ANALYSIS OF GRAPHENE SYNTHESIS ON SIO₂/SI, SIC AND TI6AL4V BY HOT FILAMENT CHEMICAL VAPOR DEPOSITION

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DEDICATED TO MY FAMILY

Abstract

Graphene, a material formed from one layer of graphite, was obtained for the first time in 2004 by Novoselov and Geim. The interesting properties of this two-dimensional (2D) sp² hybridized material have led to an increase in research to find the most efficient method to obtain high-quality graphene on a large industrial scale. The exceptional properties of graphene have converted it into one of the most studied materials in the 20+ years since its discovery. Graphene has high electrical conductivity, elasticity, flexibility, hardness, chemical resistance and others outstanding properties that has converted it into a promising material for advances in science and technology. Graphene, in combination or deposited on other materials, can extend its application in multiple areas, such as electronic, energy storage, aerospace, and biomedical. The most common method to grow graphene is thermal chemical vapor deposition on copper, and the carbon layer is then transferred to the desired material. This transfer process often results in wrinkles, breaks, and contamination in the graphene films. For this reason, this work proposes a method to grow graphene directly on SiO₂/Si, SiC and Ti6Al4V by hot filament chemical vapor deposition (HFCVD). The relation between the growth parameters and the graphene films characteristics are presented here. Three chapters of this dissertation are dedicated to the analysis of graphene growth on each different substrate with their respective structural, morphological and compositional characterizations.

The direct synthesis of graphene on SiO₂/Si by HFCVD was conducted at low pressures (35 Torr) with a mixture of methane/hydrogen and a substrate temperature of 970 °C followed by spontaneous cooling to room temperature. A thin copper-strip was deposited in the middle of the SiO₂/Si substrate as a catalyst. Raman spectroscopy mapping and atomic force microscopy measurements indicate the growth of few-layers of graphene over the entire SiO₂/Si substrate, far

beyond the thin copper-strip, while X-ray photoelectron spectroscopy (XPS) and energydispersive X-ray spectroscopy (EDS) showed negligible amounts of copper next to the initially deposited strip. The scale of the graphene nanocrystals were estimated by Raman spectroscopy and scanning electron microscopy (SEM).

A method to grow graphene on 6H-SiC substrates at low pressure (35 Torr) by the HFCVD technique is also presented. The graphene deposition was conducted in an atmosphere of methane and hydrogen at low substrate temperatures (950 °C). The graphene films were analyzed by using Raman spectroscopy, scanning electron microscopy, atomic force microscopy, energy dispersive X ray, and X-ray photoelectron spectroscopy. Raman mapping and AFM measurements indicated that few layer and multilayer graphene were deposited from the external carbon source depending on the growth parameter conditions. The compositional analysis confirmed the presence of graphene deposition on SiC substrates and the absence of any metals involved in the growth process.

An approach to grow graphene directly on Ti6Al4V pellets by HFCVD using methane as a carbon source is presented. This work establishes an analysis of graphene deposited on the Ti6Al4V alloy with the aim of reinforcing the properties of this alloy and increasing its future use in biomedical and engineering areas. Graphene deposition on Ti6Al4V was confirmed by Raman, SEM, EDS and XPS measurements and a growth mechanism is discussed.

In summary, a method for each of the graphene growth processes on SiO₂/Si, SiC and Ti6Al4V is demonstrated, allowing the possibility for graphene production by the HFCVD method, which is well established for its versatility for industrial use.

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List of Abbreviations

AFM	Atomic Force Microscopy
APCVD	Atmospheric Pressure Chemical Vapor Deposition
CCD	Charge Coupled Device
CVD	Chemical Vapor Deposition
EDS	Energy-dispersive X-ray analysis
FWHM	Full Width at Half Maximum
FET	Field Effect Transistor
GO	Graphene Oxide
HFCVD	Hot Filament Chemical Vapor Deposition
HOPG	Highly Oriented Pyrolytic Graphite
HF	Hydrofluoric Acid
LPCVD	Low Pressure Chemical Vapor Deposition
MFC	Mass Flow Controller
NGO	Nano-Graphene Oxide
PECVD	Plasma Enhanced Chemical Vapor Deposition
PMMA	Poly(methyl methacrylate)
PVA	Polyvinyl alcohol
PDMS	Polymeric Polydimethylsiloxane
SEM	Scanning Electron Microscopy
SiC	Silicon Carbide
TCVD	Thermal Chemical Vapor Deposition
TEM	Transmission Electron Microscopy

