

REVIEW OF CVD SYNTHESIS OF GRAPHENE

Abstract: This article presents an overview of the research highlights in graphene synthesis by Chemical Vapor Deposition (CVD). We discuss the growth mechanisms mainly over transition metals and alloys (with emphasis on Cu and Cu alloys), including new developments and experiments in transfer-free graphene growth on dielectric materials. We focus on the role of the different synthesis parameters, including thermodynamic aspects of the chemical process and physical, chemical and morphological properties of substrate catalyst. We discuss the relation among these parameters and the properties of the as-grown graphene. Some important relations are reviewed and addressed to the influence of the fundamental parameters and methods on the synthesis of high quality graphene.

1. INTRODUCTION

Graphene, a two-dimensional, single-layer sheet of sp^2 hybridized carbon atoms, has attracted world-wide attention and research interest, owing to its exceptional physical properties, such as high electronic conductivity, good thermal stability, and excellent mechanical strength [1].

Since the discovery of graphene by K. Novoselov & A.K. Geim [2] the “top-down” exfoliation technique has been widely used to produce two-dimensional atomic crystals including not only graphene but also many other 2D materials, as BN and MoS_2 [3]. This process of producing graphene sheets has been found to be reliable and easy and has attracted the immediate attention of the scientific community. The best quality graphene, in terms of structural integrity, has been obtained by this method up to now. However, only flat graphene flakes (tens of microns in size) can be produced and the number of exfoliated layers is not easily controlled. As in most practical applications conceived for graphene, including microelectronics, optoelectronics (solar cells, touch screens, liquid crystal displays), graphene based batteries, super-capacitors and thermal control , large area and high quality with low structural defects graphene is needed [4] other methods should be developed. CVD synthesis route could have the answer to this complex question.

The preparation of graphite from heterogeneous catalysis on transition metals has been known for years. Independently of this, the first report on CVD synthesis of few layer graphene (FLG) was published in 2006 [5]. Since then, the CVD “bottom-up” synthesis has evolved to scalable and reliable production method of large area graphene. Synthesis of large area and high quality graphene has been demonstrated by this method [6,7]. But comparing CVD graphene properties to exfoliated graphene, the latter goes on exhibiting better quality so far.

Currently the growth and development of high quality, large-area CVD graphene on catalytic metal substrates is a topic of both fundamental and technological interest. Since the large-scale graphene films synthesized so far are typically polycrystalline, the research effort is aimed to control the domain size, the number of graphene layers, the density of grain boundaries, the defects and so on. For graphene materials to realize the promise of “graphene based applications”, it is clearly necessary to solve those problems, preventing defects in fabricated devices.

There are already several and recently published comprehensive reviews dealing with theoretical properties of graphene for electronics [8] and also with future applications of graphene and graphene based materials [9-16]. The revision we are involved is aimed at people interested in practical questions in the field of synthesis and catalysis of graphene and graphene based structures.

2. CVD SYNTHESIS AND GROWTH OF GRAPHENE

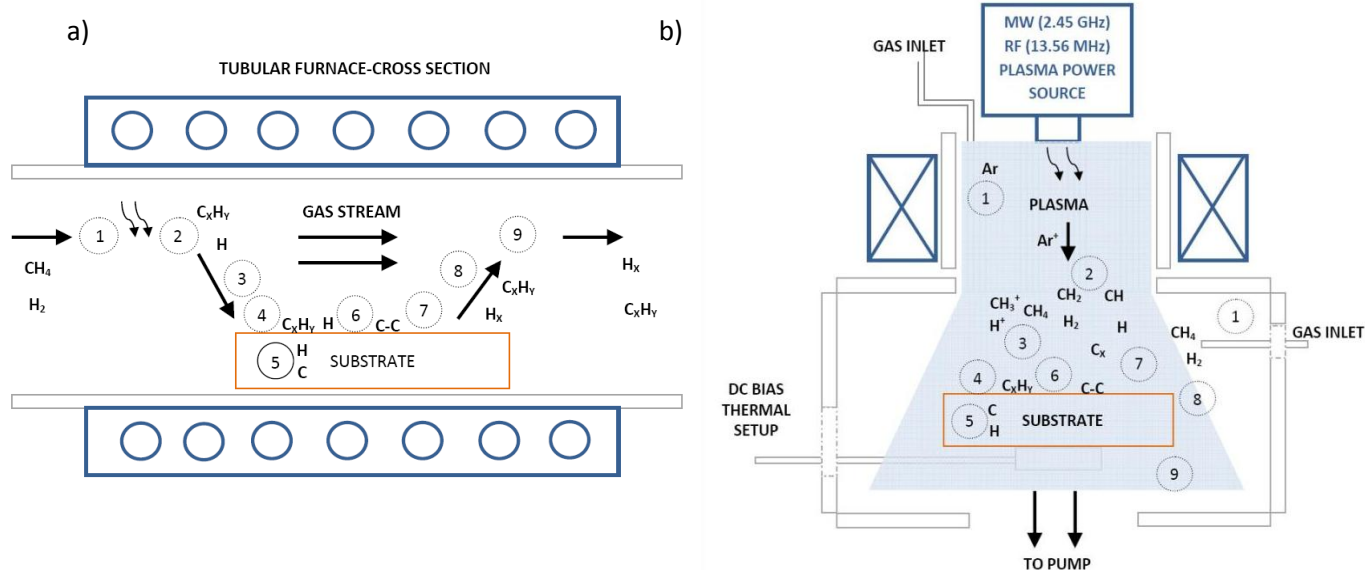
There exist comprehensive review articles and books dealing with generic aspects of the Chemical Vapor Deposition. Here we are only intent on describing elemental details of CVD applied to graphene synthesis. We encourage the readers to increase their knowledge with the fundamental aspects of Vapor Deposition Processes revisiting the cited references [17-23].

2.1. BRIEF DESCRIPTION OF CVD CHEMICAL REACTIONS AND PROCESSES

Chemical Vapor Deposition (CVD) involves the activation of gaseous reactants and the subsequent chemical reaction followed by the formation of a stable solid deposit over a suitable substrate. The energy that the chemical reaction demands can be supplied with the aid of different sources; heat, light or electric discharge are used in thermal, laser assisted or plasma assisted CVD, respectively.

The deposition process can include two types of reactions: homogeneous gas phase reactions, which occur in the gas phase, and heterogeneous chemical reactions which occur on/near the vicinity of a heated surface leading to the formation of powders or films, in each case.

Though CVD has been used to produce ultrafine powders, this review article is mainly concerned with the CVD of extremely thin graphene films. So heterogeneous chemical reactions should be favoured and homogeneous chemical reactions avoided during the designed experiments. **Fig. 1** shows a schematic diagram of a typical CVD process.



1. Transport of reactants by forced convection.
2. Thermal a) or plasma b) activation. Homogeneous gas reaction with particles and powder production should be avoided in graphene synthesis, controlling the kinetic parameters (P,T,n).
3. Transport of reactants by gas diffusion from the main gas stream through the boundary layer.
4. Adsorption of reactants on the substrate surface.
5. Dissolution and bulk diffusion of species depending on the solubility and physical properties of the substrate
6. Thermal activation mediated-surface processes, including chemical decomposition (catalytic), reaction, surface migration to attachment sites (such as atomic-level steps), incorporation and other heterogeneous surface reactions. Growth of the film.
7. Desorption of byproducts from the surface.
8. Transport of byproducts by diffusion through the boundary layer and back to the main gas stream.
9. Transport of byproducts by forced convection away from the deposition region.

Fig.1. Schematic diagram of Thermal CVD a) and Plasma Assisted CVD b) process: case of graphene from CH₄/H₂ mixtures.

2.2. PREPARATION OF CVD-GRAPHENE.

Chemical vapor deposition (CVD) of large-area single-layer graphene on metal films was explored widely in some respects up to now. Despite the significant progress, CVD graphene is a polycrystalline film made of micrometer to millimeter size domains. To date the graphene films grown on Ni foils or films did not yield uniform monolayer graphene. In most cases, a mixture of monolayer and few layers (polygraphene) was obtained. On the other hand, it was shown that Cu is an excellent candidate for making large area, uniform thickness (95%) single layer graphene films due to the low solubility of C in Cu [6]. It was suggested and even demonstrated that the graphene growth on Cu is somehow surface mediated and self-limiting.

2.2.1. PROCESSING STEPS

From a practical point of view, some critical steps have to be taken to get exposure of the catalyst surface to the gas precursors. One previous step is the substrate surface modification through cleaning processes, including chemical reduction inside the processing chamber. The detailed step by step process is basically as follows:

- **Heating step:** heating in controlled atmosphere the catalyst-substrate and gases (in hot wall reactors) up to the pre-process temperature.
- **Annealing step:** Maintaining the temperature and gas atmosphere so reducing the catalyst surface. This is the first chemical reaction of the whole process. It is performed to clean the catalyst surfaces and modify, as possible, the surface morphology including crystalline orientation, roughness (smoothing) and grain size of the metal catalyst. Metal evaporation should be avoided as possible.
- **Growing step:** Introduction of new precursors and growth of graphene over the catalyst substrate. During the growth process there are different strategies to growth the graphene film. There are one-step processes or many-step processes. During the steps is possible to modify the pressure or mix of gases, residence time, T, gas flow...It is important to take into account that depending on the nature of the catalyst (solubility, catalytic action and so on), the graphene may grow during this step or in the next one.
- **Cooling step:** After the growing step, the next step is cooling the reactor in proper atmosphere. The atmosphere commonly used is similar to that of the annealing or growing step, until the reactor temperature is under 200°C to prevent oxidation of the catalytic surface not covered or graphene functionalization with oxygen containing groups. When working with high solubility substrates, *cooling step dynamics is critical to control the growth* due to the solubility dependence.
- **Final step:** Backfill with inert gases (Ar, N) up to atmospheric pressure and open the reactor chamber.

2.2.2. GROWTH KINETICS AND REACTION MECHANISMS

Hydrocarbon based reactants, being methane (CH₄) the most mentioned, were commonly used as C source. Due to strong C-H bonds in methane molecule (440 kJ/mole) its thermal (non-catalytic or non plasma activated), decomposition (step 2 in fig. 1) occurs at very high temperatures (>1200 °C) [24]. This high temperature is not easily obtained in a typical thermal CVD setup. To reduce the temperature of methane's decomposition different transition metal catalysts (e.g., Fe, Co, Ni, Cu) were widely used. This catalytic behavior is observed when growing CVD graphene on metals at low temperatures (<900°C) in a greater or lesser extent. Therefore, non catalytic activation can be considered negligible working in thermal systems [25]. On the other hand, in the case of plasma assisted CVD, the activation and decomposition of gases prior to reach the substrate is effectively performed, but surface diffusion is a thermal-mediated process and plays a fundamental role in growth kinetics.

Growth kinetics

As the graphene synthesis process is a heterogeneous catalytic chemical reaction, the metal performs the two different roles of substrate and catalyst. Therefore, in a typical thermal catalytic CVD, the film grown over metal substrate reduces the catalytic activity due to the catalyst poisoning. This should announce the end of the reaction and the graphene film formation. If the overall process is performed on the surface (adsorption, decomposition and diffusion of molecules), monolayer graphene is preferentially grown. This is known as “self-limiting” effect and was only observed in Cu to date (and also depending on the process conditions). On Ni and other common transition metals (Co, Ru, Ir, etc.,) it was demonstrated that CVD growth of graphene occurs by carbon bulk diffusion due to the high solubility of carbon and segregation (fig.2) during cooling step. In this latter case, solid solution of a mixture of elements is formed near surface and the resulting graphene depends on the kinetic parameters selected for the synthesis. Among all the thermodynamic parameters, a fast cooling rate seems to be a critical factor to suppress the formation of multiple graphene layers [25, 26]. More complex deposition process results when an extra gas phase activation (decomposition by plasma or very high, >1200°C, temperature in fig. 2) is performed. In this case the chemical reaction evolves to a mixture of heterogeneous catalysis and decomposition in vapour phase. Then the reaction cannot be considered as totally controlled by the catalyst.

