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Chemical Vapor Deposition of Graphene

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1. Introduction

Graphene is a two-dimensional material composed of carbon atoms arranged in a hexagonal atomic structure. Tremendous amount of research has been done on digging out its excellent properties in future applications. However, the ability of fabricating large-area monolayer graphene is hindering its application. So far the graphene of the best electronic properties is synthesized by mechanical exfoliation from Highly Ordered Pyrolytic Graphite (HOPG), which is of tens of micrometers in size (Novoselov et al., 2004). Graphene can also be produced by chemical reduction of graphite oxide (Tung et al., 2009), high temperature annealing of single crystal SiC (Konstantin et al., 2009) and Chemical Vapor Deposition (CVD) on metal substrates (Reina et al., 2009). These techniques have been employed in demonstrating good quality graphene transistors. However the only one that has the promise of becoming a manufacturable technology is CVD, which has been one of the mostly used thin film fabrication techniques in silicon Very-Large-Scale Integration (VLSI).

2. CVD technology

CVD is a technique of thin solid film deposition on substrates from the vapor species through chemical reactions. The chemical reaction plays an important role and is thus one of the most distinctive features that CVD possesses compared with other film deposition techniques such as physical vapor deposition (PVD). Figure 1 shows the schematic drawing of a typical tube-furnace CVD system for graphene growth. It is composed with a gas deliver system, a reactor and a gas removal system. During the CVD process, reactive gas species are fed into the reactor by the gas delivery system that consists necessary valves, Mass Flow Controllers (MFCs) that manipulate the flow rates of the gases passing through, and a gas-mixing unit that is responsible for mixing the various gases uniformly before they are let in the reactor. The reactor is where the chemical reaction takes place and the solid materials are deposited on substrates as the purpose of the reaction. The heaters are placed surrounding the reactor to provide high temperatures for the reaction. Eventually the by-products of the reaction and non-reacted gases are removed by the gas delivery system that is made of one or more pumps that are not necessary for the CVD not operating at vacuum condition.

In contrast to the relatively unsophisticated setup, however, CVD is far away from an easy-to-control process. In addition to the control of regular parameters such as temperature, pressure, time and so on that other deposition techniques also inevitably encounter, there are other factors need to be considered carefully to conduct CVD. In a successful CVD process (Figure 2) the transport kinetics of gas species tends to be complicated with convection and
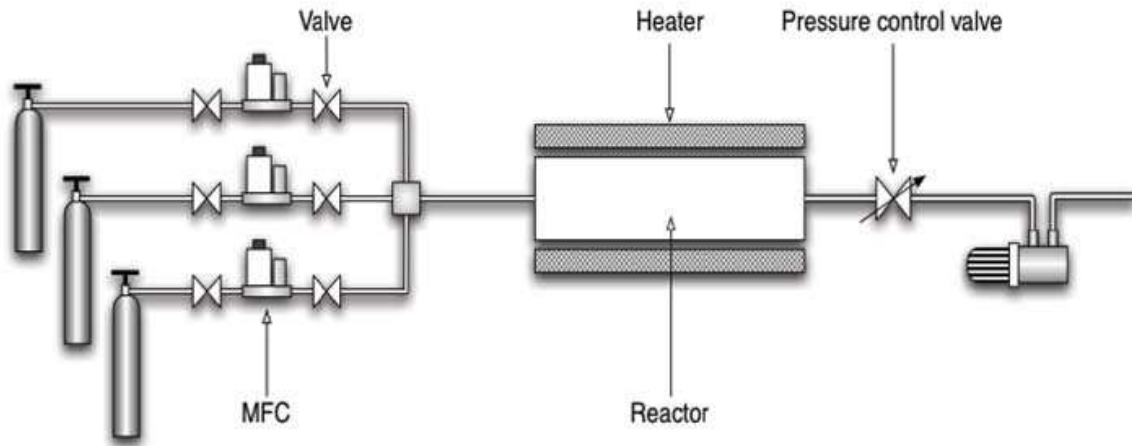
Fig. 1. The schematic diagram of a typical tube-furnace CVD system. Gas flows are regulated by MFCs, and fed into the reactor through a gas-distribution unit. Chemical deposition takes place in the reactor that is heated by the outside heaters. The exhaust gases are removed by vacuum pumps.

diffusion being dominating in different regions of a reactor. And the chemical reaction might be the most complicated because it usually involves many intermediate steps and one may not know the exact step-by-step reaction mechanism. The diffusion of reactive species to or from the substrates is also complicated in that a stagnant boundary layer of non-uniform thickness is formed above a fixed substrate surface based on the fluid dynamics (Figure 3). As a result the diffusion occurs slower at the thick boundary layer region, and results in deposition non-uniformity.
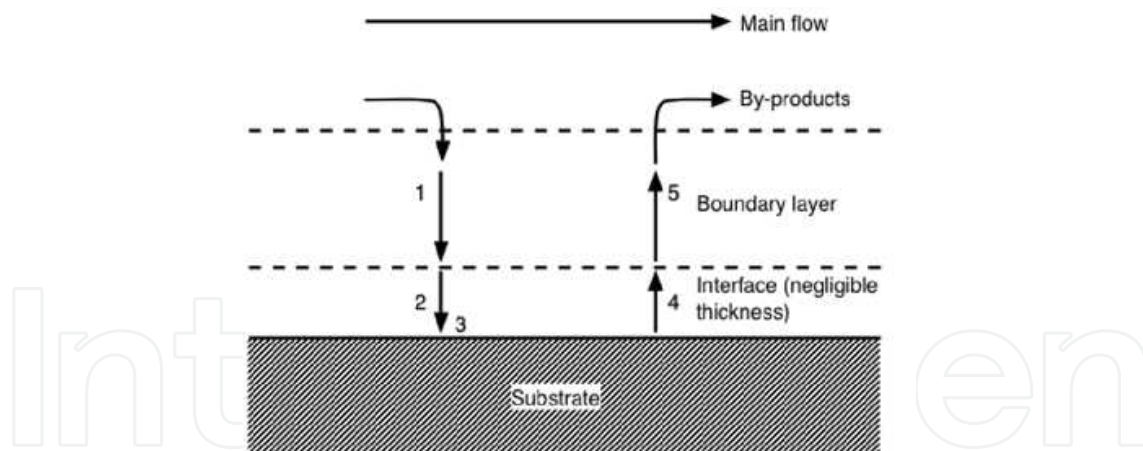

Fig. 2. The chemical deposition process in CVD. 1. Reactants diffuse through the boundary layer. 2. Reactants are adsorbed onto substrate surface. 3. Chemical reaction occurs on the surface. 4. The by-products of the reaction are desorbed from the surface. 5. The by-products diffuse through the boundary layer.

Another factor one must consider is the depletion of reactants from one end of the reactor to the other. Note that this is different from flow rate which as mentioned earlier does not affect the growth of the film; however if inert gas is hitting the wafer at the end of the reactor, then no chemical reaction will occur. This is because reaction will usually occur near the front end of the reactor and not near the end. To eliminate this issue, one can have increasing temperatures moving away from the location where reactant gas is flowed in which will cause a higher

(a)

Main flow

Boundary layer

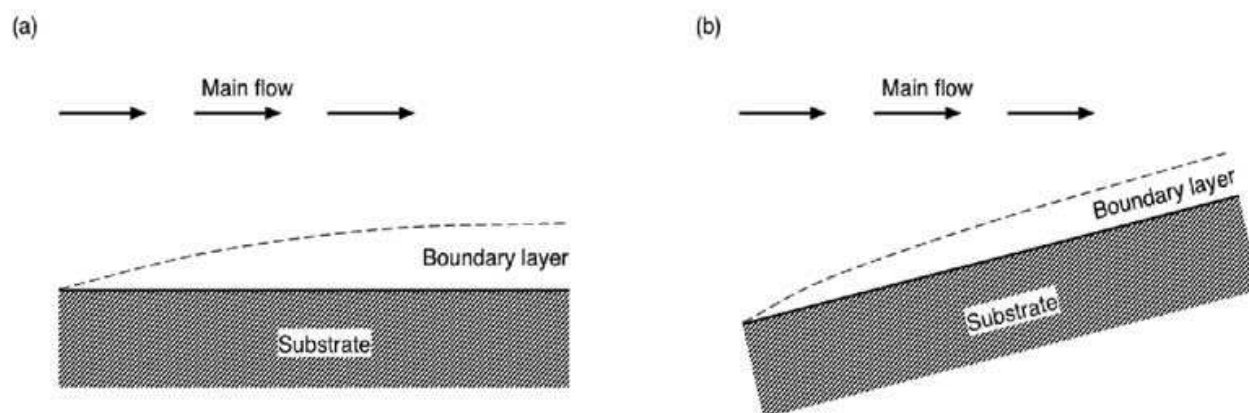Substrate

(b)

Main flow

Boundary layer

Substrate

Fig. 3. An example of a boundary layer above the substrate surface. (a) The substrate surface is parallel to the main flow. (b) The substrate is tilted to enhance the thickness uniformity of the boundary layer based on fluid dynamics.

diffusion rate to occur near the end of the reactor; this leads to better throughput throughout the reactor.

