphene exhibit a gravimetric specific capacitance of 129 and 112 F g\(^{-1}\) in 6 M KOH and 1 M TEABF\(_4\)/AN, respectively. The device work properly with the specific power was as 23.1 and 16.2 kW kg\(^{-1}\) in 6 M KOH and 1 M TEABF\(_4\)/AN, respectively displaying higher energy density performance maybe due to higher potential window in 1 M TEABF\(_4\)/AN (2.2 V) than that in 6 M KOH (0.9 V). Also, the high surface area and porous structure of VG-coated e is mainly from the VG interlayer and intersheet channels which give one order of magnitude higher than that of the bare stainless steel for charge storage performance. These result exhibit higher capacitance value compared those reported for horizontally oriented graphene and traditional activated carbon or carbon powders.

Vertical graphene nanosheets (VGN) with high surface area have been described by Ghosh et al. using microwave PECVD process. From cyclic voltammetry analyses at various scan rates, the unaltered, mirror symmetric and quasi-rectangular shape for the VGN/Na\(_2\)SO\(_4\), VGN/KOH and VGN/H\(_2\)SO\(_4\) display the near ideal capacitance behavior with good electrochemical reversibility with areal specific capacitance of 44 \(\mu\)F cm\(^{-2}\), 197 \(\mu\)F cm\(^{-2}\), and 188 \(\mu\)F cm\(^{-2}\), respectively. Among them, H\(_2\)SO\(_4\) exhibited excellent specific areal capacitance (188 \(\mu\)F cm\(^{-2}\)) and good capacitance retention up to 200 cycles with the capacitance retention of 96.8% followed by VGN/Na\(_2\)SO\(_4\) (95.93%) and VGN/KOH (98.41%). This better conductivity and high surface area of the electrode material show excellent performance to be used in supercapacitor.

Besides, rechargeable lithium-ion batteries (LIBs) have been widely utilized in energy storage devices due to their excellent capacity, remarkable charging efficiency, and long cycling life. Instead of superior characteristic, synthesis and design of novel electrode materials must take a consideration for performance lithium storage behavior\(^{159,160}\) to be used as main power sources in portable electronics, renewable energy systems, and hybrid electric vehicles.\(^{161}\)

Cho et al. reported a simple fabrication process to develop a porous silicon nanofibers (Si NFs) using PECVD technique which involves three steps\(^{162}\) which are firstly, the fabrication of polymer/Si NFs by electrospinning, secondly, by reducing the as-spun fibers with Mg at 650°C and graphene coated at 400°C to get graphene-coated Si NFs to be used as anode material in LIBs. The as obtained anode show remarkable cycling performance with higher capacity retention compared with pure Si NFs. Also, the high cycling performance graphene-coated Si NFs may be attributed by the confinement of porous-thin Si NFs with graphene. The graphene would restrain the volume change of Si NFs and enhanced the electrode electrochemical performance. This graphene coated Si NFs exhibit a stable electrochemical performance up to 50 cycles (Figure 10) with specific capacity of 760 mAh g\(^{-1}\) compared with Si NFs alone.

In recent years, graphene has attracted tremendous attention which displays unique properties including thermal, electrical, and mechanical properties.\(^{163}\) These features play an important role in various applications.\(^{164}\) Realizing the shortage of graphene, 3D graphene has been explored due to easy preparation, economical devices, and high efficiency.\(^{165}\) By controlling the structures of the carbon nanowires, Kim et al. have successfully synthesized scalable highly branched graphene nanosheets (HBGNs) electrodes using low cost DC PECVD under atmospheric pressure.\(^{166}\) The as-prepared hybrid graphene–HBGN anode showed an excellent capacity of 500 mAh g\(^{-1}\) with 10% irreversible capacity loss at a current density of C/5 even after 100 cycles. Furthermore, at high rate of 4 C, the BGN electrode retained a good specific capacity of 297 mAh g\(^{-1}\) showing a promising electrochemical performance for a large scale as anode materials in LIBs. This electrode material exhibited promising electrochemical performance due to their large surface area, unique morphology, and excellent mechanical properties. Also, this unique morphology of 3D HBGNs provides efficient diffusion of Li-ions with large surface area and many voids leading to a large number of sites for Li-ion storage.