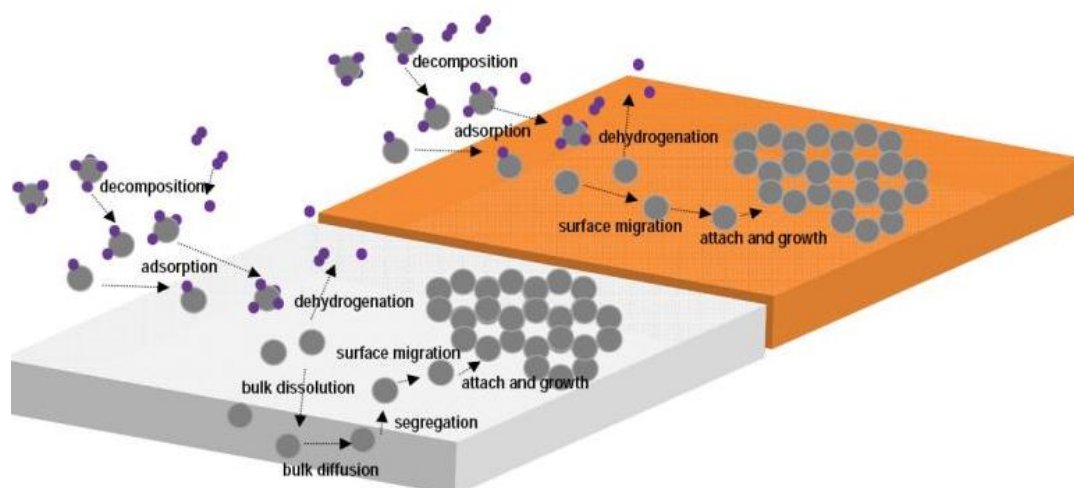


Figure 2. Growth kinetics in CVD graphene on different catalyst: Case of CH₄ on Ni and Cu.

The use of carbon isotope labeling technique in conjunction with Raman spectroscopic mapping [27,28] demonstrated effectively different kinetic behavior of CVD growth of graphene on Ni and Cu. By this technique was possible to track carbon during the growth process. The two different mechanisms of graphene growth observed on Ni and Cu can be understood from the C-metal binary phase diagram, being the most important difference that solubility of C in Cu is much lower than that in Ni. Only small amount of carbon can be dissolved on Cu. The source of C is mainly CH₄ that is catalytically decomposed (dehydrogenated in fig.2) on the Cu surface. This route facilitates surface migration and monolayer graphene growth. Experiments with high temperature cycles performed on graphene films of approximately 0.5 monolayer coverage on Cu while continuously imaged using LEEM (Low-Energy Electron Microscopy) confirmed this demonstration [29]. No C precipitation or island growth was observed during cooling in agreement with preliminary reports, suggesting that the process is confined to the surface, with negligible dissolution and precipitation of C from the substrate.

In contrast, Ni can dissolve much more carbon atoms. The graphene growth becomes mainly from the precipitation during the cool-down of the process and “polygraphene” was detected in most cases. One

opportunity for Ni is that the solubility and precipitation process can be controlled to some extent with the annealing, growing and cooling rates.

It is worthy of mention that, in the case of Cu it was published that not always the result is a graphene monolayer, there can also be a small fraction of flakes (few layers) stacked on the graphene film. To dispel doubts, termination of flake growth due to full coverage of Cu surface with graphene was observed, that suggests that the carbon species for flake growth had similar origin as those for the first graphene layer. [30, 31] One possible explanation for these small multilayer areas could be that the nature, composition and morphology of nucleation centers had an important role in the first stage of nucleation. Also is important to note that for the graphene layer in contact with the metal, the edge growth rate could be faster than the growth rate of the second and subsequent layers that may be attributed to a more difficult access of the species to upper- or lower- layers.

Reaction mechanisms

One explanation of reaction mechanism depending on the nature of the catalyst was already proposed, based on the spectroscopic ellipsometry experiments [32]. Primarily, the difference in the growth kinetics and mechanism between Ni and Cu was ascribed to the really different carbon solubility in Cu compared to Ni. But the mechanism shows more complex differences.

Graphene synthesis: reaction mechanisms

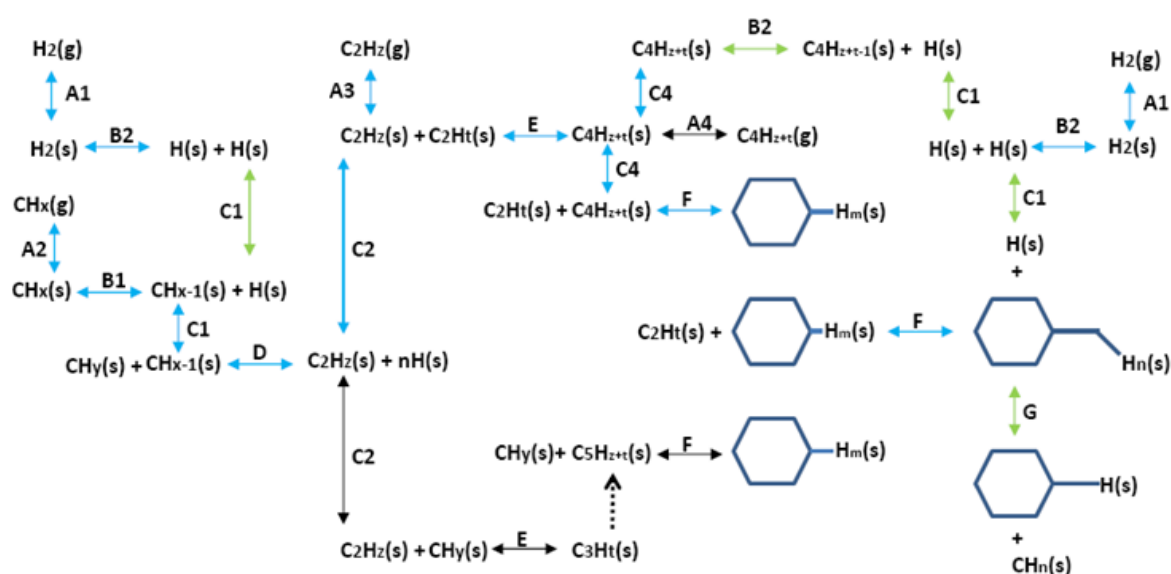


Figure 3. Reaction mechanisms in CVD graphene on transition metal catalyst. More probable (but not unique) reaction mechanisms in blue arrows and $z, t, m=0$. **Reaction type A: adsorption-desorption.** A1, A3 desorption favoured by hydrogen saturation on surface (from precursors). **B: dehydrogenation-hydrogenation.** Probable source for hydrogenation is molecular H_2 precursor. **C: surface diffusion or migration,** more favorable for dimers (C2). Dimers with high hydrogen saturation probably suffer desorption or cracking. **D: dimerization with or without simultaneous dehydrogenation - (cracking) decomposition [v].** Dimers with hydrogen are not stable at high temperatures. **E: polymerization- (cracking) decomposition.** **F: aromatization - decomposition.** More stable arm-chair edges. **G: decomposition of aromatics (hydrogen attack).** Reactions with hydrogen in green arrows.

A general picture of the reaction mechanisms during synthesis is shown in fig. 3. During annealing step, the catalyst surface is reduced by molecular hydrogen. At the end of this process the nude metal surface gets also exposed to hydrogen so, the first step to be considered should be the dissociative chemisorption

of H₂ on the metal surface, reaction (B2). At typical conditions of graphene synthesis, this process takes place on Cu and Ni surfaces with different trends. In the case of Ni is more probable for hydrogen to recombine and desorb from surface (reaction B2, A1) but this is not directly applicable for Cu that exhibits a much more hydrogen solubility [32, 47, 48]. In this case, saturation would be necessary to desorb molecular hydrogen from Cu surface. Therefore, before exposure of the catalyst to hydrocarbons a surface and/or subsurface partially covered with atomic hydrogen could be the starting point [46]. After exposure to hydrocarbons (diluted in molecular hydrogen in most cases) the next step to discuss is the competitive process between the dissociative chemisorption of H₂ and the physical adsorption and dehydrogenation of CH₄ on available surface sites (s) of the catalyst (Ni or Cu), according to reactions (A1-B2) and (A2-B1), respectively.

During next steps CH_x (CH₄) catalytic decomposition (dehydrogenation in fig 2, and reaction B1 in fig 3) takes place on the metal surface. The precise moment when the precursor dehydrogenation is completed remains an open question. According to theoretical calculations based on density functional theory (DFT) [35, 50,36] dehydrogenation reactions are probable to take place up to x=2 (fig 3) in the case of Cu, being the CH monomer dissociation the rate limiting step, difficult to complete. On the other hand, complete monomer dehydrogenation and carbon bulk diffusion is expected in the case of high solubility metals (Ni) even though CH dissociation has high activation barrier [49] even on steps [50] at the process temperatures. These monomers on Cu continue their path towards graphene nucleation, being dimer formation with simultaneous dehydrogenation a favorable reaction from an energetic point of view (reaction D, fig 3). According to first-principles calculations within density functional theory [37] C=C dimers are stable on all sites on Cu surface. Moreover carbon dimers containing hydrogen are very unfavorable on surface with low adsorption energies [39, 42, 43] even in defects [44] and desorb or immediately decompose even at very low temperatures [40, 45, 53] as demonstrated in Temperature-Programmed Desorption (TPD) and Thermal Desorption Spectroscopy (TDS) experiments [52]. Complementary studies of acetylene (CH≡CH) aromatization over transition metals also demonstrated that the benzene ring is not stable at the metallic surface [41]. Therefore, in the case of Cu, the reaction D with z=0 should be considered in carbon deposition, being this moment the most probable to complete the dehydrogenation and the formation of C=C bonds with sp² hybridization. Other routes that include carbon dimers, trimers and tetramers as a result of carbon atom by atom incorporation (reactions E,F in black fig 3) were also studied by DFT methods [51]. Important activation barriers were involved in this reaction path due to the formation of bridging-metal (BM) structures with energy barriers higher than dimers diffusion barriers and subsequent aromatization. To clarify the nucleation model on Cu (111) Riikonen et al., [38] emphasized the role of mobile carbon dimers during the growth of graphene on Cu. Several competing processes were taken into account, namely, (1) dimer formation, (2) dimer migration, (3) back dissociation of dimers into individual atoms, (4) migration of carbon along the surface and (5) migration of carbon atoms deeper into the bulk. On the basis of theoretical calculations, the processes (1) and (2) were found to be dominant. In detail, it was observed that the formation of carbon dimers was exothermic and that the migration barrier for the dimer to move on the Cu(111) surface was small (E_a = 0.27 eV). Once the dimer was formed, it cost more energy to dissociate the dimer than it to migrate around the surface. They also had shown how migrating dimers could form larger graphitic structures on the Cu (111) facet. Interplay of the substrate electronic states with the dimer σ_p-bonding orbital was observed: there should be an electronic factor that stabilizes the internal C–C bonding of the carbon dimer, while at the same time reducing its interaction with copper. This could be an important mechanism in driving the formation of stable and mobile graphitic rings and fragments on copper. Suitable selection of thermodynamic parameters during synthesis is crucial, that allow these surface carbon species to have lower chemical potentials than carbon in gas phase. Only in this way carbon graphitic rings could be stable at surface and could grow into larger graphitic structures up to graphene formation [35]. Once the nucleated graphene structure is stable at surface, further growth can be performed by attachment of carbon species onto graphene edges. Theoretical analysis of graphene edge reconstructions showed that C insertion into the front of a growing graphene patch must depend on the edge configuration. On Cu (111), a carbon dimer has lower formation energy than a

monomer. Armchair (ac) edges are also more stable than other edge possible configurations, and thus, the addition of C should occur preferentially (but not only) in the form of dimmers to armchair edges. After a C2 dimer diffuses to an armchair site and forms a hexagon on the pristine ac edge, the second hexagon then forms at an adjacent ac site by insertion of another C2 dimer [54].