All the factors in the CVD process are entangled with one another and it is extremely tedious work to single out one to look into its influence to the entire deposition process. Hence CVD is a more complex process than other processes and it is necessary that several test runs should be performed to calibrate the system before a successful deposition of thin film with desired thickness and quality.

3. Unique aspect of CVD graphene

3.1 Requirement of catalysts

Graphene deposition can be divided into two parts: precursor pyrolysis to carbon and the formation of graphitic structure from dissociated carbon atoms. The precursor dissociation should be done only on the substrate surface (i.e. heterogeneous reaction) to avoid the precipitation of carbon clusters in the gas phase which is typically in the form of carbon soot and sits on synthesized graphene, if any, to form graphene/soot mixture as well as on reactor walls. Although they are all made of carbon, the amorphous structure of carbon soot determines that their composite no longer retains the properties of monolayer graphene. To achieve the heterogeneous decomposition of precursors on surface, various catalysts of mostly elemental metals are typically used as catalysts. The function of catalysts is to lower the energy barrier of the reaction. In addition to the undesirable need for very high temperature, high energy barriers result in reaction rates to be sensitively dependent on temperature making it difficult to control the reaction rate. Because the film quality is determined by reaction kinetics, high energy barrier leads directly to the difficulty in controlling the film quality.

In the graphitic structure formation step, large area graphitic structure forms only when reaction temperature is raised to beyond 2500 °C without catalysts, which is too high that requires special setup of the deposition system and the substrate. In addition huge amount of energy consumption becomes a considerable issue. The introduction of catalysts lowers energy barriers not only for the pyrolysis of precursors, but also for the graphitic structure formation.

3.2 Impacts of catalysts

The usage of catalysts introduces new materials into the reactor chamber, leading to potential issues. Catalysts are usually metals, which may have finite carbon solubility. For example, Cu has almost zero carbon solubility (Lopez & Mittemeijer, 2004), and Ni has a non-negligible carbon solubility (Natesan & Kassner, 1973). During the growth at elevated temperature, dissociated carbon atoms on the catalyst surface may dissolve into the bulk due to the finite solubility. Things become worse when these dissolved carbon atoms precipitate back onto Ni surface as temperature drops and hence unwanted carbon deposition may occur from bottom. Different cooling rate suggests the different thickness of graphene, and one more freedom participates in the deposition process. Hence the control of deposition is of more difficulties. Figure 4 shows the schematic drawing of graphene grown on Ni with different cooling rate (Yu et al., 2008). Extreme fast cooling leads to little carbon precipitation, because not sufficient time is allowed for carbon to precipitate. Medium cooling gives graphene, and slow cooling has nothing on the surface in that carbon atoms diffuse deep into the bulk catalyst.
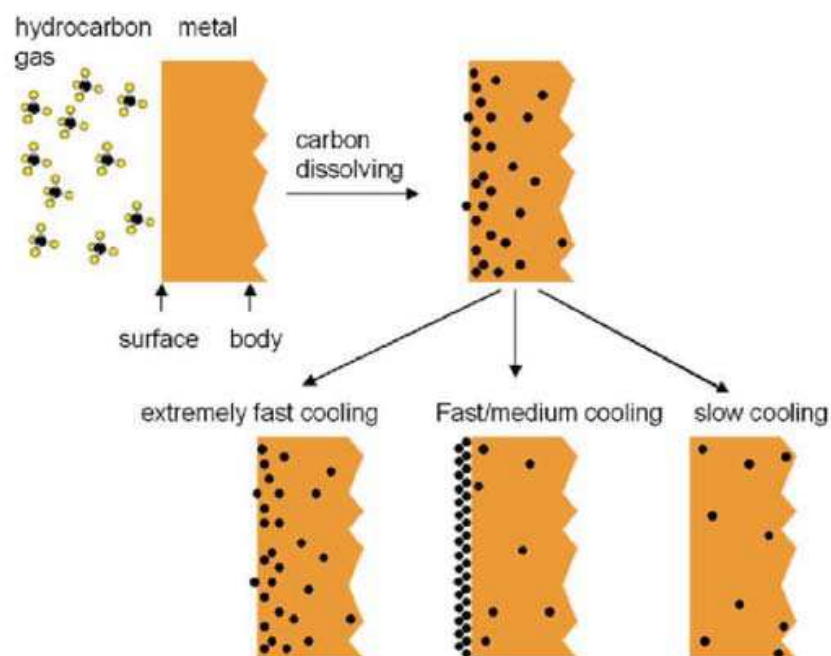

Fig. 4. Illustration of carbon segregation at metal surface (Yu et al., 2008).

Another issue with catalysts is the surface roughness, mainly due to the grain boundaries. When carbon precipitates out to the surface, they prefer to stay in the areas with higher surface energy, such as grain bounties, surface trenches and so on, for the reason that these areas have more atomic dangling bonds that could easily attract precipitated carbon atoms. Eventually the deposited graphene exhibits non-uniformity with thick graphene around grain boundaries and other surface defects, and thin sheet on the other areas. It is thus important to pre-anneal catalyst substrates in order to have large grains to reduce total length of grain boundaries, as well as other minor surface defects.

3.3 CVD graphene on Ni

Ni is one of the major catalysts that used in CVD growth of graphene. Growing graphene on Ni provides sufficient details of various concerns of deposition process with majority of this chapter being dedicated to it as a result.

The first successful graphene deposition via CVD was conducted using Ni as catalyst with the inspiration coming from the CNT growth where Ni is a well-known efficient catalyst. The crucial difference between graphene and CNT growth is that in graphene growth the precursor partial pressure is significantly reduced in that low growth rate is needed for the growth of graphene, a sub-nanometer film. High growth rate leads to over deposition. The prepared samples for graphene growth have structures show in Figure 5, i.e. $Ni/SiO_2/Si$, with SiO_2 as the diffusion barrier to prevent Ni from diffusing to Si substrate. The deposition parameters are set up as follows. After the prepared sample (Figure 5) is loaded into the furnace, the whole reaction chamber is pumped down with a vacuum pump (Figure 1) to the base pressure that should be much less than the deposition pressure for the purpose of reducing the probability of depositing residue gas molecules on graphene (i.e. graphene contamination or doping). When the base pressure is reached, hydrogen gas is let into the reaction chamber and the furnace is turned on to heat up to the deposition temperature. The temperatureis maintained for some time to anneal the catalyst Ni to initiate grain growth that may increase graphene uniformity eventually. Then the deposition begins, by letting in methane together with hydrogen. The whole chamber is then cooled down to the low temperature before taking out the sample. All the above steps are for Low Pressure CVD (LPCVD) growth. Note that graphene can also be fabricated via atmospheric pressure CVD, in which case a huge amount of argon gas is usually used to purge of the residue oxygen in the chamber to protect the metal surface from being oxidized, beside hydrogen gas, and to dilute the precursor to lower deposition rate.
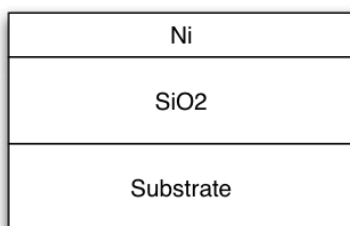
Ni
SiO2
Substrate

Fig. 5. Schematic diagram of the sample prepared for graphene growth. The top Ni layer is the catalyst, and the middle layer SiO_2 is the diffusion barrier layer to prevent Ni diffusion to the substrate that is usually silicon.