TRT	Thermal Release Tape
TiC	Titanium carbide
UHV	Ultra-high Vacuum
2D	Two Dimensional
XPS	X-ray photoelectron spectroscopy

Chapter 1. Introduction

1.1 Carbon materials

Carbon based materials have had an immense contribution in the development of materials science motivating the creation of novel technologies with exceptional applications. Carbon is a group IV element with four valence electrons that easily bonds with other atoms in order to fill the remaining 4 electrons in the second shell. Depending on the synthesis conditions, the electrons in the second shell orbitals $(2s^22p^2)$ can undergo sp, sp² and/or sp³ hybridization [1,2]. The capacity of carbon to join with other atoms to produce innumerable compounds with interesting characteristics. Furthermore, carbon bonding with itself produces a variety of materials with interesting applications such as: graphite used in pencil leads, electrodes and lubrication; diamond used for jewelry, cutting and electronics; carbon blacks and carbon fiber applied to reinforce tires and plastics [3,4]. Another important carbon-based material is activated carbon, used in the filtration of gases, water purification and electronic devices [4].

1.1.1 Classification

According to the allotropic classification, some authors describe graphite, diamond, and fullerene as the three basic carbon materials [1], while others include carbyne and amorphous carbon, which have no crystalline structure, as a fourth allotrope [3,4]. In this work, we consider graphite, diamond and fullerene as the basic carbon structures. Graphite is a planar sp² hybridized arrangement of carbon atoms, formed by parallel layers of two-dimensional carbon sheets in a hexagonal lattice (Figure 1.2) [2]. The adjacent layers of carbon sheets, separated by 3.35 Å, are weakly bound by Van der Waals forces and each carbon atom forms a covalent bond with 3 other carbon atoms in the same sheet [1]. Depending on the stacking sequence, graphite can be classified as hexagonal (ABAB...) or rhombohedral (ABCABC...) structures, where the hexagonal is the most stable phase [2]. Graphite formed by irregular parallel layers stacked in a random sequence

is known as turbostratic [2]. The carbon materials that comprise the graphite group are: Turbustratic carbon, carbon fiber, nanofibers, intercalated graphite, graphite oxide, exfoliated graphite, flexible graphite, activated carbon, carbon black and others [1]. Although carbon nanotubes form part of this group, they are a hybrid structure between the graphite and fullerene [1]. Due to the extraordinary properties of graphene, this material will be explained in greater depth in the next section.

Diamond, the second allotrope of the carbon family is a three-dimensional sp³ hybridized material formed by four covalent bonds with other carbon atoms, making this structure electrically insulating with high thermal conductivity. The best-known diamond structures are cubic, however hexagonal, zinc-blende and wurtzite forms are found [1]. The defects and incorporation of hydrogen atoms in diamond result in an amorphous structure known as diamond-like carbon [1,2,4]. Another material of the diamond family is graphane, a sp³ hybridized two-dimensional polymer of carbon and hydrogen, with insulator properties. [1].

Fullerenes have sp^{2.5} hybridized carbons, formed by hexagonal and pentagonal structures. One example (and the best known, as "bucky ball") of a fullerene structure consists of 60 carbon atoms which form 20 hexagons and 12 pentagons in a spherical shape. Many other fullerenes structures with a different number of carbon atoms have been observed. These carbon materials have applications as catalysts, lubricants and for drug delivery [1,2].



Figure 1.1 Carbon structures, (a) Graphite, (b) Diamond, and (c) Fullerene.