3. TOWARDS HIGH QUALITY GRAPHENE: EFFECT OF EXPERIMENTAL PARAMETERS

CVD chemical reactions, graphene synthesis steps and growth kinetics aspects, have just been reviewed, but growth kinetics and reaction paths are not completely known, and more complementary experimental work should be performed to get to know the actual precursor decomposition routes in each case. The detailed knowledge of the growth kinetics and the reaction paths have proven to be of great importance when working on CVD synthesis. In this section, the fundamental factors that could have great influence on high quality synthesis of monolayer, bilayer or few-layer graphene films will be discussed. The correct synthesis parameters should be selected to achieve high quality graphene.

3.1. TYPE OF PRECURSOR MATERIAL.

Gas, liquid and solid precursors were used for graphene synthesis, [55] being mainly hydrocarbons and polymers (C and H based compounds). The fundamental question to bear in mind is that they are all suppliers of C and just before reaching the surface they are always in the gas phase. Therefore, a critical parameter in graphene synthesis is the energy needed to perform the whole process depending on the type of precursor. [36][34]. One way to reduce this energy demand could be the use of low C-H bond energy precursors, being other way the use of catalysts, not discussed in this section. Accordingly, a key parameter to take into account should be the dehydrogenation energy of the precursor (CH_x to CH_{x-1}). This is a highly endothermic process in the gas phase although on the metal surface, there is a significant reduction of the energy required, owing to the presence of strong M- CH_{x-1} and M-H interactions. [36]

As we have seen above, the decomposition (dehydrogenation) in gas phase can be performed by high temperature or plasma assisted processes. On the other hand, when the species are adsorbed the decomposition is a catalytic process. The gas phase decomposition, always performed before adsorption, was widely used in typical reactions in horizontal CVD quartz hot-reactors. But in some cases, as in CH_4 graphene synthesis, the effect of the thermal heating of the gas is negligible, so thermo-catalytic decomposition on metal surface is crucial. Later it will be discussed that currently in experimental work, plasma CVD (activation of gases with electromagnetic energy) combined with thermal heating of the catalysts is being widely used. Therefore, there are two possible routes in synthesis: gas pre-activation-dissociation before reaching the substrate or only thermo-catalytic decomposition (see figure 1).

3.1.1. GASES

Hydrocarbons

Methane (CH_4), ethylene ($\text{CH}_2=\text{CH}_2$) and acetylene (C_2H_2) being the dehydrogenation energies of CH_4 (410 kJ/mol=98.4 Kcal/mol), ($\text{CH}_2=\text{CH}_2$) (443 kJ/mol=106.32 Kcal/mol) and (C_2H_2) (506 kJ/mol=121.44 Kcal/mol) [56] were used as typical gaseous carbon precursors. The C-H bond energy is a key parameter to control the decomposition temperature and required energy. Methane, the most used, is highly stable saturated molecule so the dehydrogenation in the gas phase of CH_x to CH_{x-1} is highly endothermic, the calculated values being $\text{CH}_3\text{-H}$, 4.85 eV ; $\text{CH}_2\text{-H}$, 5.13 eV; CH-H , 4.93 eV); C-H , 3.72 eV [36]. On the metal surfaces, there is a significant reduction in these values and theoretical calculations explained that over some transition metals even exothermic dehydrogenation processes could take place.

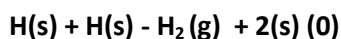
Hydrogen content

Hydrogen (H_2), were widely used in the cleaning and crystallization of the metallic substrates (annealing step), via oxygen reduction ($Mx-O$, $M-Ox$, oxides are always present in the catalyst surface). Molecular Hydrogen (H_2), used as diluent gas of the carbon precursor (typically CH_4 , various ratios of CH_4-H_2 have been reported in the literature) undoubtedly has to have a role in the graphene CVD growth. [57] As we have discussed in previous sections, its interaction with the substrate could affect the subsequent CH_4 chemisorption kinetics [32], i.e.,

- (i) H_2 and/or atomic H could diffuse into the catalyst depending on the solubility (metals of high hydrogen solubility and low surface diffusion) and compete with CH_4 for the initial physical adsorption;
- (ii) atomic H could create sites for sticking hydrocarbon and carbon radicals on the surface by subsequent H-abstraction reactions, removing hydrogen from the surface;
- (iii) hydrogen could passivate defects and grain boundaries, that were believed nucleation sites;
- (iv) atomic hydrogen could be active in the competition of CH_x deposition or C-etching, and
- (v) it could play an important role in the C sp^3 - sp^2 transition.

Indication of the important role of hydrogen in determining the graphene growth kinetics and in limiting the graphene thickness comes from previous observations such as that when the fraction of CH_4 with respect to H_2 is increased, the graphene growth on Cu is no longer self-limiting [58]. But the contrary has also been published (depending on other synthesis conditions) [59].

Another question that it is worthy to emphasize is the differences detected on the role played by hydrogen during the pretreatment and the whole process depending on the metal used (Cu or Ni). As an example, a reversible phenomenon with respect to hydrogen for Cu was observed. Hydrogen readily bulk-diffuses into Cu, and it out-diffuses to surface when hydrogen is turned off and pressure decreased but it does not desorb from surface, unlike Ni. This is consistent with different diffusion coefficients in Cu and Ni. At the typical growth temperature of graphene by CVD of approximately 900 °C, the in-diffusion coefficient of hydrogen in Cu is approximately one order of magnitude higher than for Ni, implying a lower hydrogen solubility in Ni than in Cu [33]. So the reaction (0) below is highly favored for Ni but not for Cu. So the role of hydrogen and its benefits or damages during growth remains an open question.



3.1.2. LIQUIDS

A recent publication reported the use of toluene and LPCVD to grow continuous monolayer graphene films at 500°C to 600°C on flat and electropolished Cu foils (after 980°C annealing) [64]. The consideration that motivated the choice of toluene, along with the fact that it is considerably less toxic than others as benzene, was its actually weak bonds. In this work, particularly it should be highlighted the results about the rectangular shape graphene domains. The authors related it to the hydrogen partial pressure of the reactor. Comparing the partial pressure of hydrogen reported in the literature and the partial pressure of these results, the higher the partial pressure of hydrogen, the easier the domain shapes tend to be equiaxed shape due to more sharp edges and corners of the graphene flakes etched. This means that sharp four or six lobe domains can grow under lower partial pressure of hydrogen and the hexagonal domains under higher hydrogen partial pressure. The partial pressure of hydrogen for growing rectangular domains that were observed was between them.

3.1.3. SOLIDS

There were published many experimental works dealing with the use of solid precursors in graphene synthesis. It was demonstrated that large area, high quality graphene can be grown from solids. Among these precursors, there are polymer films, small molecules, evaporated solids etc... Interestingly, even food, insects, and waste were used as solid carbon source to generate high-quality monolayer graphene. [60]

One first approach was the use of solid polymers (polystyrene) as the carbon source because of its relatively weak C-H bonds and low decomposition temperature [61]. The C-H bond in polystyrene is comparatively weak, with a bond energy in between 292–305 kJ/mol, much lower than that in typical gaseous carbon precursors such as methane (410 kJ/mol), ethylene (443 kJ/mol) and ethyne (506 kJ/mol). Varying H₂ flow and heating polystyrene up to 280°C, it is possible to grow hexagonal graphene domains (up to 1.2 mm) with low nucleation density 100 n/cm² in AP (Atmospheric Pressure) CVD.

Other example dealing with spin-coated poly methyl methacrylate (PMMA) and small molecules (fluorene (C₁₃H₁₀) and sucrose, table sugar, C₁₂H₂₂O₁₁) deposited on Cu at temperatures from 800°C to 1000°C were reported under LP (Low Pressure) CVD conditions [55]. It was found that the thickness of PMMA-derived graphene can be controlled—to give a monolayer, a bilayer, or a few layers—by changing the diluent gas flow rate. In the case of small molecules, although containing potential topological defect generators (the five-membered ring in fluorene) or high concentrations of heteroatoms (oxygen in sucrose), they also produce high quality pristine graphene [55]. Other substrates—such as Ni, Si (100) with native oxide, and 200-nm-thick SiO₂ thermally grown—were also tested. The Raman spectra confirm that Ni is an efficient catalytic substrate that converts PMMA into highly crystalline graphene. Under the same growth conditions, neither graphene nor amorphous carbon was obtained on Si or SiO₂ substrates.

Also Hofrichter et al. published the fabrication of graphene on silicon dioxide by solid-state dissolution of an overlying stack of a silicon carbide layer (50 nm) and a nickel thin film (500 nm) [62]. The carbon dissolves in the nickel by rapid thermal annealing. Upon cooling, the carbon segregates to the nickel surface forming a graphene layer over the entire nickel surface. By wet etching of the nickel layer, the graphene layer was allowed to settle on the original substrate. The SiO₂/Si substrate was annealed at 1100°C, 30 seconds in AP of Nitrogen. When cooled, the carbon segregates to the interface forming graphene layer resulting in few layer and monolayer mix (polygraphene). Further optimization to obtain larger monolayer coverage should be possible via carefully tuning the ratio of SiC to Ni film thickness in conjunction with an optimized cooling rate [63].

Homogeneous single-layer graphene can be growth by simply annealing crystalline Cu (111)/c-plane sapphire at 900 and 1000 °C, due to graphitization of amorphous carbon previously deposited on the surface or coming from furnace walls desorption [65]. But the published results confirm that only if sufficient carbon source is supplied, graphene can be formed, irrespective of growth temperature (800–1000°C) and nature of the metal, suggesting that the carbon supply is an important influencing factor of graphene nucleation. So, surface induced graphitization has not proved suitable for synthesis of high quality material.

3.2. SUBSTRATE

Since the metal exert a key role, as catalyst, in the formation of graphene layers, in this section we take a look at the critical issues concerning the substrate material. Chemical and physical properties, crystallography and morphology of the catalyst are reviewed. We address the differences due to the metallic or dielectric character of the substrates.

3.2.1. MATERIALS

Transition metals

The formation of few layered graphene resulting from industrial heterogeneous catalysis on transition metal surfaces has been known for years. The catalytic power of transition metals and some of their compounds is well known and arises from their partially filled d-orbitals or from the formation of intermediate compounds that favors the reactivity of the precursor gases. Therefore, catalysis by metals results from their ability to provide low activation energy pathways for reactions either by the facile change of oxidation states or formation of intermediate compounds.

The CVD method on transition metals such as Ni [66], Pd [67], Ru [68,70], Ir [69,70] and Cu [6] foils or evaporated films, revealed that the properties of the as-grown graphene films such as quality, continuity, and layer number distribution are dependent on the catalyst used. The different catalytic activity and solubility were detected to lead to different growth mechanisms.

Catalytic activity is related to decomposition of hydrocarbons on metals, which produces active carbon species and is a critical step lowering the activation energy for decomposition of precursor gases. As an example, the fact that graphene can grow on Pt at a relatively low temperature (750 °C) indicates that Pt has a stronger catalytic ability for CH₄ dissociation than Cu [71], which is consistent with reported theoretical calculations [36]. Pt also has a much stronger catalytic ability for H₂ dissociation to form active atomic H. The lower activity of Cu also compared to Ni and other transition metals in the catalytic dissociative chemisorptions of CH₄ can be rationalized considering that it occurs by the electron transfer from the C–H bonds to the 3d orbitals of the catalysts, with Ni having two 3d unpaired electrons and Cu having only one unpaired electron available for the interaction (Cu has electron configuration [Ar]3d¹⁰4s¹, since an electron passes from the 4d-orbital to 3d to generate a filled 3d electron shell, which is the most stable configuration) [32]. Copper has not been observed to form any carbide phases, so the low reactivity with carbon could be attributed to the fact that copper has a filled 3d-electron shell, the most stable configuration (along with the half filling 3d⁵) because the electron distribution is symmetrical which minimizes reciprocal repulsions [30].

The carbon solubility also revealed as a key parameter to control the growth of graphene over metals. Different growth kinetics were proposed depending on the solubility of the catalyst. Also the growth conditions determine the deposition mechanism defining the morphology (domain size and boundaries) and thickness of the graphene films. Cu, e.g., has very low carbon solubility compared to Co and Ni (0.001–0.008 weight % at 1084 °C for Cu, 0.6 weight % for Ni at 1326 °C, and 0.9% weight for Co at 1320 °C).