Figure 7 shows the images of the CVD graphene grown on Ni as deposited at 900 °C, 3 minutes and the corresponding spectra of Raman spectroscopy, which has been shown to be a valuable tool for characterizing graphene (Ferrari et al., 2006). Figure 6 shows the Raman spectra (2D peak) of graphene of different thickness (Ferrari et al., 2006). Graphene film grown on Ni is not uniform in thickness all over the substrate surface as indicated by the color contrast (the dark areas correspond to thick graphene). Instead, the monolayer areas are small in size and randomly distributed among the multilayer graphene regions. To better illustrate its morphology, graphene is transferred from Ni to SiO_2 oxide substrate of 300 nm thick on which graphene is visible under optical microscopeso one can observe its uniformity without the disturbance of Ni surface (Ni et al., 2007). Figure 8 shows the image of the transferred graphene on SiO_2 surface together with Raman spectra. In Figure

7 and 8, the upper-right Raman spectrum peak indicates a monolayer graphene, and the lower-right spectrum corresponds to a thick graphene layer, based on Raman spectrum analysis. Therefore, the graphene growth on Ni is confirmed to be non-uniform in thickness over a large area, but monolayer graphene can be found in small areas. One might notice that the backgrounds in Raman spectra are different when graphene is on Ni and on SiO$_2$. This is due to the interaction of graphene and its substrate (Wang et al., 2008).
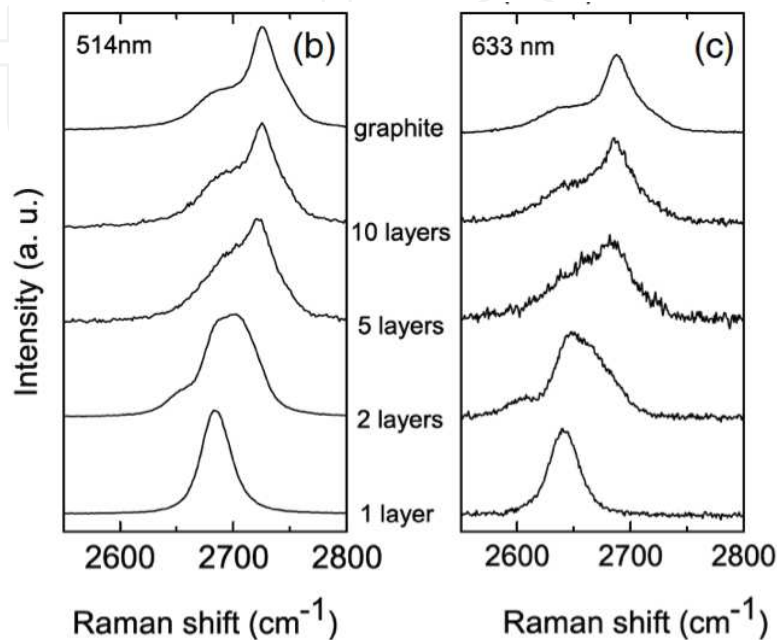
Fig. 6. Raman spectra of 2D peaks of graphene of different thickness (Ferrari et al., 2006).

Like CVD growth of CNTs, the achievement of graphene on nickel was not based on the solid understanding of the mechanism. It is proposed briefly (Li et al., 2009) that when the precursor decomposes into carbon ad-atoms on the Ni surface, they soon dissolve into the bulk Ni, because Ni has a finite solubility of carbon at high temperatures (e.g. 900 °C). At the cooling step, the bulk Ni is subject to temperature decrease, leading to the solubility reduction since the solubility of carbon in Ni is temperature-dependent, and hence the excessive dissolved carbon atoms have no way out but to precipitate back onto the top surface, where they form graphene sheet (Figure 9). The thickness of graphene is therefore controlled by the carbon solubility difference in Ni at the deposition temperature and the rate of cooling at the last growth step.When carbon atoms precipitate out, they do not arrange themselves uniformly on the Ni surface. Instead they precipitate onto the sites with high surface energy such as rough areas and grain boundaries. That is the reason why graphene sheets deposited on nickel is non-uniform as seen in Figure 7 and 8. In summary, this is a "bottom-up" process rather than a "top-down", leading to difficulties in control graphene thickness precisely.

3.4 Challenges of graphene synthesis on Ni

The first challenge comes from the pyrolysis of the precursor species. Hydrocarbon species are typically used as precursors for graphene growth, such as methane (CH$_4$), acetylene (C$_2$H$_2$) and so on. CH$_4$ is one of the most commonly used precursors, as it is comparatively stable (i.e. low pyrolysis rate) at high temperature (e.g. 800-1000 °C for most graphene growth)and has simple atomic structure. Most other hydrocarbons have a very high pyrolysis rate at high temperature, resulting in large amount of carbon deposition that is not preferred for
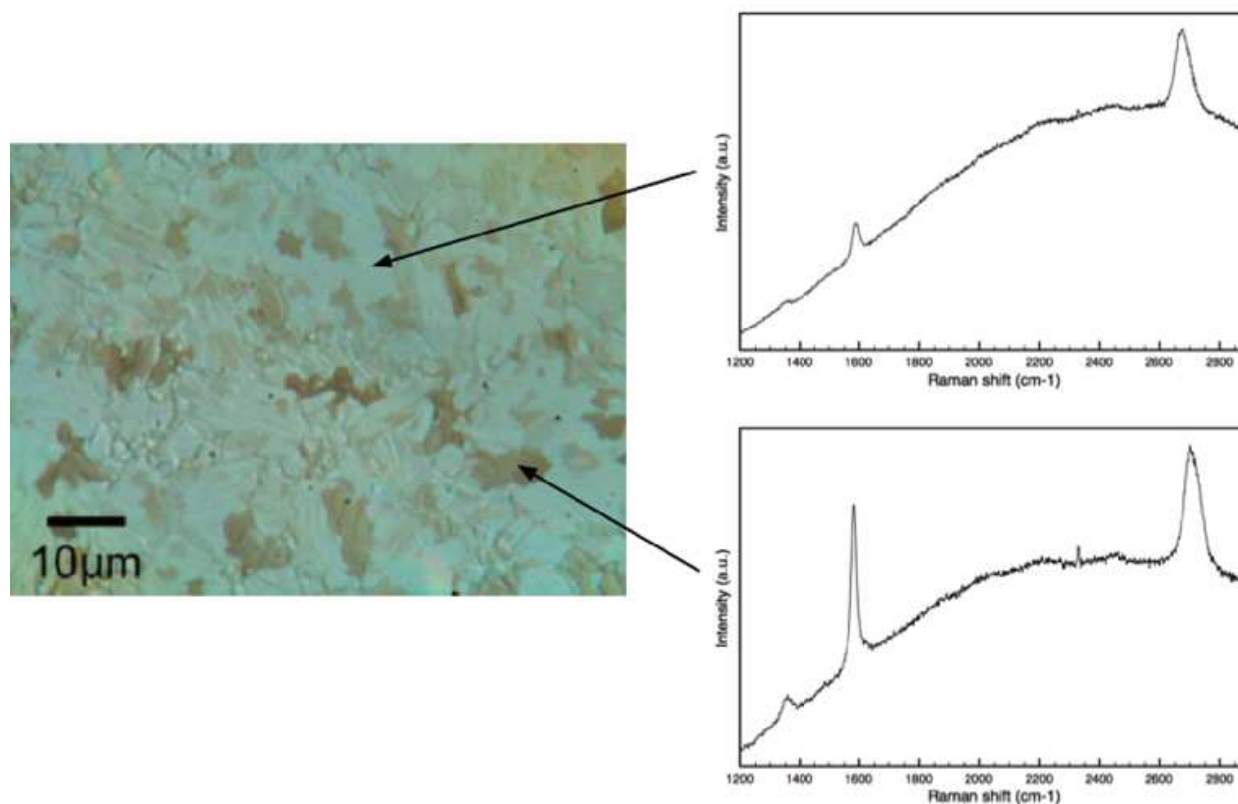
Fig. 7. Optical image of ad-deposited graphene on Ni (left). And the Raman spectra measured at certain points (see arrows). The dark areas correspond to the multilayer graphene, based on Raman spectroscopy analysis.

sub-nanometer graphene. However, even with CH_4, the process of how it is decomposed thermally is still not absolutely understood because of the intermediate steps in CH_4 pyrolysis. A possible dissociation path of CH_4 is CH_3-CH_2-CH-C. The more intermediate steps of the decomposition of the precursors, the more freedom get involved in supplying carbon atoms for the subsequent graphene formation. Hence difficulties inevitably arise to control the carbon supply rate.