Furthermore, 3D Si thin film supported on a graphene scaffold (GSSSE) was successfully prepared by Wang et al.\(^{167}\) to be used as an anode electrode for high energy LIBs by using MPCVD. At current density of 797 mA g\(^{-1}\) the as-prepared Si anode exhibit a gravimetric capacity as high as 1560 mAh g\(^{-1}\) with capacity retention of 84% after 500 cycles. Also, after 1200 cycles, the result show the specific capacities of 1083 and 803 mA h g\(^{-1}\) at 2390 mA g\(^{-1}\) and 7170 mA g\(^{-1}\), respectively. These high specific capacities, excellent cyclability and rate performance could be due to the highly porous 3D architecture of the graphene scaffold, which possesses good electrical conductivity as well as mechanical flexibility. Also, the 3D architecture of the graphene scaffold 3D architecture of the graphene scaffold can essentially accommodate the volume changes of Si during lithium insertion and extraction processes. Meanwhile, for electrochemical performance, the excellent cyclic stability of the GSSSE may be attributed to the unique designed architecture structure: (1) large volume change of Si during charge–discharge processes may be attributed by the macro porosity of graphene scaffold. (2) large surface area of graphene scaffold provides more active sites for electrochemical reactions, which lead to faster kinetics and higher utilization of the active electrode material. (3) highly porous and excellent conductivity of graphene scaffold deliver a good pathway for lithium ions and electrons between the current collector and electrode.

For supercapacitor application, the cyclic voltammetry analyses of vertically-oriented graphene electrode in 6 M KOH and 1 M TEABF\(_4\)/AN resulted in gravimetric specific capacitance of 129 F g\(^{-1}\) and 112 F g\(^{-1}\), respectively. These excellent specific capacitance value are higher compared with 3D VFG-nanoplate (1052 mF cm\(^{-2}\) which is three times than VFG-plane 337 mF cm\(^{-2}\)) and vertical graphene nanosheets/H\(_2\)SO\(_4\) (188 \(\mu\)F cm\(^{-2}\) up to 200 cycles with the capacitance retention of 36.8%). Meanwhile, vertical graphene-bridged supercapacitor displays power capability up to 112.6 kW kg\(^{-1}\) at a high current density of 600 A g\(^{-1}\) with capacitance retention of \(\sim 90\%\) (at 100 A g\(^{-1}\)).
Table III. Summarized performance of electronic and energy storage devices based utilizing graphene grown from PECVD.