As a result of the low solubility and low catalytic activity, Cu can form only soft bonds with carbon via charge transfer from the π electrons in the sp² hybridized carbon to the empty 4s states of copper [14, 71,72]. This combination of very low affinity between carbon and copper along with the ability to form intermediate soft bonds could facilitate graphitic carbon formation. As the 3d⁷ and 3d⁸ orbitals of Co and Ni are between the most unstable electronic configuration (Fe) and the most stable one (Cu), it could be postulated that the most suitable catalysts for graphitic carbon formation are those transition metals that have low affinity towards carbon but that are still able to stabilize carbon on their surfaces by forming weak bonds [14].

Previous results of growth on polycrystalline Ni [66,74,75] and Cu [6] substrates triggered interest in graphene synthesis by CVD for large area deposition. In the case of Ni, the fundamental limitation was that polygraphene was mainly obtained. This lack of control over the number of layers was partially attributed to the fact that the segregation of carbon from the metal carbide upon cooling due to high solubility (~0.6%), occurred at different rates within the Ni grains and at the grain boundaries [73]. There

are some reports [63] of graphene films composed mostly of one or two layers of graphene grown by controlled carbon precipitation on the surface of polycrystalline Ni thin films during atmospheric (CVD). Controlling both the methane concentration and the substrate cooling rate during growth can significantly improve the thickness uniformity.

In contrast to Ni, uniform deposition of high quality, single layered graphene over large areas was recently achieved on polycrystalline copper foils [6]. The initial [6] and subsequent follow-on [7] studies demonstrated the growth of single layered graphene over areas as large as 30-inches with 95% coverage of monolayer graphene. CVD growth of graphene on Cu is generally attributed to thermal decomposition of hydrocarbons on the surface and the subsequent surface diffusion of carbon atoms due to the low solubility of carbon (<0.001 at.%) in Cu. Furthermore, thin copper foils are inexpensive and can be easily etched with solvents available in most laboratories so that transfer onto desired substrates can be readily achieved.

A recent publication [71] claimed the growth of millimeter-sized hexagonal single-crystal graphene flakes and graphene films on single crystal and polycrystalline Pt by ambient-pressure CVD. In this case, single-crystal Pt substrate showed similar growth behavior for graphene as that on polycrystalline Pt. Solubility of carbon in Pt is high, 0.9% in weight, so growth temperature of lower than 800°C was enough for graphene nucleation. Low CH₄ concentration was used because the size of the graphene grains was related with this parameter. Single crystal grains of a perfect hexagon shape with very smooth edges and lateral size of up to 1.3 mm were obtained at 1040°C.

Compared to Cu or Ni catalyst systems, Fe is favorable in terms of low cost. However, there were only a few studies in this area maybe due to the complex Fe–C phase diagram that also offers great versatility [76]. Lowering T^a below 912 °C results in phase transformation of the Fe-C binary mixture to body-centered cubic alpha-ferrite and a decrease in the solubility of C, due to the eutectic phase formation at 727°C with a very small solubility of about 0.022 wt%. In this case, few-layer graphene were grown by APCVD with CH₄. The layer number distribution were tuned by varying the procedure of heating/cooling temperature, cooling rate and CH₄ flow rate.

Metal-catalyzed crystallization of a-C to graphene by thermal annealing (deposition of a layer of a-C, 2.5–40 nm thick by electron-beam evaporation on Si-SiO₂ substrates, followed by nickel or cobalt metal thin film, 100–300 nm deposition) was also performed [77]. These samples were annealed at 650–950°C using a tube furnace under argon flow.

In conclusion, up to now the best approach to control the number of layers via metal catalysis was the monolayer growth on very low solubility metal, as Cu, since it was quite difficult to control the growth of monolayer graphene via fast cooling processes on high solubility metals (Ni). It was also observed a lack of control in growing bilayer graphene, which is actually important because bilayer films seem to be the most useful in electronic applications.

Metal Alloys

Cu-Ni

Recently, more experimental efforts were made with the intention of controlling the number of layers of nucleated graphene films that would be a real breakthrough. Thin Ni films and fast-cooling processes were used to hinder carbon precipitation. Not uniform graphene but polygraphene with only monolayer regions and a wide range of thicknesses was grown by these methods. It was widely observed that monolayer graphene grows on the “flat” dimension boundaries of the metal grains while multilayer

graphene ($n > 3$) preferentially forms at the metal grain boundaries. This lack of control was the main reason to study the growth of graphene on metal alloys.

Since Cu and Ni are well-known binary isomorphous systems, Cu-Ni alloy is an ideal system which has moderate as well as controllable carbon solubility by tuning the atomic fraction of Ni in Cu. To elucidate the behavior of these binary systems, Robinson et al., [79] studied Cu-Ni foils (90/10% in weight) from the catalyst point of view. Ni surfaces are more catalytically active than Cu surfaces so the rate of dissociation of the hydrocarbon precursor should be much higher on the alloy than on pure Cu surfaces. In principle, this could mean lower graphene growth temperatures. Nevertheless, relatively small, 100 μm , substrate grains were observed for the 90/10 Cu–Ni foils annealed at 1050°C. Therefore, either much longer annealing times or higher annealing temperatures are needed to grow centimeter sized substrate grains. In addition, an experimental study of the equilibrium surface composition of Cu-Ni alloy substrates by Sakurai et al. [80] found strong Ni segregation for Cu rich alloys, which may enhance the catalytic activity further.

Growing experiments with different atomic fractions were also performed. A cold-wall chamber (8 Torr pressure and 100% CH_4) were used [78] to obtain monolayer, bilayer, and multilayer graphene as well as ultrathin graphite on commercial polycrystalline Cu-Ni (31.00% Ni, 67.80% Cu). In this case, the foil showed millimeter grains size after annealing. Different cooling rates (5 or 100 $^\circ\text{C}/\text{s}$) and temperatures (930°C to 1030°C) were used. The observed uniformity of monolayer graphene on this Cu-Ni alloy surface was much better than the reported results on polycrystalline Ni up to now.

Liu et al. [81] reported a facile segregation approach for this purpose using Cu-Ni mixtures with different percentages. Bulk nickel generally contains a trace amount of carbon species, which can be brought into the thin Ni film during electron beam deposition process. A sandwiched structure of Cu(370 nm)/Ni(20–130 nm)(C)/ SiO_2/Si , where the Ni layer was used as the carbon source (carbon content about 2.6 at%) and the Cu layer was employed as a favorable segregation medium was grown. To date over 95% monolayer and 91% bilayer graphene films were prepared by only changing atomic percentage of Ni in Cu-Ni alloy. For a Cu-Ni alloy having 5.5% Ni component, monolayer graphene occupied over 95% of whole film. When Ni component in the alloy was increased to 10.4% the segregated film was dominated by bilayer graphene over 89%. Further increasing the Ni percentage lead to thicker graphene.

Ni-Au

One more novel experiment was performed by Weatherup et al. [82]. This group was working in the design of alloy catalysts for low temperature synthesis of graphene. They showed that alloying polycrystalline Ni with Au (Ni films ~ 550 nm thick on $\text{SiO}_2(300 \text{ nm})/\text{Si}$ substrates covered with various thicknesses of thermally evaporated Au up to 10 nm) allows MLG CVD at temperatures of 450°C with reasonable crystallinity and domain sizes. This low-temperature would be compatible with back-end CMOS integration. AP, scalable chemical vapor deposition of predominantly monolayer (74%) graphene films with an average D/G Raman peaks ratio of 0.24 and domain sizes in excess of 220 μm^2 was demonstrated. The Au alloying thereby drastically lowered the graphene nucleation density, allowing more uniform and controlled growth and highlighting the role of step edges. They also found that 3–5 nm Au gave the best graphene uniformity with regards to their CVD reference conditions with thicker Au layers leading to more inhomogeneous graphene layers. One drawback could be the preannealing that should be applied at higher temperatures to mix the alloy, although one advantage could be that mixing can be promoted by metal co-deposition.

Dielectric substrates

Generally CVD graphene is transferred onto a desired substrate for further applications. Thus, it is of great interest to directly prepare continuous graphene films on dielectric substrates such as BN, Si, SiO₂, Al₂O₃, GaN, MgO, Si₃N₄ and so on. Considerable efforts were made to directly grow graphene films on these substrates, [83-88] but so far continuous and highly conductive films were very difficult to synthesize. Important applications were reported for the replacement of conventional transparent conductive films (TCFs), including In₂O₃:Sn (ITO), SnO₂:F (FTO) and so on for graphene films. However, the highest efficiency achieved in solar cells was only 4.17%, [89] which can still not compete with conventional solar cells.

There are some examples of experimental work on the synthesis of graphene over dielectric substrates. Bi et al. [90] reported the direct growth of graphene films on dielectric substrates by ambient pressure CVD (APCVD) at 1100–1200°C using a gas mixture of methane (CH₄), hydrogen (H₂) and argon (Ar). It is important to mention that at 1200°C over BN, Si, SiO₂ and AlN substrates, not monolayer but few-layer graphene growth were reported.

Other singular approach was the direct chemical vapor deposition of a single or few-layer graphene film on dielectric surfaces via a sacrificial copper film [91] by Ismach et al. Working on the CVD growth of graphene on micrometer-thick copper foils they noticed that a significant amount of the copper evaporates and deposits at the edges of the fused silica tube used in the CVD.

Considering the melting temperature of the copper, ~1084°C, along with the high temperature during the growth, ~1000 °C, and the low pressure in the chamber, 100-500 mTorr, the significant evaporation of the metal is not surprising. They proposed that if long processing time is used (up to 300 min) the Cu film can evaporate completely. This CVD few-layer graphene exhibits the characteristics similar to that of turbostratic graphene, that is, lack of long order in the perpendicular direction. The results showed that the continuity of the metal film on the surface depends on its thickness, the metal-dielectric wetting properties, and the heating temperature and time. Typically, 100 to 450 nm thick Cu films on quartz and other insulating substrates were used. After the initial heating, the dewetting and evaporation rates of the metal decreased, presumably, due to the graphene growth that increases the coverage of the copper surface. Single to few-layer graphene film was obtained, but the film was highly defective and composed of thicker graphitic-like material and highly damaged graphene layers.

In conclusion, up to now many approach to control the number of layers via metal alloys catalysis were performed. There were some important advances on this subject with controlled few layers growth over alloys catalyst. Nevertheless, physical, optical and electronic properties of these films still have to be necessarily improved. Also it would be highly desirable to directly growth graphene layers on dielectric substrates. More experimental work should be performed in these areas for graphene to be competitive on practical applications.

3.2.2 CRYSTALLOGRAPHIC STRUCTURE OF METAL SURFACE

In the choosing of the catalyst, other parameters more than the material or chemical nature have to be taken into account. Crystal structure, texture, mono and polycrystalline character and the evolution of the surface morphology during synthesis, among others, were demonstrated to be critical aspects for graphene nucleation and growth.

Single crystals, polycrystals and grain size

There are examples of experiments where, even on a single metal grain (single crystal) different orientations of graphene domains were observed [92]. Moreover, in a recent work of Gao et al [71], they observed that a single-crystal Pt substrate showed similar growth behavior for graphene as that on

polycrystalline Pt. Nevertheless, the size and orientation of the metal substrate grains were expected to have a large impact on the defect density of the graphene films grown by the dissociation of hydrocarbon molecules on metal substrates. The larger the grain size the higher-quality graphene films were demonstrated [7].

Crystal structure orientation, texture and lattice match

Graphene has a hexagonal-honeycomb lattice character in surface. Regardless of graphene can grow on several hexagonal or other crystallographic surfaces, growth on hexagonal substrates was frequently referred to as “epitaxial” even if significant lattice match was absent between the graphene and the substrate. Lattice mismatch of less than 1% is present on Co (0001) and Ni (111) surfaces. In contrast, lattice mismatch between graphene and Cu(111), Pt(111), Pd(111), Ru(111) and Ir(111) is >1% [14]. For systems with only a small lattice mismatch, a strong interaction can result in a pseudomorphic growth resulting in a large coincidence lattice and a “Moiré pattern” type of growth as a result of different rotational alignments [94].