The main challenge originates from the unique dimension of graphene. Graphene differs from other materials in a way that it is a sub-nanometer-thick material, whereas the typical CVD deals more with the film much thicker than graphene. The deposition technique of graphene should essentially provide extremely precise control of the thickness of the deposited film analogous to the atomic layer deposition (ALD) with the deposition resolution of a single atomic layer.Such high precision has never been achieved in the past in CVD, reasons being mentioned earlier, and thus raises great challenges. In details, the depositionmust be terminated right after the first layer of graphene is formed on the substrate. Over deposition leads to the undesired nucleation of the second layer graphene and eventually multilayer graphite, while insufficient deposition sparks off many isolated graphene flakes rather than a continuous sheet.In order to have perfect graphene sheet deposited, the deposition rate-limiting step needs to be seriously considered as the slow rate implies more control of graphene growth, which may not be good for the deposition of other thick films.Typically the deposition rate in CVD is limited either bychemical reaction rate or by mass transportation.
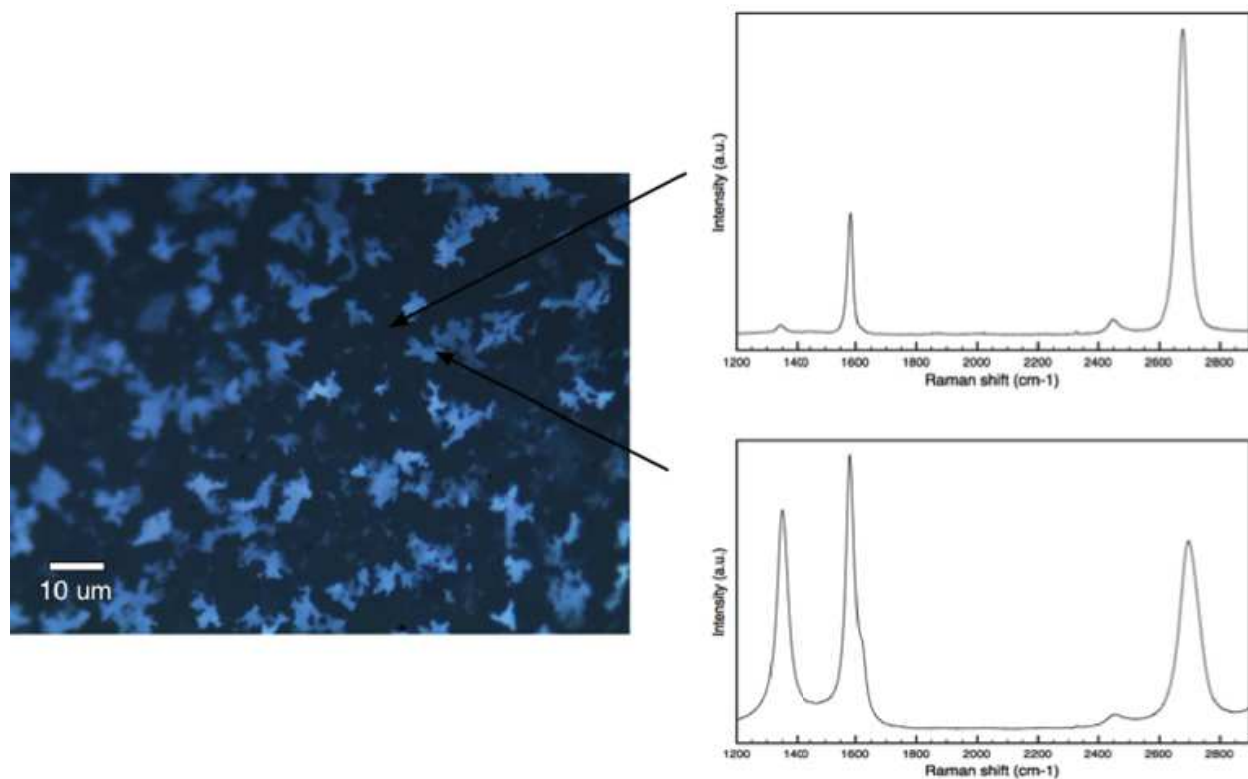
Fig. 8. Optical image of transferred graphene on SiO_2 of 300 nm thick. And the Raman spectra measured at certain points (see arrows). The bright areas correspond to the multilayer graphene, based on Raman analysis.

In the chemical reaction controlled process, the reaction rate is the limiting factor, which is related to the reaction temperature and the concentration of the reactants. Hence it is helpful to reduce the deposition temperature in case of graphene deposition with hydrocarbon pyrolysis, or to decrease the partial pressure of the precursor species from the perspective of the reaction kinetics. However, temperature affects not only the reaction rate, but also the microstructure of the deposited film. Low temperature leads to fine-grained graphene sheets, by decreasing the diffusion length of the dissociated carbon ad-atoms after the reactionaccording to the surface kinetics, which is desired for some film depositions, but not for the graphene. The low partial pressure has been widely applied in the recent graphene growths for this reason. In fact the total pressure during the CVD process is also decreased to minimizethe diffusion effect by minimizing the boundary layer above the substrate due to the inverse relation of the boundary layer thickness and the pressure, and enhance the graphene uniformity.

Besides the regular manipulation of the deposition parameters, the replacement of effective catalysts with low-efficient materials is a good idea in CVD growth of graphene by slowing down the pyrolysis of precursors. Ni significantly reduces the energy barrier to form graphene, but it also promotes the deposition rate. Recently the effort has been shifted to Cu partly because it is not as efficient as nickel in lowering the energy barrier, and the results were proved to be promising.

All the above measures are effective, but do not guarantee precise growth control in sub-nanometer scale. The most important reason encouraging people to use CVD to grow graphene is that the growth is a self-limiting process. Assuming a graphene sheet has
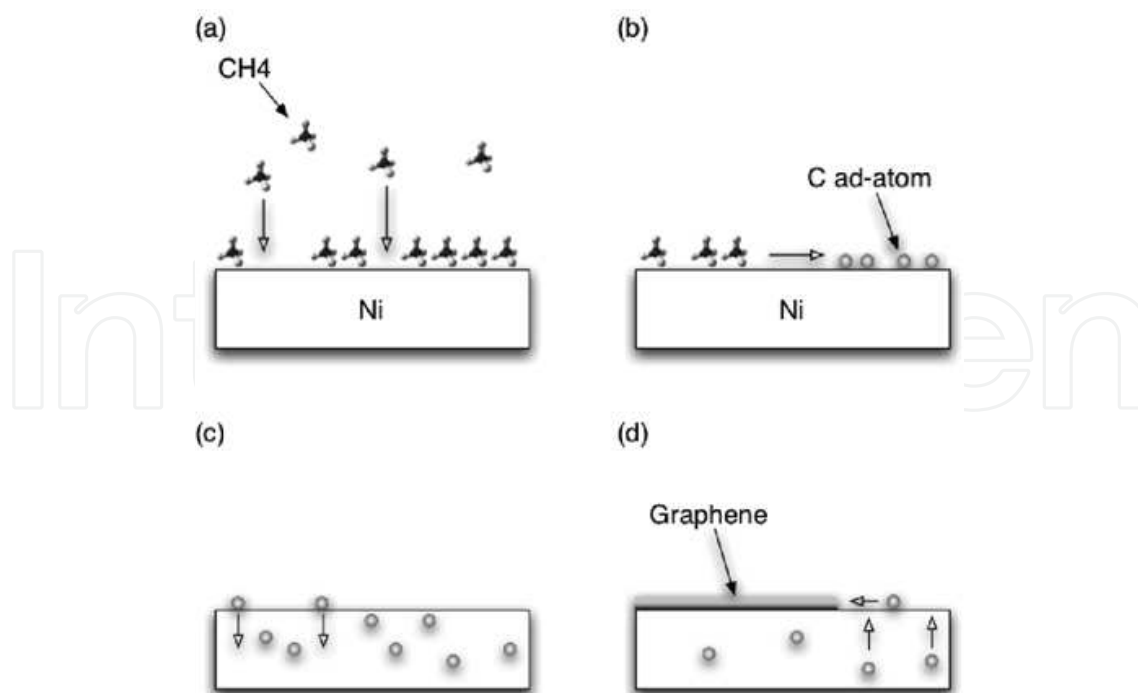
Fig. 9. Schematic drawing of the graphene growth mechanism with nickel as catalyst. (a) Methane molecules diffuse and adsorb on nickel surface. (b) Methane pyrolysis to carbon ad-atoms on nickel surface. (c) Carbon ad-atoms dissolve in bulk nickel. (d) Carbon atoms precipitate back to nickel surface at low temperature and graphene is formed.