1.2 Graphene properties and applications

Graphene is a material formed from one sheet of graphite and was obtained for the first time in 2004 by Novoselov and Geim. These authors used the mechanical exfoliation method to obtain graphene and they were able to measure the electrical properties of this carbon material [5]. The electrical, mechanical and optical properties of this two-dimensional material with sp² hybridization have led to an increase in the number of investigations to find the best method to obtain high-quality graphene on a large industrial scale. Carbon has four unpaired electrons, three of them are bonded to other carbon atoms in the horizontal plane to form σ bonds, while the remaining electron is delocalized across the hexagonal ring structure [6]. This is one of the special characteristics of graphene that makes it an excellent electrical conductor [7]. Furthermore, this single carbon layer has a thickness of 0.34 nm and a carbon-carbon bond distance of 1.42 Å (Figure 1.2).



Figure 1.2 The hexagonal structure of graphene and its respective unit cell.

1.2.1 Graphene properties

The excellent properties of graphene, such as high electron mobility of 200,000 cm²V⁻¹s $^{-1}$ [6], surface area to weight ratio of 2,630 m²/g [5], modulus of elasticity of 1TPa [5], thermal conductivity on the order of 5300 W/ mK [8], and good electrical conductivity [9] makes this material an excellent candidate to improve current technology and novel applications [10,11,12]. Graphene could be employed in high-speed electronics [10,11], field effect transistors [13], photonics [10,11], supercapacitors [14,15], hydrogen storage [16], solar cells [17,18], electromechanical systems [19], strain sensors [20] and energy storage [11]. The structure of graphene can be found in different configurations; these assemblies are known as nanoribbons [21], quantum dots [22], hydrogels [23] and foams [12,24,25]. An important consideration for low dimensional materials is that point defects can have a detrimental effect in the energy transport process compared to bulk [26]. As a consequence, the two-dimensional carbon lattice in graphene, which in principle should be free of defects and disorder, has extraordinary electrical properties.

1.2.1.1 Electronic properties

Graphene has the highest electron mobility known with a carrier concentration of 1012 cm⁻² [6] and good electrical conductivity. Furthermore, graphene shows a half-integer quantum Hall effect, and the charge carriers have a zero effective mass behavior known as massless Dirac fermions [27]. The particular electrical properties of graphene are the result of the interactions of the four valence electrons in the carbon atom with three other carbon atoms in a two-dimensional lattice. Three of the valence electrons forms σ bonds in the sp² plane (2s, 2p_x and 2p_y orbitals in the plane of the carbon lattice) with three other carbon neighbors. The fourth valence electron in the 2pz orbital forms a π bond perpendicular to the carbon lattice. This electron is delocalized and free to move on the two-dimensional carbon lattice. As a result, graphene is electrically conductive

and optically transparent [26]. The band structure of graphene is described by the nearest neighbor tight binding model that only consider the π electron (Equation 1.1) [28].

$$E^{\pm}(K_x, K_y) = \pm \gamma_0 \sqrt{1 + 4\cos\frac{\sqrt{3K_x a}}{2}\cos\frac{K_x a}{2} + 4\cos^2\frac{K_y a}{2}}$$
(1.1)

Where *a* corresponds to $\sqrt{3a_{c-c}}$, (*a* _{c-c} =1.42 Å) and the nearest neighbor overlap is represented by γ_0 and has values of 2.5 and 3 eV [29]. According to this approach, the valence and conduction bands coincide at the high symmetry k-points (shown in Figure 1.3) essentially making graphene a zero-bandgap semiconductor. In addition, the Fermi energy level is positioned in this point, called Dirac or charge neutrality points [28].



Figure 1.3 The calculated band structure of graphene with the Dirac points (Figure adapted from reference 28).

1.2.1.2 Optical properties

As described previously, the σ -bond contributes in the majority to the graphene crystalline structure, while the π -bond determines its electronic and optical properties [30]. This carbon material has a special optical absorption governed by interband transitions at higher energies, from mid-infrared to ultraviolet and at lower energies by intraband transitions, in the far-infrared spectral range [31-33,34].