In the case of copper, the role of Cu orientation and lattice mismatch was also more important than expected after the preliminary successful experimental results on polycrystalline Cu (100) foil surface [6]. A detailed study of the as-grown graphene showed that graphene had distinctive four-lobed islands and substantial in-plane rotational disorder [29]. The in-plane orientations were around two crystallographically equivalent Cu directions, a consequence of placing the sixfold graphene on the fourfold Cu (100) substrate. Furthermore, each nucleation site typically generated four graphene crystals, each with a different in-plane orientation. Island morphology was strongly determined by substrate temperature.

More recent works demonstrated that although Moiré patterns were observed on both Cu(111) [93] and Cu (100) [65], the hexagonal lattice of Cu(111) favored the high quality of as grown graphene. There were observed two predominant Moiré patterns in Cu(111) which could suggest that the graphene have preferred orientations with the underlying Cu(111). The results observed comparing the different orientations led to speculate that graphene could prefer nucleation on Cu(111) crystal plane than Cu(100) and (110), because of the similar crystallographic geometry in Cu(111) reducing so the nucleation barrier, since the lattice mismatch between graphene and underlying metal causes an additional energy cost.

Zhao et al. [94] also investigated the influence of the surface structure of single Cu crystals in UHV from ethylene at 900°C. The over graphene had a hexagonal superstructure (Moiré) on Cu (111) and linear superstructure with a periodicity of 11 Å and an angle of 0° on Cu(100) square lattice. The graphene film properties were confirmed to be much poorer on the Cu(100) surface when compared to the Cu(111) surface.

Wood et al. [95], using different characterization techniques, found that substrate crystallography affects graphene growth even more than facet roughness. They determined that (111) containing facets produce pristine monolayer graphene with higher quality and growth rate than (100) containing facets, especially in Cu (100). This could be attributed to the high diffusion [93, 94] and improved adsorption of carbon-containing species on Cu(111) [96]. Since Cu(111) is the lowest-energy Cu surface,[97] longer pre-growth annealing treatments under Ar/H₂ flow at 900 °C could help for the production of Cu(111) facets on the polycrystalline Cu substrate. So, engineering Cu to have (111) surfaces is expected then to cause monolayer, uniform graphene growth.

Recently, “Orientation-controlled growth of graphene” was performed by an epitaxial CVD approach using heteroepitaxial Co,[98] Ni,[99] Cu,[100,101] Ir,[102] and Ru[103,104] films deposited on single-crystal sapphire (α Al₂O₃(0001)) or MgO (111) substrates. This approach gave as a result crystalline metal films

suitable for large-area graphene growth with much lower cost than single crystals, not only for low carbon solubility metal like Cu but also for Co and Ni whose carbon solubility is high. Ogawa et al. [105] compared domain structures of large-area, in single-layer graphene films grown on heteroepitaxial Cu(111) and (100) films both deposited by magnetron sputtering on single-crystal MgO(111) and (100) substrates, respectively. It was demonstrated that domain structure and size, as well as the orientation were strongly influenced by the Cu crystalline plane and that the Cu(111) was preferable for the orientation-controlled graphene growth. Graphene was epitaxially formed on Cu(111)/MgO(111) but graphene/Cu(100)/MgO(100) showed a more complex LEED pattern where graphene covered the Cu surface with two preferential [10] orientations with angles of $0 \pm 2^\circ$ and $30 \pm 2^\circ$ with respect to the underlying Cu[011] lattice. LEEM measurements for the as-grown single-layer graphene on Cu(100) also showed that the as-grown graphene possessed a clear multidomain structure with patches of small domains.

In conclusion, it is worth to mention that even though in some experiments different orientations of graphene domains on a single metal grain were obtained, the hexagonal lattice of Cu(111) favored the high quality of as grown graphene. Moreover, during the CVD heteroepitaxial growth on Cu(111), the orientation of graphene nuclei became well controlled with domain boundaries atomically connected. This could represent a new alternative. Therefore, it could be advantageous to develop techniques for producing foils of these materials with a (111) surface texture.

3.2.3. THICKNESS, ROUGHNESS AND MORPHOLOGY

Thin films and Foils

Standard processes in Si technology include, among others, the deposition of Cu and Ni thin films on Si substrates and wafers. The evaporation of metals is performed in HV systems and is not a cheap process to manage in lab research. Therefore, a lot of lab research in graphene synthesis was performed using different catalyst configurations as thin foils (up to 25-30 μm thick). These foils were cheaper than films deposition processes and all the processes developed on foils can be translated easily to thin films and their standard processes. Another advantage is that foils are flexible and even though their initial high roughness, it is also well known that annealing the foil metal can lead to very large grain size, with a flattened surface that rivals or even exceeds the flat surfaces typically obtained by cutting and polishing single crystals. After a typical annealing process, the spaces between single atomic steps in the case of Cu are often greater than 100 nm, indicating surface normal less than 0.1° from the [100] azimuth. [29].

It is worthy of mention that the lateral dimensions of the Cu grain boundaries were observed to vary with the annealing pre-treatment time and also with the Cu foil thickness [14]. H_2 embrittlement of Cu could also limit diffusion and minimizes grain growth during annealing.

In this connection, the pioneering work of large area graphene growth on Cu foils [6, 31,59] developed in low pressure (LP) CVD at 1000°C from CH_4 and H_2 mixtures on foils of various thickness (12.5, 25, 50 μm) to check precipitation mechanism, did not show evidence of differences in graphene quality. Moreover, the cheap copper foils revealed ideal for large area graphene synthesis, up to 30 inch demonstrated [7]. On the other hand, it is commonly accepted that commercial Cu foils are (100) textured after annealing (and due to the cool rolling fabrication process) and as seen above, the crystallography strongly affects the graphene growth. Pregrowth low-energy electron diffraction (LEED) analysis of the Cu surface also showed that annealing resulted in a (100) texture in the foil plane [29].

Returning again to standard processes, in high performance electronic devices, the graphene must be electrically isolated from its surrounding environment. In the case of copper, this is generally achieved by etching the underlying metal substrate, with subsequent transfer to an insulating substrate, such as silicon oxide [6]. However, such a layer transfer process is non-ideal for nanoelectronic applications due

to microcracking and the potential for interfacial contamination between the graphene and the substrate. Levendorf et al [106] demonstrated a transfer-free process for fabrication of CVD graphene transistors. Instead of utilizing a bulk copper substrate, an evaporated copper film on an oxidized silicon wafer was grown. One problem with the evaporated Cu/SiO₂/Si system is that, although stable at temperatures <800°C, it was unstable at the temperature used on the synthesis. One approach to ensuring stability at the Cu/SiO₂ interface could be to minimize the graphene synthesis temperature. Another approach presented evidence of significant Cu-Si interdiffusion during graphene synthesis and evaluated the use of metal and insulating diffusion barriers as a means of prevention at the Cu/SiO₂ interface [107]. Diffusion barriers (W, Cr, Ni, Al₂O₃, HfO₂, SiN_x) were demonstrated to reduce interfacial diffusion, but often the Cu/Si interdiffusion was not completely suppressed. To solve this, instead of using a similar process to grow on freestanding foils, the pre-growth annealing of the foil at a lower T (typically 700°C) was carried out to achieve Cu grain growth, that also minimized the copper evaporation occurring at high temperature. Moreover, excessive exposure to high temperatures can result in the formation of voids in the copper film and decomposition of the film into islands.

Another reason for using thin films, mostly in the case of Ni and other metals with high solubility, was that the large amount of carbon sources absorbed on nickel foils usually formed thick graphite crystals rather than graphene films [66,108]. To solve this problem, very thin layers of nickel of thickness down to 300 nm were deposited on SiO₂/Si substrates using electron-beam evaporators. It was demonstrated that very thin films and rapid cooling proved critical in suppressing formation of multiple layers.

Macro-roughness and morphology

It was often found that the topography of the surface strongly affects the uniformity of grown graphene. Also it was widely discussed that the purity of the film determines the number of layers, mainly at low pressure conditions [30]. Luo et al., [109] published that the use of very flat, electropolished Cu catalyst surface and extremely low methane concentration enables the growth of a very uniform graphene film. Boundary structures of the standard Cu foil led to thickness variations in the graphene film. Raman measurements of the graphene film regions that replicate the Cu grain boundary regions revealed carbon atoms in disordered sp³-bonded networks in these areas. The correlation of graphene thickness variation with the topography of the catalytic Cu foil motivated the idea that smoothing the Cu through polishing would lead to more uniform and better quality graphene. Moreover, first principles calculations indicated that, in contrast to graphene growth on other metals, Cu-catalyzed graphene nucleation was particularly favoured at surface irregularities (i.e., metal step edges and other defects) but also occurs over the flat regions [110]. Therefore, nucleation was also found to proceed readily on the crystal plane and to be favoured at high partial pressures.

Micro-roughness, boundaries, step edges

It was published in theoretical works that carbon binds stronger at the step edges than on the terraces for transition metals as Ni, Co, Ru, and Rh [111]. Even with full coverage along the step edge, carbon still binds most favorably to the step sites [112, 113, 114]. Metal atomic step edges were also demonstrated to be important for graphene island nucleation in the case of Cu, but not unique and in some cases not the most desired.

Regarding this, Wofford et al., [29] published that the minimum temperature of ~790 °C is sufficiently high to induce significant motion of Cu steps due to sublimation on Cu (100) foils in LP CVD. Real time observations during synthesis demonstrated at high temperatures above 960°C, that the surface of each Cu grain consists of a propagating array of monolayer-height steps before growth. Subsequently, when a segment of a Cu step edge collides with a growing graphene island, it decelerates and incoming step

edges become bunched under the graphene. As a consequence incoming steps wrap around under the interior of the four-lobed graphene island. This process creates four-lobed Cu hillocks draped by graphene. Indeed, at very high temperatures surface roughening can be so dramatic that individual hillocks can be easily visible with an optical microscope. While single Cu step edges was not observed to have a perceptible effect on the growth, large bunches were observed to distort island evolution, to induce rotational disorder by altering growth trajectories and to decrease the graphene quality.

In the case of graphene islands grown on Cu (111) in UHV conditions it was also observed that Cu (111) step bunches led to rotational disorder in two ways [115]. First, they can cause islands to be nucleated with different in-plane orientations. Second, step bunches can generate new rotational boundaries as islands expand. Change of island orientation was observed when crossing a step bunch. Thus, fewer step bunches led to fewer rotational boundaries, consistent with the work of Zhao et al. [94] These high angle rotational boundaries could be minimized using higher growth temperatures in this Cu(111) case.

The tendency to introduce rotational boundaries during growth differentiates Cu (111) and (100) from other surfaces. For example, graphene sheets were observed to grow without changing orientation across boundaries between rotationally misoriented Ru (0001) grains [116] and even across different facets of Ni grains. It is worthy of mention that temperature and pressure dependence of this processes have to be taken into account. As we discuss below, compact hexagonal shapes were observed in high-pressure CVD by several groups. The carrier and carbon-source gases in CVD suppress Cu evaporation so that a higher temperature can be employed compared to that used with UHV growth. At high temperatures in UHV experiments, the surface morphology is evolving quickly due to sublimation, causing large step bunches to collect at graphene edges. Rearranging these step bunches is likely difficult, impeding the processes that lead to hexagonal shapes. Therefore, pressure and temperature seem to have a critical role in evaporation and propagation of metal atomic steps.