| Application                      | Materials                          | Findings                                                                 | Ref |
|----------------------------------|------------------------------------|--------------------------------------------------------------------------|-----|
| Field effect transistors         | High quality monolayer nitrogen doped graphene crystals | √ FET mobility: 100 to 400 cm² V⁻¹ s⁻¹                                  | 133 |
|                                  | Graphene crystal growth             | FET mobility of the hexagonal graphene crystals with graphene materials prepared by: | 134 |
|                                  |                                    | √ Cu-CVD: 600–1500 cm² V⁻¹ s⁻¹                                           |     |
|                                  |                                    | √ Peal-off graphene: 850–2200 cm² V⁻¹ s⁻¹                               |     |
|                                  |                                    | √ High transmittance: ~89% at 450°C, sheet resistances: 1855 Ω/sq      | 136 |
|                                  | High quality monolayer graphene    | The best sheet resistance: 590 Ω/sq at 750°C                            | 137 |
|                                  | Patterned graphene                 | √ Low FET mobility: 105 cm² V⁻¹ s⁻¹                                    |     |
|                                  | Vertically standing graphene films | √ Low turn-on electric field: 1.3 V μm⁻¹                               | 139 |
|                                  |                                    | √ Low threshold field: 3.0 V μm⁻¹                                      |     |
|                                  |                                    | √ Large field-enhancement factor: 1.1 × 10⁴                            |     |
|                                  | Vertically-oriented graphene sheets| At 10 mA cm⁻²:                                                         | 142 |
|                                  |                                    | √ Turn-on electric field: 2.3 V mm⁻¹                                   |     |
|                                  |                                    | √ Threshold field: 5.2 V mm⁻¹                                           |     |
|                                  | Multiwall carbon nanotube (MWCNT)-graphene | √ Minimum threshold field: 3.6 V mm⁻¹                                 | 143 |
|                                  |                                    | √ Field enhancement factor: 3164 at 20 Torr                             |     |
|                                  |                                    | √ Maximum threshold field: 0.12 mA cm⁻²                               |     |
|                                  |                                    | √ Field enhancement factor: 3356 at 5 Torr                             |     |
|                                  |                                    | √ Low turn-on electric field: 2.42 V μm⁻¹                              |     |
|                                  |                                    | √ Large current density: 3.49 mA cm⁻²                                  |     |
| Supercapacitors                  | Vertically oriented few-layer graphene | √ Cₜ₀: 1052 mF cm⁻² which is three times than VFG-plane (337 mF cm⁻²). | 153 |
|                                  |                                    | √ Good cycling stability: 93% capacitance retention (3,000 cycles)     |     |
|                                  | Vertical graphene nanosheets       | At scan rate from 20 to 1000 mV s⁻¹ and galvanostatic charge/discharge measurement at 1 to 100 A g⁻¹: | 154 |
|                                  |                                    | √ Power capability: 112.6 kW kg⁻¹ at a high current density of 600 A g⁻¹. |     |
|                                  |                                    | √ Capacitance retention: ~90%                                         |     |
|                                  | Vertically-oriented graphene       | In 6 M KOH;                                                           | 155 |
|                                  |                                    | √ Cₜ₀: 129 F g⁻¹                                                      |     |
|                                  |                                    | Power density: 23.1 kW kg⁻¹                                             |     |
|                                  | Vertical graphene nanosheets (VGN) | Cₜ₀: 112 F g⁻¹                                                         | 156 |
|                                  |                                    | √ Power density: 16.2 kW kg⁻¹                                           |     |
| Li-ion batteries                 | Graphene-coated Si NFs             | Capacity: 760 mAh g⁻¹ compared with Si NFs without the graphene     | 160 |
|                                  | Highly branched graphene nanosheets| √ At a current density of C/5                                       |     |
|                                  |                                    | √ Good specific capacity: 500 mAh g⁻¹                                  |     |
|                                  |                                    | √ 10% irreversible capacity loss (100 cycles)                         |     |
|                                  | 3D Si thin film supported on a graphene scaffold | √ Good specific capacity: 297 mAh g⁻¹                                 | 164 |
|                                  |                                    | √ At current density of 797 mA g⁻¹                                    |     |
|                                  |                                    | √ High gravimetric capacity: 1560 mA h g⁻¹                             |     |
|                                  |                                    | √ Capacity retention: 84% (500 cycles)                                |     |
|                                  |                                    | √ High gravimetric capacity: 1083 mA h g⁻¹ at 2390 mA g⁻¹ & 803 mA h g⁻¹ at 7170 mA g⁻¹ (1200 cycles) | 165 |

maximum specific power of vertically-oriented graphene electrode in 6 M KOH and 1 M TEABF4/AN were 23.1 and 16.2 kW kg⁻¹, respectively. The as-prepared 3D Si thin film supported on a graphene scaffold anode exhibit a gravimetric capacity as high as 1560 mA h g⁻¹ with capacity retention of 84% after 500 cycles at current density of 797 mA g⁻¹. Also, after 1200 cycles, the result shows the specific capacities of 1083 and 803 mA h g⁻¹ at 2390 mA g⁻¹ and 7170 mA g⁻¹, respectively. These result show high gravimetric capacity compared with graphene coated Si NFs (760 mA h g⁻¹, 50 cycles) and as-prepared hybrid graphene–HBGN anode with gravimetric capacity of 500 mA h g⁻¹ (100 cycles) and 297 mA h g⁻¹ at a current density of C/5 and 4 C, respectively. Table III in specific summarized the
performance of electronic and energy storage devices utilizing graphene grown from PECVD technique.