been deposited on catalyst surface, the "catalyst-poisoning" effect (i.e. catalyst looses its catalytic feature) takes place because the catalyst is now hidden under the first-layer graphene, preventing the precursor species to access the catalyst. Hence the chemical deposition should stop automatically after the first layer is synthesized. This may be questionable, however, because the first layer graphene itself is a catalyst for the second layer to be deposited, which is true in the deposition of graphite via CVD. Compared with the origin catalyst, graphene is less effective, reason being that the energy barrier of the second-layer graphene nucleation is huge in that the second-layer nuclei are "floating" on the bottom graphene layer with the weak Van Der Waals force as the bonding force. In other words, the critical size of the nuclei is so huge that the probability of the second layer nucleation is negligible, especially with the limited super-saturation of carbon ad-atoms and the reasonable temperature. The CVD growth of graphite is a counter example where high temperature is preferred to initiate layer-by-layer growth. Therefore, as long as the partial pressure and temperature are controlled, the second layer growth could be minimized.

The mass transportation controlled process rarely is the case in graphene growth. Mentioned earlier, the low pressure is typically used, and hence precursor diffusivity to substrate surface is high because it is inversely related to the pressure.

The other challenge is the obscure mechanism. Using hydrocarbon precursor to grow graphitic materials has been studied for decades, but the secret of what is happening in the deposition process is never indeed revealed for the reason that it is a complex process as mentioned above. As a result, try-and-error method is commonly used to grow graphene and thus the production yield and repeatability are not so high as that of thick material deposition.

3.5 Graphene synthesis on Cu

While nickel encounters problems as a catalyst, the second-generation graphene was synthesized with Cu as catalyst. Cu has almost zero solubility of carbon even at $1000\,^\circ$C, so the amount of carbon participating in dissolution-precipitation process is not sufficient to form a single layer of graphene. As a result, the dissolution-precipitation mechanism is negligible for Cu. The carbon atoms form a graphene sheet on the copper surface during the growth step directly. This mechanism suggests easier control over the deposition of graphene on the copper surface as the cooling rate at the last step does not affect the graphene thickness. One can roughly estimate the amount of precursor gas needed for monolayer graphene fabrication at a certain temperature and pressure, and then predict the CVD recipe to start with.
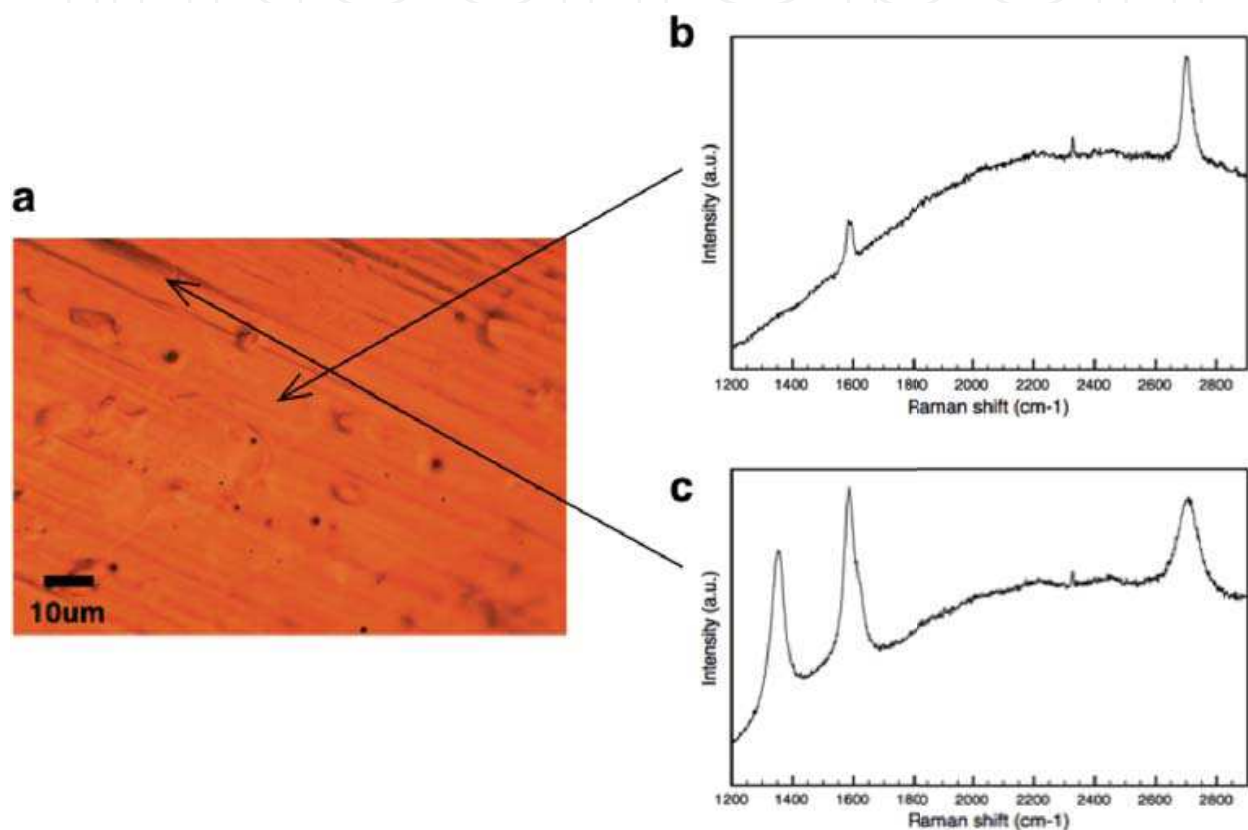

Fig. 10. (a) OM image of graphene growth on Cu foil surface. (b) and (c) Raman spectrum measure at the flat area (see arrow) and corrugated area at graphene surface, respectively.