Other defects and impurities

It was observed that graphene initially nucleates on the Cu surface impurities, imperfections, step edges and grain boundaries. So, reducing the density of nucleation sites can effectively increase the graphene domain size [65]. It was also observed that the type of nucleation site can affect whether the graphene island was single crystal or not [29] that gives rise to a mean grain number much smaller than the nucleation density. Polycrystals are preferentially formed on defective nucleation sites whereas single crystals do preferentially at the less defective regions. On Cu (111), single crystal graphene firstly nucleated inhomogeneously at defects such as steps, step bunches, and impurities [115] but changing to proper synthesis conditions can lead to secondary single crystal nucleation, more difficult to achieve because of the more difficult nucleation on less defective regions. The metal purity was considered as a meaningful aspect to yield higher quality graphene. It was published that higher purity copper foils (99.999%) yield higher quality graphene with room-temperature mobility closer to those reported for exfoliated graphene [117]. Kalbac et al. [28] suggested that the graphene growth begins by the formation of a multilayer cluster due to complex defects or polycrystalline impurities. This seed was observed to increase its size but the growth speed of a particular layer depends on its proximity to the copper surface.

Liu et al., [30] found that the purity of the Cu film clearly determined the number of synthesized graphene layers at low pressure conditions. Multilayer graphene was observed to nucleate from the impurity clusters and merge into a 1–2 layer graphene film away from the nucleation centers.

The above discussion reveals that it is crucial to reduce the number of imperfections, roughness and impurities and make the surface as uniform as possible to obtain high-uniformity graphene on Cu. It is clear that the roughness and imperfections initially enhance graphene nucleation, but also defective graphene later. It is also possible that the impurity atoms in the bulk diffuse to the Cu surface during annealing. These surface impurities dramatically enhance the catalytic capability of Cu resulting in high

concentration of carbon atoms that are decomposed from precursors. Hence, it can be concluded that the purity of Cu surface plays a critical role in determining the number of graphene layers.

3.2.4. SEEDED GROWTH AND CONTROLLED NUCLEATION

Recently, new approaches dealing with pre-patterned graphene seeds were investigated. Substrate surface seeding was a common surface pretreatment method used to modify and control the surface nucleation density and the growth rate of diamond films [118]. In the case of diamond, powder or particles littered on the substrate surface, were used as the predominant nucleation sites and the material gradually was grown owing to the C ad atom concentration.

In the case of graphene on Cu, these new experiments were performed in different ways, either using seeds of prepatterned multilayer graphene flakes or controlling nucleation by locally providing a high concentration of carbon. In the former method [119] however, an extra CVD process was firstly required to obtain a continuous multilayer graphene film on Cu used for the following lithographic patterning of the growth seeds (multilayer graphene). In the latter method [120], polymethylmethacrylate (PMMA) was used as a carbon source for enhancing local nucleation. This latter method demonstrated controlled graphene nucleation and synthesis of single crystal graphene arrays and offered a promising route to fabricate graphene-based devices free of grain boundaries and with more reliable performances. Atmospheric pressure CVD (APCVD) was used in this method. Occasionally, polycrystalline islands or few-layer domains, nucleated and grown from one single such nucleus, were also observed.

Some experiments with highly oriented pyrolytic graphite (HOPG) flakes as seeds transferred to the Cu foil surface, simply by pressing against the patterned HOPG were also performed. After the CVD synthesis, a preferential nucleation of graphene on HOPG sites was also observed. However, due to the roughness and flexibility of the surfaces of those thin Cu foils, transferred graphite flakes differ significantly in size, thickness and shape affecting graphene growth. In addition, it was nearly impossible to fabricate well-defined arrays by the pressing method.

This seeded growth could be a very interesting alternative for high quality and performance graphene layers with applications in several fields. Nevertheless, very high complex processes with important economical implications are involved.

3.3 THERMODYNAMIC AND KINETIC PARAMETERS

Pressure and temperature revealed as key factors during graphene growth. Other dynamic factors, such as gas flow and gas residence time inside the processing chamber, also play important roles that will be reviewed in this section. We will also refer to other important aspects of the synthesis such as plasma assisted deposition and different time profiles during all the steps of the graphene deposition.

3.3.1. PRESSURE

Vacuum level prior synthesis should be minimized to the limit in order to get high purity layers. The lower the base pressure of the reactor, the lower density of impurities and residual oxygen may remain. Working in low pressure CVD, a few mTorr vacuum level has been commonly used. On the other hand, recipes with diluents (H_2) of the precursor gases have been proposed for reducing residual oxygen during annealing and growing stages of the synthesis.

Up to now, a lot of experimental work was published in a extensive pressure range, HV (High Vacuum, 10^4 - 10^6 Torr), LP (Low Pressure 0.1-1 Torr) and AP (Atmospheric Pressure). It was possible to grow-graphene with acceptable quality in all ranges, but great differences in graphene domain size and morphology were

observed. In LP CVD flower like-four to six lobed structures were commonly grown [6, 59]. In contrast, in AP CVD, hexagonal structures of graphene were synthesized [121]. Concerning the domain size, both cases offer graphene flakes near millimeter size and continuous monolayer films when using Cu catalyst. Bhaviripudi et al., [121] studied, under the same experimental setup, the role of the total pressure on Cu. The results revealed that even though the thermodynamics of the system remains the same, whether the process was performed at AP,LP or under UHV conditions, the kinetics of the growth phenomenon was different.

Although in LP, monolayer graphene was grown (up to 95% monolayer coverage), in the case of AP growth, results varied from a monolayer at lower methane concentrations (parts per million concentration) to multilayer domains with a monolayer graphene background at higher methane concentrations (5-10% by volume). This seems to indicate that either the growth was not self-limiting under higher methane concentrations or only partial coverage was achieved. This lack of control over the number of layers and the different domain shapes promoted further investigations performed to determine the detailed growth mechanism.

The more exciting difference between LP and AP maybe, the morphology and shape of the graphene domains, already were extensively studied in real time LP experiments [29, 115]. In the case of AP the tendency for the graphene grown into AB Bernal few-layer hexagonal stacks was also studied [122]. It was discussed that the growth of top graphene layers with no contact with the copper surface could be due to the high local supersaturation of carbon at high methane flow rates with an excess of precursor supply. Higher precursor supersaturation should lead to considerably faster graphene growth. However, low graphene coverage rate of $0.2 \mu\text{m}^2$ per minute was monitored, whereas considerably higher rates of up to $100 \mu\text{m}^2$ per minute were observed for low pressure growth by Li et al. [31] It could be hypothesize that the lower growth rate could be due to lower lateral diffusion rate of species that favour multilayered graphene instead of monolayer fast growth.

To better support the discussion of the formation of multi-layer graphene at an early stage and the limited further growth of the top layers Wu et al., [123] developed a two-step ambient pressure CVD process with similar strategy as Li et al. The result was consistent with the point that, once a continuous graphene film formed on the catalytic Cu surface, growth of extra graphene layer was inhibited because of the absence of Cu to catalytically decompose the carbon precursor gas [27].

Another significant factor related to the experimental pressure is the sublimation-evaporation during the process due to the vapor pressure (V_p). The vapor pressure of the substrate was demonstrated to have a strong influence on the growth rate and orientation of the graphene grains [29] [79]. V_p of Cu and Ni are $6 \cdot 10^{-5}$ and $1 \cdot 10^{-7}$ Torr, respectively. For the Cu(111) surface, this represents a loss of 4 monolayer (ML) of Cu per second from the surface at 1000°C under ultrahigh vacuum conditions, whereas the sublimation rate from a Ni(111) surface is approximately 7×10^{-3} ML/s. For graphene growth on Cu substrates in LP regime the pressure of the source gas is typically in the mTorr or higher pressure range, which should slow the sublimation rate of Cu from the surface. Even so, sublimation of metal during growth was reported due to high temperature commonly used, close to the melting point of the copper, 1084°C , and even more in LP regime. Significant amount of the copper evaporates and deposits at the edges of the fused silica tube used in the CVD. However, once graphene growth was initiated, the graphene covered regions of the surface were observed to suppress sublimation.

Sublimation of the metal catalyst during the growth was used to deposit monolayer graphene, although this parameter should be precisely controlled, [91] [124]. Defective films were grown using sacrificial copper films. One cause of the defective film could be that the grown graphene can break under stress due to the Cu morphology change during its evaporation.

It is worth mentioning that Liu et al., [30] noticed that decreasing the annealing pressure (from 80 to 20 mbar) could have a positive effect on the quality and uniformity of graphene. It was observed that the surface of Cu became smoother due to the increasing sublimation of Cu at lower pressure. Low pressure during annealing could greatly enhance the uniformity of Cu surface and decrease the number of the sharp structures, thereby making the Cu surface smoother. But it was already demonstrated that in the growing stage [29] Cu sublimation should be avoided due to roughening of the Cu surface and, thus, the conformal graphene film.

Partial pressure of precursor gases and hydrogen

Recent studies on the graphene growth optimization [31, 123] indicated that hydrocarbon pressure is one of the major factors affecting the graphene growth. A minimum partial pressure of hydrocarbon is required in most of the experiments for graphene to cover the Cu surface during growth. The pressure of the hydrocarbon determines the concentration of the carbon species on the Cu surface during graphene growth. So, a controlled and relatively low precursor (CH_x) partial pressure is highly recommended in all pressure ranges [109, 121]. It was also demonstrated by Li et al., the synthesis of high quality graphene working at very low total pressure (mTorr range) with almost only carbon precursors and low quantity of H_2 .

Zhang et al., [125] investigated the correlation between the grain morphology and the total pressure and methane to hydrogen ratio in LP. With methane-to-hydrogen ratio of 1:12.5 and at different total pressures, the graphene grains changed from irregular small flakes (80 mTorr) to mostly four-lobe grains (100 mTorr) and finally to mostly six-lobe flowers (150 and 200 mTorr). When increasing the total pressure to 300 mTorr, the six-lobe graphene flowers turned to irregular shape. Interestingly, similar results were obtained when keeping the total pressure at 150 mTorr and gradually increasing the methane to hydrogen ratio from 1:30 to 1:2. All these observations indicated that increasing the total pressure of the CVD system had a similar effect on the morphology of graphene grains as increasing the methane-to-hydrogen ratio.

The role of hydrogen partial pressure was already commented (see section 3.1). Gao et al., [71] observed that the graphene edges become regular and straighter, because edges with a low stability were selectively etched away by an active atomic H when the CH_4/H_2 ratio is low. Wang et al., [126] also published about the role of hydrogen. They observed that when only the CH_4 supply was shut off and the sample was cooled, after the growth stage, in a high concentration H_2 atmosphere (300 sccm Ar and 40 sccm H_2), the graphene domains would appear to be etched into rectangular openings. In accordance with the copper-catalyzed etching mechanism proposed by Zhang et al. recently, [127] they proposed that low concentration H_2 could reduce the etch rate considerably and result in no significant etching damage.

The whole section reveals that the pressure regime is crucial in high quality graphene synthesis. It seems that more regular graphene domains are synthesized in AP CVD. LP CVD regimes enhance evaporation of catalyst and etched domains, but more precise control of the number of layers is achieved. The role of hydrogen remains an open question to be resolved, although etching effects were demonstrated. The partial pressure of the precursor gases reveals as crucial and dependent of each reactor setup although some relation between this partial pressure and the total pressure of the system was detected.

3.3.2. TEMPERATURE

One important effect, widely detected in tubular reactors is the temperature gradient along the radial direction inside the reactor. It can result in inhomogeneous growth of the graphene. To solve this, two

quartz tubes, one suspended inside the other, were used in large area synthesis experiments, wrapping the small tube with a metal foil [7].

Heating treatment of the catalyst

In catalysis, it was demonstrated an enhanced dissociation of carbon precursors at high temperature and also surface smoothing via metal grain growth, being this a fundamental step in graphene synthesis over metal foils. Depending on the catalytic activity of the metal, the process temperatures can vary between 800-1100°C. Ni is intensively studied because the phase diagram of Ni and C reveals that at high temperature solid solution is formed (above 800°C) and that the metastable formation of Ni₃C phase promotes the precipitation of carbon out of Ni. Co and Fe show also carbon solubility at 850°C-1000°C although graphite precipitation from Fe can be obtained only under very specific conditions. Working with Cu and Ni is common to use 900-1050°C temperature. It was demonstrated that high T (>1035 °C) yields a low density of graphene nuclei when growing and, as a consequence, large domain size. But the problems with high T(°C) were that more metal was observed to evaporate depending on pressure conditions and that the roughness of the surface was promoted.