Conclusions
This review presented a systematic study on synthesizing high quality graphene by using PECVD and its specific usage in electronic and energy storage devices. Throughout comprehensive research on graphene growth technique including substrate materials or catalysts, experimental conditions, growth dynamic, etc, it has proven that there is a very promising future in science and application of this unique carbonaceous material. Graphene growth by PECVD is a potential method to produce high quality of graphene with low synthesis temperature. Among various metal catalysts, Cu and Ni are the most promising candidates for PECVD graphene growth. It is the structural quality of their films that is crucial for the controlled synthesis of monolayer or bilayer graphene films. Growth mechanism and decomposition of hydrocarbons in producing high quality graphene can be controlled by altering the CVD parameter. For example, partial pressure of hydrocarbon and CVD temperature could be vital for carbon solubility of the metals as well as to determine the coverage of graphene on metal surface.

In addition, the graphene synthesized from PECVD for electronics and energy storage devices have been analyzed. A green and facile method is highly required to synthesize graphene based electronics and energy storage devices with designed compositions, porosity, pore sizes, and shapes to enhance the performance of material. By employing various plasma sources in PECVD such de-charges, microwave, and radio frequency, PECVD system proved to have the most reliable ability to produce high quality graphene and better performance in desired applications. Further understanding of development and design a novel graphene electrode material as well as controlling the PECVD parameters for large production of high quality graphene is another interesting and demanding matter. This observation provides useful insights in understanding the growth process of CVD graphene and its optimization to further explore the ability of the grown graphene.

Acknowledgments
The authors are grateful to the Ministry of Higher Education, Malaysia, for the research financial support under the Long Term Research grant Scheme (LRGS) Nanomite Project. And special thanks to Zamalah Scheme of UTeM for the PhD financial support for NN Zulkapl and RNAR Seman.