The conductivity of graphene at T = 0K behaves independent of frequency, then the value of its conductance is described by equation (1.2) leading an absorbance of $\approx 2.29\%$ described by Equation (1.3) where the α corresponds to the fine structure constant defined by $\alpha = \frac{e^2}{hc} \approx 1/137.036$ value [27,30,31,32,34-37].

$$\sigma(\omega) = \frac{\pi e^2}{2h}$$
(1.2)
$$A(\omega) = \frac{4\pi}{c} \sigma(\omega) = \pi \alpha \approx 2.29\%$$
(1.3)

As a graphical interpretation, Figure 1.4a shows the interband optical transitions of graphene and in Figure 1.4b the optical sheet conductivity and sheet resistance for three graphene samples in an energy range of 0.5 to 1.2 eV is depicted [35,36]. In multilayer graphene samples the absorption of light for N number of layers is given by N $\pi\alpha$, reaching 10 % of absorption at higher frequencies because of the van Hove singularities in the edge zone [26]. However, the optical property of graphene depends on the perfection of the atomic lattice. Defects in the structure generated by the synthesis method can lead to negative effects in the material and change its electronic and optical properties [30].



Figure 1.4 Optical properties of graphene, (a) representation of interband optical transitions in graphene, (b) graph of the optical sheet conductivity and the sheet absorbance of three different samples of graphene (Figures adapted from reference 36).

The modifications in the graphene structure can be involuntary like defects and contamination or they could be intentional, such as electron/hole chemical doping to modify its optical properties [30, 35]. One example of this experimental approach is observed in field effect transistor (FET), where the doping level can be modified by the application of a gate voltage through the SiO₂ substrates or electrolyte layer. Typically, the limit of the doping concentration is about 5×10^{12} cm⁻² and depends on the breakdown of the oxide layer. However in the electrolyte layer, it is possible to induce carrier concentrations as high as 10^{14} cm⁻² [35,38,39]. In summary, the optical properties of graphene makes this material nearly transparent, this absorbs 2.3% of light, making detectable in the visible range on a smooth surface without a microscope.

1.2.1.3 Chemical properties

Graphene is chemically inert, and even has shown resistance against hydrogen peroxide.

Chen et al. in 2011 studied the protection of metal surfaces (Cu and Cu/Ni alloy) to air oxidation using a coating of graphene. They found that the surface is protected from oxidation after a thermal exposition at 200 °C for 4 hours [28,40]. Some contaminant compounds such as polymethylmethacrylate (PMMA) and hydrocarbons can be thermally removed off the graphene surface at 350 °C for 48 hours under air environment [28]. Some atomic species can be functionalized with graphene such as fluorine to form fluorographene, which has a bandgap of 3 eV, and is inert and stable in air over 400 °C [41]. The functionalization of graphene leads to compounds with tunable properties allowing for more applications where the quality of graphene play an important role in chemical processes [42,43]. In addition, electrochemical methods i.e. oxidation, is a good option as a controllable process for molecular attachment with graphene [44].

1.2.1.4 Thermal properties

A material free of defects and impurities can reach its highest or intrinsic thermal conductivity when the phonons are only scattered by itself. This property can be affected by phonon interactions with defects or rough boundaries, that are more critical in nanoscale materials [28]. The measurement of the thermal conductivity of low dimensional materials, such as graphene, is a difficult process. The first measurement of this property was obtained by an optothermal Raman technique conducted by Balandin et al. [8]. The experiment started with the study of the temperature dependency of G peaks on the Raman signal of graphene, where the G peak frequency decreased from 1584 cm⁻¹ at 200 °C to 1578 cm⁻¹ at 100 °C. The thermal conductivity of mechanically cleaved graphite is on the order of ~3000 W/ mK⁻¹ [8].