The “hot-wall” reactor consisting in a quartz tube located inside a furnace is the most used configuration in graphene synthesis so far [7,129,130]. On the other hand, it is believed that, in this type of reactors, the thermal gas activation and dissociation in gas phase may be considered as not specially noticeable. Therefore, if the reaction is surface limited (heterogeneous reaction) there is no need to heat the gas up to this high temperature before reaching the surface. There is another possibility, a design called “cold-wall type” apparatus where only the substrate is heated and in less time. The cold wall type reduces completely gas phase reactions resulting in no particulate contamination. Synthesis of high quality graphene films on a Ni foils using a cold-wall reactor with a rapid thermal processing (RTP) heater was reported [128]. RTP provided a fast heating & cooling rate and temperature control. The reported results differed from previous observations in the growth of graphene on Ni substrates by CVD due to the rapid process, even allowing new discussions about growth kinetics. These results suggested that two different growth mechanisms could exist in the case of Ni. While portion of carbon atoms may be dissolved into the nickel film, many carbon atoms also migrate on the nickel surface and bond with each other to form graphene. Therefore, this could explain the graphene synthesis in a very short growth time (30 s); this direct growth-surface migration mechanism may play a larger role than the precipitation mechanism. To verify the direct growth mechanism of CVD process very short growth time (10 s) and different H₂ gas flow rates during the growth stage were investigated. The defect density decreased with decreasing the H₂ flow rate. It could be postulated that hydrogen is not necessary to synthesize high-quality graphene by RTP direct growth mechanism using a Ni catalyst, consistent with the previously observed in the case of CVD growth of graphene on Cu foils [131].

Geng et al., [132] demonstrated in AP that the use of liquid Cu (T>1084°C, Cu melting point) can be particularly effective for controlling the nucleation process in graphene CVD systems. It was observed that the grain boundaries were eliminated and the results showed the production of uniform, self-aligned, large-sized, single-domain, hexagonal graphene flakes (HGF) and continuous monolayer films. This new route involved the formation of liquid Cu phase on quartz and W substrates at growth temperature above Cu melting point. The evolution from well-separated HGFs, to closely packed structures and to continuous film was documented. Typically, HGFs well dispersed on the surface and self-assembled were observed. Liquid Cu surface could be involved in the translation or rotation of HGFs, while minimization of surface energy may be responsible for the alignment. The average size of individual HGFs determined by both nucleation density and growth rate was about 20–30 μm. Increasing growth temperature led to HGFs with average sizes of approximately 50 μm; and lowering CH₄ flow rate led to approximately 120 μm. The average growth rate of HGFs was estimated to be 10–50 μm/min on flat Cu/W, which is much higher than the rate of 0.1–0.2 μm/min observed for the case of HGFs grown on a Cu solid surface [133].

Low temperature synthesis (Plasma assisted processes)

Low temperature processes for graphene synthesis are highly recommended for industrial applications. There is still a need to develop a reliable and reproducible method for low temperature synthesis of high-quality graphene for the full exploitation of graphene properties and application potentials. One game-changing breakthrough [134] would be the development of graphene growth on arbitrary surfaces at low temperatures (for example, by means of plasma assisted deposition) with a minimal number of defects. So, plasma assisted deposition could be a fundamental player in graphene future development.

Different works using surface wave plasma (SWP)-CVD and remote plasma assisted CVD [135] exhibited a capacity to synthesis graphene at lower temperatures and over substrates other than used in standard processes (Al foil). In the former method no monolayer graphene was deposited but few layer, graphene was synthesized at a relatively higher temperature of 650°C in the latter method. In another approach by Kim et al., [136], graphene films were synthesized on polycrystalline nickel foil using a cold-wall type microwave MPCVD system with a heating stage. A substrate temperature of 450 to 750°C and a total pressure of 20 Torr under various mixing ratios of H₂ and CH₄ were used. The dependence of monolayer graphene synthesis on temperature was investigated and it was clearly shown that the higher the temperature the higher quality graphene was grown so far.

Teresawa et al., [137] investigated multilayer graphene grown on Cu foils by radio frequency plasma enhanced (RF) chemical vapor deposition (PE-CVD). The growth of graphene was investigated at various conditions, changing the plasma power, gas pressures, and the substrate temperature (from 500°C to 900°C). At high substrate temperatures, the growth of the first layer of graphene was affected by the catalytic action of Cu, while the growth, at low temperature, of multilayer graphene was dominated mostly by radicals generated in the plasma. Outstanding differences in the grain size, number of layers and growth rates on few layer graphene between 500 and 900°C respectively were observed. It was also observed that the grain size of graphene decreases with the thickness. The growth rate of the subsequent layers in multilayer graphene was measured approximately five times slower than that of the first layer graphene. In thermal CVD, the difference in the growth rate between the first layer and the second layer was more than 10 [27]. This more rapid growth comparing with thermal CVD is one of the features in PE-CVD. In contrast to thermal CVD, the activated carbon fragment such as C₂ radical is formed in PE-CVD and the graphene growth occurs even at 500 °C.

Rapid synthesis radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD) [138] revealed as a very powerful technique for the synthesis of large-scale graphene at relatively low temperature in a short time. Large-area single- or multilayer graphene of high quality was synthesized on Ni films deposited on a thermally oxidized Si, at a relatively low temperature (650°C). In the deposition process, trace amount of CH₄ was introduced into the PECVD chamber and only a short deposition time (30-60 s) was used. Single or multilayer graphene were obtained due to carbon atoms from the discharge diffuse into the Ni film and then segregate out at its surface. Increasing number of graphene layers were obtained with longer deposition times using larger CH₄ flows at a cooling rate of about 10°C/s. Kalita et al., [139] reported direct synthesis of nanographene films (very small domain size) on silicon (n-Si) and glass (SiO₂) substrates by microwave assisted surface wave plasma (MW-SWP) CVD at 400-560°C. The technique is a rapid growth process (70-120 s) and the film can be deposited on different substrates. The directly grown deposit consisted of triangular shaped nanographene domains with sizes of 80–100 nm in lengths that interconnect to form a continuous film. For the deposition process, a gas mixture of C₂H₂ and Ar at a pressure of 45 Pa was used. Kumar et al., [140] reported a unique process for rapid synthesis (100 s duration) of few-layer graphene films on Cu foil by microwave plasma chemical vapor deposition (MPCVD). The process can produce films of controllable quality from amorphous to highly crystalline by adjusting plasma conditions during growth and with no supplemental substrate heating (plasma-metal

coupling for rapid heating of the foil). The hydrogen plasma was also used to remove the native oxide layer enabling graphene growth on metal Cu. It was suggested that the same process could be used for rapid synthesis of primarily single-layer graphene.

Great advances are being published in this area of graphene synthesis. Monolayer high quality graphene on metal was already synthesized at lower temperatures. Synthesis of small domain graphene on dielectric substrates was also published. Therefore, low temperature processes for graphene synthesis are being developed by means of plasma assisted deposition. This will be an extensive area of research in the near future with the intention to synthesize controllable number of graphene layers on arbitrary substrates with a reliable and reproducible method.

3.3.3. FLOW RATE AND RESIDENCE TIME

Gas flow regime revealed as an important factor to be taken into account during graphene synthesis. It was also observed [31] that the density of graphene nuclei decreased as T (°C) increased or as methane flow JMe (sccm) and methane partial pressure PMe (mTorr) decreased. Therefore, high T and low JMe and PMe were found to yield a low density of graphene nuclei and thus large domain size. Different vapor trapping methods have been reported. Li et al. [59] demonstrated the CVD growth of graphene single crystals up to 0.5 mm in size in quasi-static flow regime (vapor trapping method), using a copper enclosure in LP. Subsequent experiments [125] in quasistatic flow achieved the growth of large-grain, single-crystalline six-lobe graphene flowers with grain size up to 100 μm. SEM images of these six-lobe graphene flowers grown on the bottom side of Cu foil placed inside a vapor trapping tube were shown. Interestingly, the graphene that grown on a Cu foil placed outside the small vapor trapping tube did not show any “flower” shape, but continuous graphene film with slight etching. This result indicated that the vapor trapping tube changed the local environment inside the tube, especially in reducing the carbon supply and creating a quasi-static reactant gas distribution that resulted in large flower shaped graphene grains.

Following this line of experimentation, when methane flow rate decreased (from 300 sccm to 180 sccm) using Fe foils while keeping the other parameters unchanged [76] bilayer graphene instead of multilayer was obtained, likely due to the smaller amount of carbon dissolved and segregated from the catalyst.

3.3.4. HEATING/COOLING TREATMENTS AND PROCESS IN STEPS

Annealing time

Reducing the nucleation density was a feasible route to prepare large-size single-crystal graphene domains [59]. The presence of impurities and defects on the surface of a substrate proved to affect the nucleation behavior considerably. Regarding the importance of surface defects, Gao et al. [143] demonstrated that the graphene nucleation rate near a step edge may be 10^4 – 10^7 times greater than that on a terrace due to a significantly lower nucleation barrier. As known, high temperature treatments of the substrate revealed to be helpful for the reduction of volatile impurities, contaminants, and defects on a copper surface, thus leading to the hindering of graphene nucleation. Very longtime annealing (3 h) was also used by Wang et al., [126] to reduce the nucleation density on copper foils resulting in large hexagonal domains about $0.4 \times 0.4 \text{ mm}^2$.

The effects of total annealing time and temperature on the orientation and size of grains within Cu foils and Cu–Ni alloy foils were also studied [79]. As above discussed, alloying metals is often performed in order to control the number of graphene layers. The annealing process could be summarized in two stages. During the grain growth, the first step is to incorporate and order atoms from the disordered regions, resulting in some ordered regions. The second step is the growth of large grains at the expense of

smaller ones. As the temperature increases to a value close to the melting point of the metal, the diffusion coefficient of the atoms within the foil becomes very large (atomic diffusion is a thermally activated process), resulting in the growth of grains with macroscopic dimensions. The obtained results showed typical lateral dimensions ranging from a few millimeters up to approximately a centimeter for Cu foils annealed at 1030°C for 35 min and from tens of microns up to a few hundred microns for the 90/10 Cu–Ni foils annealed at 1050 °C for times ranging from 45 to 90 min. The smaller grains within the Cu–Ni foils were attributed to the higher melting point of the Cu–Ni alloy. Then at these temperatures, more density of grain borders and subsequent defects on as-grown graphene can be possible to occur on alloys.

Concerning the effect of H₂ during the annealing treatment, it is believed that H₂ can eliminate certain impurities such as sulphur (S) and phosphorus (P) that may cause local variations in the carbon dissolvability in the metal substrates [144].

Therefore, it seems clear that long annealing times at low pressure of reducing gases combined with high temperature, yielded low nucleation density and subsequent large domains. This route is highly desirable in high quality graphene synthesis.

Growing step profile

In the pioneering work of Li et al., [31] a two step process in LP CVD, varying the partial pressure of methane for large domain graphene synthesis, has been proposed. For a given temperature (usually 1035 °C) nuclei were formed in a first step at low methane partial pressure and flow. In a second step, the partial pressure of the methane was increased to promote full surface coverage. It is important to note that for a temperature and partial pressure given, once the nuclei density was set, no significant new graphene nuclei were detected. According to this work, other groups [126] employed the same strategy during the growth process. It was clearly observed that diminishing the CH₄ concentration leads to a reduction of graphene nucleation. Wu et al., [123] also developed a two-step AP CVD process with similar strategy as Li et al. Graphene growth was carried out at 1050 °C introducing different amounts of CH₄. Initially, with low CH₄ concentration (5 ppm) low nucleation density was guaranteed. After 20 min, the growth was continued by increasing CH₄ concentration (55 ppm) without changing any other conditions to get complete graphene coverage.

Finally, other studies [145] were developed including a two-step, AP CVD process, combining surface catalyzed process with segregation from bulk to grow bilayer graphene. Carbon atoms were firstly dissolved into the quasi-melting Cu metal and then segregated on the Cu surface to form nucleation centers.