References
1. H. P. Boehm, R. Setton, and E. Stumpf, Pure Appl. Chem., 66, 1893 (1994).
2. H. Raza, Nanosci. Technol., 1, (2012).
3. R. Raccichini, A. Varzi, A. Passerini, and B. Scrosati, Nat. Mater., 14, 271 (2014).
4. P. Allpress Release, “The New CVD Parameter Of 2010” (2010).
5. L. Jiang and Z. Fan, Nanoscale, 6, 1922 (2014).
6. H. Ramachandran, Inter. J. Adv. Eng. Tech., 1, 12573 (2012).
7. K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, and G. Kim, Nature, 490, 192 (2012).
8. Z. Yanwu, S. Murali, C. Weiwei, L. Xuesong, J. W. Suk, J. R. Potts, and R. S. Ruoff, Adv. Mater., 22, 5226 (2010).
9. M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science, 287, 637 (2000).
10. M. A. Azam, N. H. Jantan, N. Dorah, R. N. A. R. Seman, N. S. A. Manaf, J. Appl. Phys., 103, 094302 (2008).
11. K. Teii, S. Shimada, M. Nakashima, and A. T. H. Chuang, J. Phys. D: Appl. Phys., 47, 094302 (2009).
12. Z. Bo, Y. Yang, J. Chen, K. Yu, J. Song, and K. Cen, J. Phys. Chem. Lett., 10, 490 (2010).
13. S. K. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, and B. H. Hong, Nature, 457, 706 (2009).
14. A. R. Zie, X. Jia, J. D. Neizich, S. H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, Nano Lett., 9, 30 (2009).
15. Q. Yu, L. Jian, S. Pirringler, H. Li, Y. P. Chen, and S. S. Pei, Appl. Phys. Lett., 93, 113103 (2008).
16. X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. R. Piner, L. Colombo, and R. S. Ruoff, Nano Lett., 9, 4359 (2009).
17. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutt, S. K. Banerjee, L. Colombo, and R. S. Ruoff, Science, 324, 1312 (2009).
18. M. Hiramatsu, K. Shoji, H. Amano, and M. Hori, Appl. Phys. Lett., 84, 4708 (2004).
19. A. T. H. Chuang, B. O. Boskovic, and J. Robertson, Diamond Relat. Mater., 15, 1103 (2006).
20. S. Kondo, M. Hori, K. Yamakawa, S. Den, H. Kano, and M. Hiramatsu, J. Vac. Sci. Technol., 26, 1294 (2008).
21. K. Teii, S. Shimada, M. Nakashima, and A. T. H. Chuang, J. Phys. Appl., 106, 084303 (2009).
22. Z. P. Wang, M. Shoji, and H. Ogata, Appl. Phys. Lett., 25, 9082 (2011).
23. M. Y. Zhu, R. A. Outlaw, M. Bagge-Hansen, H. J. Chen, and D. M. Manos, Carbon, 49, 2526 (2011).
24. J. J. Wang, M. Y. Zhu, R. A. Outlaw, X. Zhao, D. M. Manos, B. C. Holloway, and V. P. Mammana, Appl. Phys. Lett., 85, 1256 (2004).
25. N. G. Shang, F. C. K. Au, X. M. Meng, C. S. Lee, I. Bello, and S. T. Lee, Chem. Mater., 23, 15202 (2012).
26. M. Hiramatsu, K. Shoji, E. Tutt, S. Deng, and J. Chen, and X. Nu, Nanotechnology, 23, 015202 (2012).
27. M. W. Shoji, M. Hiramatsu, A. Enomoto, N. Nakamura, H. Amano, and M. Hori, Diamond Relat. Mater., 14, 831 (2005).
28. B. C. P. Rao, R. Maheswaran, S. Ramaswamy, O. Mahapatra, C. Gopalakrishnan, and D. J. Thiruvadigal, Carbon Nanostruct., 17, 625 (2002).
29. A. N. Obraztsov, A. P. Volkov, K. S. Nagoytsev, K. Nishimura, K. Moroswa, P. Molina-Morales, and H. Nakai, J. Appl. Phys., 97, 103205 (2005).
30. W. Takeuchi, H. Sasaki, S. Kato, S. Takashima, M. Hiramatsu, and M. Hori, J. Phys. Appl. Phys., 35, 113305 (2008).
31. S. Kondo, S. Kawat, W. Takeuchi, K. Yamakawa, S. Den, H. Kano, M. Hiramatsu, and M. Hori, J. Appl. Phys., 106, 094302 (2009).

Downloaded on 2018-07-20 to IP 207.241.231.81 address. Redistribution subject to ecsdl.org/site/terms_use unless CC License in place (see abstract).
161. C. Zhong, J. Z. Wang, X. W. Gao, D. Wexler, and H. K. Liu, *J Mater Chem A*, 1, 10798 (2013).
162. D. Cho, M. Kim, J. Hwang, J. H. Park, Y. L. Joo, and Y. Jeong, *Nanoscale Res. Lett.*, 10, 424 (2015).
163. K. A. Geim and S. K. Novoselov, *Nat Mater*, 6, 183 (2007).
164. H. Chang and H. Wu, *Energy Environ Sci*, 6, 3483 (2013).
165. S. Nardeccchia, D. Carriazo, M. L. Ferrer, M. C. Gutierrez, and F. D. Monte, *Chem Soc Rev*, 42, 794 (2013).
166. H. Kim, Z. Wen, K. Yu, O. Mao, and J. Chen, *J Mater. Chem.*, 22, 15514 (2012).
167. C. Wang, Y. S. Chui, R. Ma, T. Wong, J. G. Ren, Q. H. Wu, X. Chen, and W. Zhang. *J. Mater. Chem. A*, 1, 10092 (2013).