Figure 10 shows the results of graphene deposition on copper foil surface. Different from the graphene on nickel, the graphene grown on copper has less obvious color contrast, indicating better uniformity in graphene thickness. The uniformity can also be seen on the transferred graphene on silicon oxide of 300 nm thick (Figure 11). According to the Raman spectra in most areas, graphene is monolayer. But on the rough surface areas, the graphene is thick and defective because the D peak is high and the G peak is higher than the 2D peak. One might want to polish the Cu foil surface before the deposition, but the thin dimension and softness of the foils are obstacles that render this not a good idea. In addition, the polishing will also introduce a lot of contaminates onto the copper surface. Fortunately, the artificial trenches and other textures are reduced in transferred graphene, meaning the pretreatment of polishing the
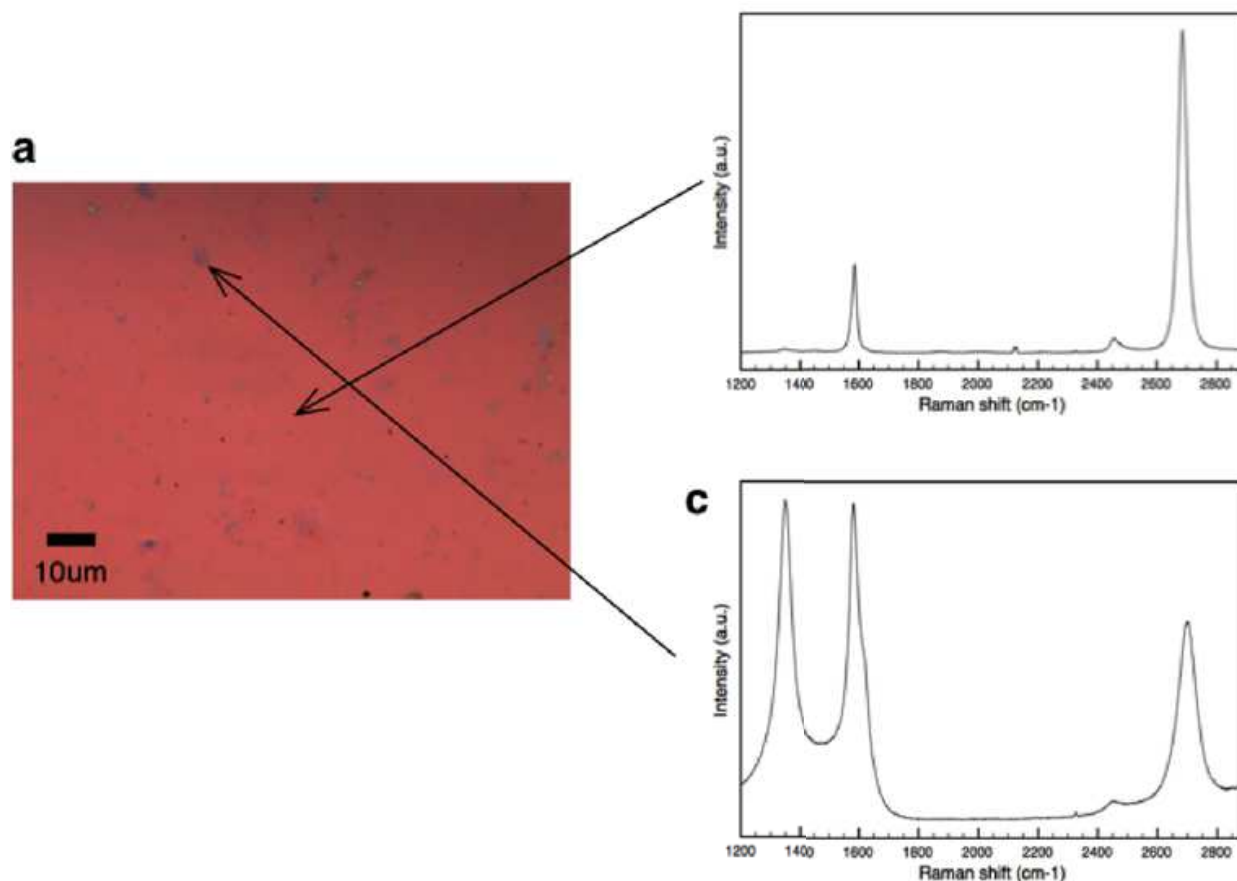
Fig. 11. (a) OM image of graphene transferred onto SiO_2. The graphene was initially deposited on Cu foils. (b) and (c) Raman spectrum measure at the flat area (see arrow), and non-uniform area at graphene surface, respectively.

copper foils may not be necessary if the transfer graphene is good enough for the potential applications.

So far most successful deposition of graphene on copper surface is done with copper foil, which is commercially available with a large size of grains, basically greater than 100 μm, one order of magnitude larger than that of typical copper thin film deposited via e-beam evaporation or sputtering. The large grain size guarantees more crystalline and higher average surface flatness, improving the synthesized graphene uniformity.

The largest production,roll-to-roll graphene production has been achieved (Bae et al., 2010) with Cu foil as catalyst (Figure 12), which shows that CVD is indeed a scalable technique capable of producing large-area graphene.

3.6 Challenges of graphene synthesis on Cu

Cu is a metal not so reactive as Ni. So attention needs to be paid during the deposition process to avoid it to be oxidized. It requires much lower base pressure of the system, and the lower temperature at which the sample could be unloaded after deposition. In the subsequent graphene transfer step (see next section), stronger etchants should be used to remove Cu, subject graphene to higher possibility to be damaged by the etchant. As a result, the properties of graphene might not be comparable to that synthesized with Ni.
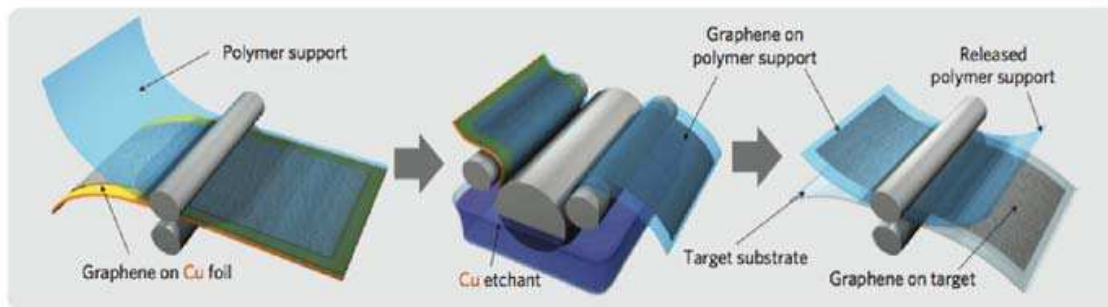
Fig. 12. Roll-based production of graphene films grown on a copper foil and graphene transfer process with thermal release tapes (Bae et al., 2010).

The second challenge is the crystalinity of as-deposited graphene, which is applied to both Ni and Cu. The graphene deposited via CVD is still far from the perfect crystalline materials. It has something to do with the catalysts. Catalysts like Ni and Cu are all metals, which are difficult to format to single crystalline materials. Instead, the catalysts deposited via a sputtering machine or an e-beam evaporator arenano-crystaline materials. Although the annealing treatment may induce grain growth that significantly enlarges the grains, the catalysts are still polycrystalline materials with many grain boundaries and different crystalline orientations on the surface. Consequently, graphene grows in a polycrystalline fashion, as illustrated in Figure 13. On the left side shows the carbon ad-atoms sitting on catalyst surface. The middle figure shows the nucleation of graphene occurring at certain points. One must know that the crystalline orientation of the nuclei may not be the same, which may be dependent on the crystalline structure of the catalyst they sit on. Finally when the nuclei keeps growing, the polycrystalline graphene is formed as shown in the image on the right side of Figure 13. It is also possible for a second layer nucleation to occur at some conditions (e.g. higher super-saturation).
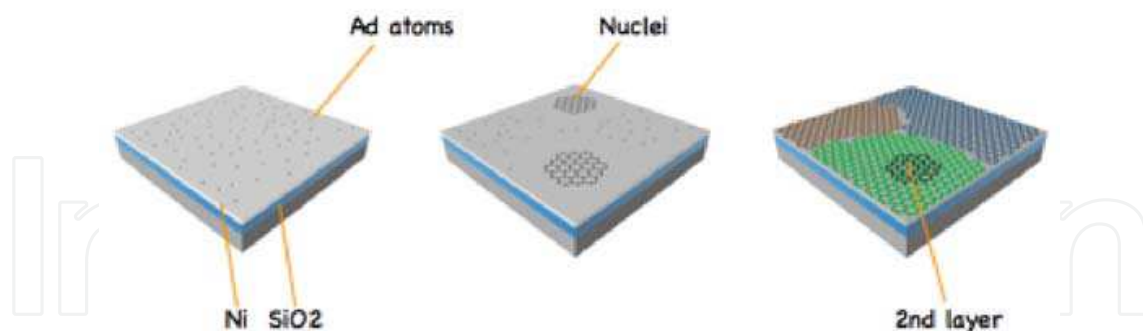

Fig. 13. Schematic diagram of carbon growth on catalyst forming polycrystalline graphene.

With all the challenges discussed, graphene growth by CVD is still a promising process compared with others. Its intrinsic properties stimulate more and more people to involve in the field of CVD graphene.