1.2.1.5 Mechanical properties

Graphene has a high modulus of elasticity of 1TPa [5], a large surface area to weight ratio

of 2,630 m²/g [11], hardness (200 times stronger than steel) [11] and other outstanding mechanical properties. These properties have converted this material into an excellent candidate to be used alone and as a supporting material in composites [12]. The most important graphene mechanical characteristics are its stiffness strength and toughness. The hexagonal lattice formed by the sp² sigma bonds is the primary reason for the mechanical properties of graphene. The first measurements done by Hone et. al revealed that graphene is the strongest material ever measured [45] and concluded that the elastic stiffness was about 340 ± 50 N m⁻¹ [12, 45], with an effective thickness of 0.335 nm and a Young's modulus of about 1.0 ± 0.1 TPa [12,45]. The strength measurement for high quality graphene has an intrinsic value of 42 N m⁻¹ that corresponds to 130 GPa [45]. Incorporation of defects in this carbon material can have detrimental consequences on its excellent properties. Zandiatashbar et al. [46] conducted experiments to study the effect of defects on the strength and stiffness properties of graphene. They used Raman and AFM nanoindentation techniques to quantify the level of defects, as a function of the stiffness and strength values, respectively. The authors induced defects in the graphene using oxygen plasma. These modified surfaces were categorized as sp³ -type and predominantly vacancy type based on the Raman signal [46]. The results showed that in sp³ type defect samples, the mechanical properties (strength and stiffness) of graphene yielded a breaking strength of 14% lower than the pristine graphene. For samples with the vacancy-defects the strength measurements dropped considerably [12,46]. The presence of wrinkles in the graphene film are a crucial factor in the performance of its mechanical properties. Measures of tensile stiffness on a wrinkled surface resulted in lower values than on unwrinkled films. Min and Aluru [47] conducted theoretical studies to understand the effect of wrinkles on the fracture stress behavior. They calculated a fracture stress value of 97.5 GPa for flat graphene surfaces and 60 GPa for wrinkled graphene [12, 47]. The fracture toughness is a critical factor for structural applications. Zhang et al. [48] fabricated a testing device using a micromechanical and SEM nanoindenter system to determine the fracture toughness of CVD synthesized graphene [48]. They found that the fracture stress decreased with increasing crack length and that the critical strain energy release rate was about of 15.9 Jm^{-2} . The fracture toughness of graphene was measured by the critical stress intensity factor, showing a value of 4.0 ± 0.6 MPa [48]. This study concluded that this property is influenced by the weakest link, originating in the initial failure, and is expected to be found in similar membranes [49-52]. Buehler et al. investigated the fracture mechanics of polycrystalline graphene by atomistic simulations, where the mean grain size has a key role in this parameter [49]. They found that the fracture toughness of polycrystalline graphene was 20 - 35% higher than pristine graphene as a consequence of larger energy release rates [12].

1.2.2 Graphene applications

The exceptional electrical, optical, thermal, and mechanical properties of graphene lead to numerous applications such as electronic devices, energy storage (batteries and supercapacitors), optoelectronics, transistor, displays, photodetectors, optical modulators, water filtration, biosensors, and solar cells [53, 11]. Some graphene applications are discussed in more detail below.

1.2.2.1 Electronics

The outstanding electronic properties of graphene allows its usage in many electronic applications, such as, transistors, transparent conductive electrodes [55,56], frequency multiplier, optoelectronics, organics electronics, spintronics and conductive ink [53]. Many of these applications have been amply reviewed and cited in Reference 53. One notable example is by Lemme et al. who showed that graphene field-effect transistors achieved better field effect

characteristics than in silicon transistors [57]. Field-effect graphene transistors are used as sensors to identify proteins, biomolecules, cells, gas, and DNA [53]. Similarly, graphene-based Hall effect sensors have been demonstrated to have high sensitivity, two times superior to current silicon-based sensors [58].

1.2.2.2 Energy

The large surface area to mass ratio of graphene opens the possibility for high energy density storage devices, such as batteries and supercapacitors. This carbon material has shown record-breaking capacitance in supercapacitors and has also been used in lithium-ion batteries with three times higher storage capacity than conventional graphite electrodes [53, 11]. Batteries with a graphene composite anode allows an improvement in the charge and recharge rates, which permits fast redox reactions, leading to lithium batteries with a cycling stability of more than 250 cycles [53,54]. Graphene is also used in the generation (charge conductor, light collector, solar cells, fuel cells) and transmission (conductive wire) of energy. The incorporation of this carbon material in solar cells has allowed the fabrication of new technologies such as dye-sensitized solar cells and in regular photovoltaic cells has been implemented as a counter electrode to increase efficiency [56,59,60].