Cooling ramp

The role of the temperature gradient during the cooling step after the synthesis process was demonstrated as a critical factor specially when working with high carbon solubility catalyst (e.g. Ni) [25]. Considering Fick's laws of diffusion, the area of FLG should dramatically increase in samples subjected to a slow cooling process. Therefore, high cooling rates, among other strategies, were commonly used to avoid (or make more difficult) carbon segregation in high solubility metals to success in the growth of high quality few layers graphene. As commented above, high quality monolayer and bilayer graphene were synthesized by using rapid processes and high cooling rates. Even when thin layers of nickel are deposited on SiO₂/Si substrates to avoid the large amount of carbon diffused into nickel foils, a fast cooling rate is critical in suppressing the formation of multiple layers [26]. Unexpected results were also published where the contrary was also observed in graphene samples fabricated using a slow and fast cooling rate (0.3 and 3 °C/s) [129]. A possible explanation could be that at particular experimental conditions, the surface mediated mechanism (as for the Cu case) plays a larger role in final film formation than the precipitation mechanism. Likely, both mechanisms will occur simultaneously during graphene growth. It

was pointed out that the growth mechanism proposed for Cu systems [6], may be applicable to the Ni system in some cases, if the synthesis conditions are suitable to control the bulk-diffusion of the carbon into the metal to the minimum and the catalysis of the decomposition of the precursor gas is effectively achieved.

Interestingly, it was also found that the cooling rate may control the segregation behavior, strongly affecting the thickness and quality of the graphene deposit [141]. Because the concentration of carbon decreases exponentially from the surface into the bulk, an extremely fast cooling can have a quenching effect reducing the rate of carbon migration to the surface. Otherwise, extremely slow cooling rates can result in carbon with enough time to diffuse into the bulk, subsequently avoiding the carbon to segregate at the surface, strongly affecting the crystallinity. These results suggested that several layers of high quality graphene can be synthesized on Ni surface with optimized medium cooling rates. It was also observed that the same gas mixture should be used during the cool-down to prevent the loss of carbon from the graphene over layer (e.g., formation of CO and CO₂), which can occur at temperatures higher than 300 °C [79].

Published results of graphene synthesis on Cu also shown that high vacuum, depletion of hydrogen, and slower cooling rate (18 °C/min) compared to previous single-layer graphene synthesis can produce CVD growth of bilayer graphene[142]. It was also found that in AP CVD on Cu, the cooling rate can significantly affect the layers number in graphene domains. High-quality monolayer graphene domains were only obtained with low cooling rates, while high cooling rates result in multilayer graphene domains with more defects, [126].

4. SCALABILITY

One favorable aspect of graphene synthesis by CVD is the ability to maximize the scale without losing the homogeneity of large area films, as published by Bae et al., [7]. An 8-inch-wide double tubular quartz reactor was used in this CVD system, allowing a monolayer graphene film to be synthesized on a roll of copper foil with dimensions as large as 30 inches in the diagonal direction. Excellent optical properties were measured on these films after layer-by-layer transfer to dielectric substrates, achieving bilayer, trilayer and four-layer graphene.

Roll-to-roll microwave plasma (CVD) was also used for the continuous deposition of graphene films in industrial mass production [146]. A deposition area of 294x480 mm was demonstrated. Few layer graphene films, which consist of flakes with a nanometer size, were deposited onto a Cu foil, although it was expected that graphene films can be obtained on other substrates by optimizing the deposition conditions.

5. BILAYER GRAPHENE

Bilayer AB (Bernal) stacked graphene became a very interesting option in electronic applications. The stacking order and coupling in few-layer graphene were demonstrated to affect the electrical properties of the material [147]. However, a process of layer-by-layer transfer could not produce AB (Bernal) stacked graphene due to the random orientation between the transferred layers. On the other hand, by means of better control of the CVD process, bilayer graphene was grown directly on metal substrates. [55,142,148] Typically, bilayer graphene was grown by feeding the growth system at higher rate of carbon or a lower rate of (H₂) but the exact growth conditions vary from one system to other due to process differences.

Lee et al., [142] reported the first synthesis of wafer scale bilayer graphene film over at least 2 in. × 2 in. area, limited only by synthesis apparatus. The method was based on CVD growth of bilayer graphene on a

copper thin film surface and was characterized by the depletion of hydrogen, high vacuum, and, most importantly, slower cooling rate compared to previous single-layer graphene synthesis. The optimal bilayer graphene film was grown at 1000 °C, with growth pressure of 0.5 Torr, CH₄ flow rate of 70 sccm, and a cooling rate of 18 °C/min (0.3 °C/s) Characterization results confirmed highly homogeneous bilayer graphene film, with only a very small fraction corresponding to possibly three layers. The authors speculated that the key parameter for bilayer growth was the slow cooling process in comparison with publications of bilayer growth on other substrates.

More recently Bi et al., [145] developed a two-step, AP CVD process, combining surface catalyzed process with segregation from bulk to grow bilayer graphene. The yield of the bilayer graphene was demonstrated over 90%. The Cu foil was firstly placed in a horizontal quartz tube and heated to 1080 °C under H₂ flow and the CH₄ flow was secondly introduced in the chamber at 1080 °C. Then the furnace was switched off and cooled to a certain temperature. Finally, the CH₄ flow was turned off and the Cu foil in the quartz tube was withdrawn for a rapid cooling. The graphene domains were prepared varying only the growth time between 3-10 min. These graphene crystallites spontaneously act as templates to induce the carbon atoms to form hexagonal bilayer graphene domains, size-tunable by controlling the growth conditions. The yield of the bilayer graphene over 90% with defect-free domains 100 μm in size, was demonstrated.

6. GRAPHENE RIBBONS AND MESHES

Theoretical and experimental data suggest that, like bilayer graphene, a band gap could be opened in sub 10 nm width graphene ribbons [149]. The first synthesis of graphene nanoribbons (GNRs) was performed through mechanical exfoliation in solution. Carbon nanotubes (CNTs) were also proposed as precursors for higher yield [150]. Another interesting approach is microscopy-based patterning limited by the wavelength of light and high cost.

An interesting approach in the case of graphene nanomeshes synthesis was proposed by Bai et al., [151] by means of self-assembled colloid spheres and a metal mask deposited to fill the space between them.

7 OTHER CONCEPTS: LASER CVD AND RAPID SYNTHESIS

Although the CVD can achieve scalable growth of graphene using a roll-to-roll method, fabrication of graphene patterns can only be performed with the aid of expensive and time-consuming post-lithographic processes. Therefore, a convenient approach to achieve fast, scalable and affordable production of graphene patterns for electronic applications is widely required. A recent overview of laser-assisted techniques developed for fabricating carbon nanostructures, including graphene, nanotubes and nanooxions was presented by Zhou et al., [152]. Rapid single-step fabrication of graphene patterns was achieved using laser direct writing. Line-shaped graphene ribbons of controlled widths and lengths were precisely fabricated on a Ni foil without extra annealing and lithographic patterning procedures. The localized laser heating resulted in a rapid thermal process at the laser beam focal point. Surprisingly, the growth rate of graphene was 1000 times faster than a conventional CVD method. Graphene patterns could be fabricated at a high scan speed up to 200 μm/s, much faster than a traditional fabrication approach. Direct writing graphene patterns using the LCVD method could expand the capability of CVD approaches in rapid and controllable fabrication of graphene for a wide range of application. High quality of the as grown graphene was demonstrated by Raman spectroscopy. The number of graphene layers could be strictly controlled by the scan speed of the laser beam. Micron size nanoribbons with limited width were also synthesized.

8. SUMMARY

An in-depth review on the synthesis of graphene by CVD techniques is presented, compiling the last more meaningful results obtained in numerous laboratories around the world. The preparation of graphene deposits necessarily requires to follow some definite steps, such as slow enough supply of carbon species to the growing surface that allows surface diffusion of carbon atoms over the substrate. Different precursors (in solid, liquid or gas forms) may be used as carbon atoms source for the preparation of graphene. Among them, a mixture hydrocarbon-hydrogen and particularly methane-hydrogen is most widely used.

Following these guidelines, firstly it is noteworthy the importance of the presence of a metal for catalysing the decomposition of precursor molecules. In this way, it is possible to control the decomposition process that supplies carbon atoms. As shown, the deposition mechanism strongly depends on the characteristics of the specific metal used as substrate/catalyst. Among these characteristics, it has to be highlighted the catalysing efficiency as well as the solubility of carbon into the metal bulk. Thereby, for metals with high carbon solubility (Ni, Co....), the main growth mechanism is the segregation and precipitation of carbon atoms located through the metal bulk immediately after the catalytic CVD process. However, for low carbon solubility metals (Cu), the deposition mechanism is mainly dominated by the metal surface and the graphene is formed outwards from the surface. Hence, the metal used as substrate/catalyst determines the main mechanism for the graphene growth. Moreover, the characteristics of the metal surface, where the growth process takes place, result essential for the final number of layers in the graphene deposit. So, the metal substrate has to be properly treated in order to chemically reduce the metal surface and modify its structure by controlling the crystal orientation, increasing the grain size and therefore becoming smoother the metal surface.

Currently some approaches to control the number of layers of the graphene deposit via metal alloys catalysis (involving Ni) were performed. There were some important advances controlling the growth of few layers varying the composition of the metal alloy catalyst, although physical, optical and electronic properties of the films still have to be necessarily improved. Also it would be highly desirable to directly growth graphene layers on dielectric substrates. More experimental work should be performed in these areas for graphene to be competitive on practical applications.

Up to now the best approach to control the monolayer growth is performed on very low solubility metal, as Cu, since it was quite difficult to control the growth of monolayer graphene via fast cooling processes on high solubility metals (Ni). However rapid synthesis could give an opportunity to these metals. From theoretical point of view, as copper substrates are used, CH is the most favorable carbon species coming from methane decomposition. Subsequently, on the metal surface the energetically favorable dimer formation from the CH species will occur. The dimer formation, as well as the diffusion of the dimer over the copper surface are dominant processes respect to the back dissociation of dimers and the migration of carbon atoms either over the surface or towards the metal bulk. Therefore, when graphene is grown on copper foils, the main growth mechanism includes dimers as intermediate species.

Also, it is worth to mention that, in Cu CVD graphene growth, the hexagonal lattice of Cu(111) favored the high quality of the as grown graphene. Moreover during the CVD heteroepitaxial growth on Cu(111), the orientation of graphene nuclei became well controlled with domain boundaries atomically connected. Therefore, it could be advantageous to develop techniques for producing foils with a preferential (111) surface texture. Also it has been shown that for obtaining high-uniformity graphene, it is crucial minimizing the number of imperfections, roughness and impurities, becoming the surface as uniform as possible. It is clear that initially the roughness and imperfections on the growing surface enhance graphene nucleation. However, during subsequent growth stages, the formation of a huge amount of defects is evident and thus the final deposit contains too much structural defects. Lastly, during annealing,

the impurity atoms likely diffuse towards the Cu surface, often enhancing the decomposition of the gas precursor.

Finally, pressure and temperature are also decisive parameters for the successful growth of CVD few-layer graphene from hydrocarbon/hydrogen gas mixtures. Low pressure (LP) CVD regimes enhance evaporation of catalyst and etched domains, although the control of the number of layers seems to be more precise. It should be highlighted that the role of hydrogen remains an open question to be resolved, although etching effects were demonstrated. As expected, the partial pressure of precursor gases reveals as crucial and dependent of each reactor setup. Another significant remark is that long annealing periods of the metal substrate/catalyst at low pressure in a reducing gas combined with high temperature, leads to a low nucleation density and afterwards large domains, both facts highly desirable for high quality graphene synthesis. Lastly, low temperature processes for graphene synthesis are being developed by using plasma assisted processes. This will be an extensive area of research in the near future with the intention to synthesize controllable number of graphene layers on arbitrary substrates with a reliable and reproducible method. Also the seeded growth can be an interesting alternative for high quality and performance graphene layers with applications in several fields. Nevertheless, very high complex processes with important economical implications are involved.

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