Although CVD of graphene has advantages such as low cost and scalable production, recall that graphene is deposited on metal catalysts. Since many applications of graphene (e.g. graphene MOSFET) require it to be on an insulator, the graphene needs to go through a transfer process to move graphene, without damaging or degrading its performance, to a

suitable insulator substrate; the current catalysts are not insulators. Therefore the transfer process plays an important role in graphene fabrication.

3.7 Growth mechanism comparison

To compare the growth mechanism on Ni and Cu straightforwardly, the Texas group has come up with a smart idea that utilities the characteristics of ^{13}C, an isotope of regular ^{12}C. During the growth, ^{12}CH$_4$ and ^{13}CH$_4$ are fed into the chamber in turns (i.e. ^{12}CH$_4$ is fed in for 1 minute, followed by ^{13}CH$_4$ for 1 minute and so on). Note that the Raman signatures of the two carbon isotopes are not exactly the same and the difference is distinguishable. Hence it is feasible to use Raman spectroscopy/mapping to tell ^{12}C- and ^{13}C-graphene patterns. If the clearly distinguished ^{12}C- and ^{13}C-graphene patterns are shown, the graphene must be formed immediately during the adsorption of carbon atoms onto the graphene nucleus edge (i.e. surface kinetics). And the randomly mixed ^{12}C- and ^{13}C-graphene patterns should be caused by the dissolution and surface segregation mechanism.

After the experiment, the grown graphene shows ^{12}C- and ^{13}C-graphene patterns separately in case of Cu, but they are uniformly distributed on the Ni surface (Figure 14) (Li et al., 2009). Hence it is suggested that graphene growth on Ni is through dissolution-precipitation mechanism, while graphene growth on Cu is a surface process.
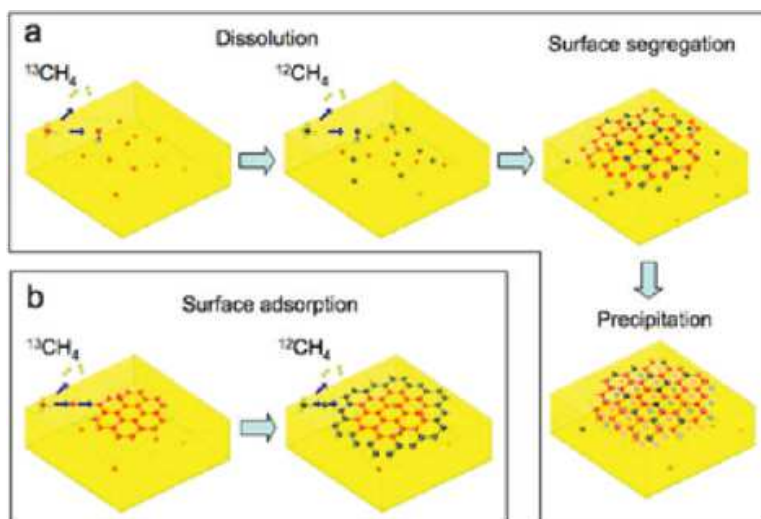

Fig. 14. Schematic diagram of the growth mechanism of graphene on metal catalysts (Li et al., 2009). (a) Graphene is grown with ramdomly distributed C isotopes due to surface segregation and/or precipitation. (b) Graphene is grown by surface adsorption where C isotopes is obviously seperated.

The second different between Ni and Cu is their chemical reactivity. Cu is more sensitive to O$_2$ to form Cu oxide than Ni, suggesting more attention needs to be paid when dealing with Cu. For example, after growth, graphene/Cu sample should be unloaded out of the reactor at room temperature, while graphene/Ni sample is safe to be taken out at 300 °C, as both Ni and graphene are of high oxidation resistance.The reactivity difference also affects the graphene transfer process that will be discussed later.

The third difference lies in their melting points. Cu has a relatively lower melting point 1083 °C and Ni 1453 °C. In the deposition process, Cu evaporation is more significant than that of Ni, leading to more deposition on reactor walls. Therefore the reactor should be cleaned more frequently with Cu. The high evaporation is not preferred for thin film deposition, owing to

the fact that evaporation of substrate material is a competing process with deposition of new material. In case of Cu, its high evaporation may result in the difficulty of graphene growth, especially for extreme thin film deposition.

The last difference is their catalytic capability. Ni is a widely used catalyst in CNT growth where high deposition rate is desired. From scientific perspective, Cu is not as effective as Ni to lower the overall energy barrier to form graphene. Hence it is suggested to use Cu as catalyst to lower the entire graphene deposition rate in growth of sub-nanometer material, so that one can gain more control.

It has to be mentioned that neither Ni nor Cu is an ideal catalyst for graphene growth, although they are most popular ones in the community of graphene deposition. The catalyst issue is the one that scientists have to face and seeking right catalyst is left as one of the future research topics.

4. Graphene transfer

The transfer of CVD-grown graphene films is very crucial, as we have mentioned previously; in order for electrical current to flow through graphene devices as opposed to being shorted out by a conducting substrate, graphene must be removed from the conducting catalyst surface and transferred onto an insulating surface (Kedzierski et al., 2009).

Not all the transfer techniques are applicable for CVD graphene. Graphene transfer techniques that are suitable for CVD graphene, are usually done by etching the underlying catalyst and then scooping the graphene directly or using some kind of media such as Poly(methyl methacrylate) (PMMA), Polydimethylsiloxane (PDMS) and thermal tape. Other techniques are not suitable such as mechanical exfoliation or chemical exfoliation dealing with multi-layer graphite as precursor material.

4.1 Direct transfer

The etching and scooping method is a straightforward transfer method to move graphene from the surface of metals to the target substrate. The key idea is to get rid of the catalyst film underneath the graphene so that the graphene sheet can be separated and scooped. An example process is shown in Figure 15. After the CVD growth, graphene is not isolated; it sits on the catalyst that is again on the substrate. The whole sample is submerged in an etchant, depending on the type of catalyst, to etch away the metal. After the catalyst is gone, the graphene sheet is floating on the liquid surface because of its hydrophobic nature (Leenaerts et al., 2009). One needs to be extremely careful to use the target substrate to scoop the floating graphene while letting the graphene sheet to sit uniformly on the surface. Finally after the graphene is dried, the transferred graphene is ready.

The advantage of this technique is that it is a simple process with few steps which reduces the possibility of introducing potential environment impacts. However, the direct scooping method requires high stability of the transferring setup to avoid the fragile graphene sheet from breaking during the process. Therefore it is of low yield. In addition, the etchant goes in between transferred graphene and its target substrate, which behaves as chemical dopants and enhances carrier scattering to degrade the electrical properties of graphene.

4.2 Transfer with media

To increase the throughput, a media is introduced to protect graphene. The mechanism is similar that the catalyst film underneath graphene is etched.Figure 16 shows an example of
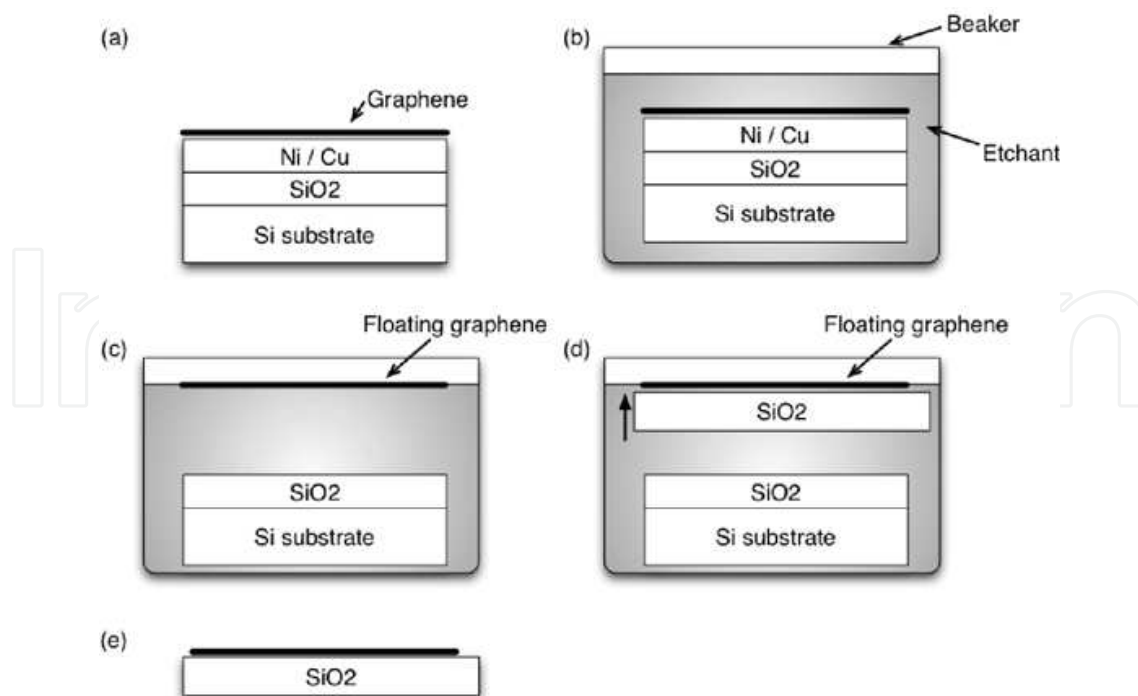
Fig. 15. Schematic diagram of the etching and scooping method without using a support. (a) The CVD-grown graphene on Ni or Cu catalyst. (b) The graphene sample is submerged into the metal (Ni or Cu) etchant. (c) The Ni or Cu is etched and the graphene is floating on the etchant surface, while the remaining SiO_2 and Si substrate sinks to the bottom of the beaker. (d) Another SiO_2 is used to scoop the floating graphene out of the etchant. (e) After drying, graphene is sitting on SiO_2, ready for future processing.

transfer graphene using PMMA as a media. Beside PMMA, PDMS and thermal release tape are commonly used as support materials too.

The only difference between PDMS and the other two is that PDMS and thermal tape are not dissolved at the last step (Figure 16f); instead they are pilled off by hand. It is crucial that the interface bonding between graphene and substrate is greater than that between PDMS and graphene to ensure graphene is left on substrate while being peeled off. However, the quantified values are unknown now. The current solution is that the PDMS stamp is applied onto graphene that is on catalyst surface when it is sticky, i.e. partially cured (Figure 16e). Then the PDMS is completely cured to reduce the adhesion before the PDMS stamp is peeled. It works because the adhesion strength of PDMS surface can be approximately linearly related to the degree of cross-linking of elastomers (Shanahan & Michel, 1991). Beside the effort on PDMS, the surface treatment on the substrates where graphene is transferred may be helpful by increasing its bonding strength with graphene, thus improving the yields. For example, surface activation with plasma, which is commonly done in wafer bonding for SOI fabrication, could be performed to help enhance the surface adhesion.

5. Summaries

Deposition of graphene on catalysts is demonstrated using thermal CVD process. Monolayer graphene is formed on catalyst through the surface catalytic pyrolysis of carbon-containing precursors, and it is transferred to arbitrary substrates via a transfer process with or without support media. Color contrast using optical microscope and Raman spectroscopy distinguish
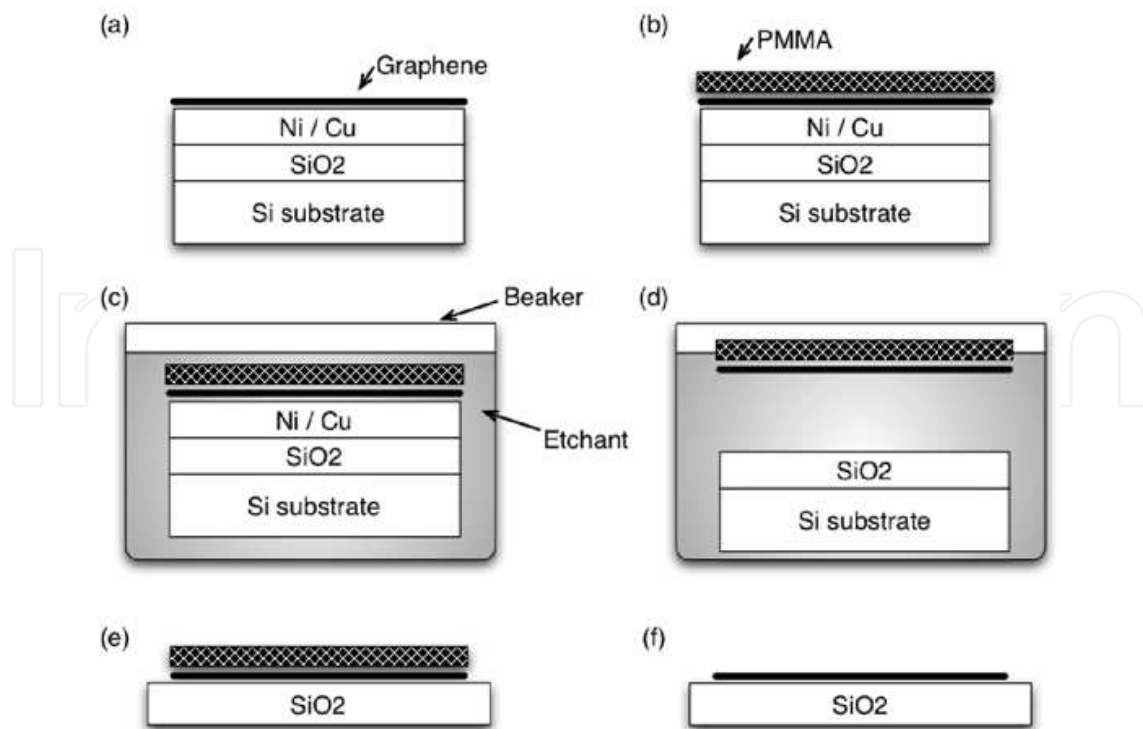
Fig. 16. Schematic diagram of graphene transfer with PMMA as a support. (a) The CVD-grown graphene on Ni or Cu catalyst. (b) A PMMA layer is spin-coated on top of graphene. (c) The graphene sample is submerged into the metal (Ni or Cu) etchant. (d) The Ni or Cu is etched and the graphene is floating with PMMA on the etchant surface, while the remaining SiO_2 and Si substrate sinks to the bottom of the beaker. (e) The floating graphene/PMMA is transferred onto a SiO_2 substrate. (f) The PMMA top layer is removed by acetone or other PMMA remover and graphene remains on SiO_2.

the number of graphene layers. It shows that the graphene morphology is closely dependent on the catalyst material, and thus the selection of right catalyst is crucial. Although the overall deposition process is not exactly scientifically known in terms of mechanism, the knowledge of the effect of carbon solubility in catalyst already leads to the upgrade of catalyst from Ni to Cu that significantly improves the surface uniformity of graphene.

CVD plays an important role in graphene fabrication, as the progress in development of graphene-based products is largely stalled by a lack of supply of high-quality large-size graphene sheets and CVD is a solution compatible with massive production. It is a milestone in CVD history that the fabrication of sub-nanometer materials has been successfully achieved.

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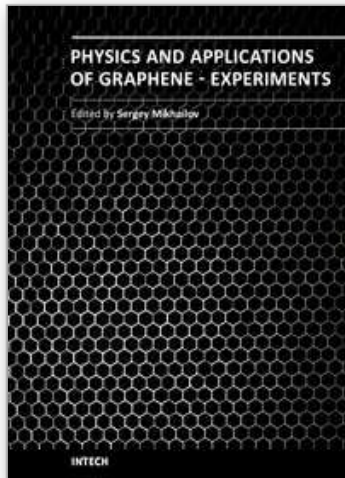
Physics and Applications of Graphene - Experiments

Edited by Dr. Sergey Mikhailov

The Stone Age, the Bronze Age, the Iron Age... Every global epoch in the history of the mankind is characterized by materials used in it. In 2004 a new era in material science was opened: the era of graphene or, more generally, of two-dimensional materials. Graphene is the strongest and the most stretchable known material, it has the record thermal conductivity and the very high mobility of charge carriers. It demonstrates many interesting fundamental physical effects and promises a lot of applications, among which are conductive ink, terahertz transistors, ultrafast photodetectors and bendable touch screens. In 2010 Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". The two volumes Physics and Applications of Graphene - Experiments and Physics and Applications of Graphene - Theory contain a collection of research articles reporting on different aspects of experimental and theoretical studies of this new material.

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