1.2.2.3 Light processing

The combination of high optical transparency (absorbs 2.3% of visible light) and excellent electrical properties of graphene makes it a good candidate for photodetectors [61], optical modulators, ultraviolent lens, infrared detection and displays [11]. Zhang et al. reported a monolayer graphene photodetector with high photoresponsivity of 8.61 AW⁻¹, three orders of magnitude higher than conventional devices, with a broadband photoresponse in the visible to the mid-infrared range [61].

1.2.2.4 Sensors

The large surface area to mass ratio and electrical properties of graphene allows the production of high sensitivity chemical (gas phase sensors), biological (biosensors, molecular absorption), physical (pressure sensors, piezoelectric devices) and radiological sensors [11,53]. Due to surface modification capacity of graphene, it can be adjusted to detect organic molecules, microbial cells, and biomolecules [53]. Graphene-based electrochemical sensors are capable of identifying heavy metal ions in soil and water with nanomolar limits of detection [11].

1.2.2.5 Medicine and environmental

Graphene's properties lead to extensive biomedical and environmental applications in bioimaging, tissue engineering, drug delivery, testing, and even a graphene-based platform for Covid testing [62]. Graphene has been to improve the efficiency of biosensors, stress wearable sensors [63], cancer detention sensors [64], contaminant removal, and water filtration [53]. Nanoplatelets of graphene have been used in the development of imaging and photothermal therapy. Due to its excellent optical properties in the near infrared region, and coupled with its low toxicity, graphene has been shown to be efficient in tumor targeting [65]. The combination of PEGylated (polyethylene glycol, PEG) and nano-graphene oxide (NGO) allows cellular imaging, while nano-graphene sheets (NGs) bound to PEG were injected into mice for whole tumor imaging. Experiments demonstrated that the tumors remained unchanged after the exposition to PEG/NIR laser system, but the NGs-PEG compound and laser treatment resulted in the elimination of the tumor [53]. The modification of graphene sheets by electrodeposition and electronic doping methods allows the fabrication of different types of biosensors, i.e., glucose sensors and resonance biosensors used in medical diagnostics as well as environmental monitoring. Graphenebased biosensors for protein and DNA testing have been fabricated, as well [66]. The implementation of nanographene as carriers for gene and drug delivery has opened a window of for many medical applications. The large surface area to mass ratio of this carbon material is the key property and driver that allows the effective binding to biomolecules [67]. For example, graphene oxide and multiwalled carbon nanotubes are used as adsorbent for hydrophobic [68,69]. molecules and hydrogels drug delivery systems, respectively in as Graphene nanoporous membranes have potential applications for water desalination and filtration systems, where pore size and applied pressure can influence the efficiency of the device. In the desalination process, graphene membranes are capable of rejecting 97 % of NaCl from seawater, when appropriate chemical composition, applied pressure and pore size are employed [53].

1.3 Graphene synthesis

To take advantage of the exceptional properties of graphene, an effective and efficient industrial scale synthesis method is necessary. Based on this motivation, many methods have been investigated and developed to achieve a high quality single carbon layer. Mechanical exfoliation was the first method to produce graphene in experiments conducted by Novoselov and Geim in 2004. Since their discovery, new thermal and chemical processes have been investigated, which can be classified with respect to their synthetic approaches. For this discussion, the synthesis methods are classified as either top-down or bottom-up approaches. The first corresponds to procedures that use the separation/exfoliation of graphite or its derivatives, while the latter focuses on thermal treatments applied to the substrate for graphene formation [53,70].

1.3.1 Top-down method

Mechanical exfoliation was the first process to obtain graphene and the best example of the top-down method. Subsequent efforts have included chemical exfoliation and other chemical synthesis processes under this classification.

1.3.1.1 Mechanical exfoliation

In 2004, Novoselov and Geim were able to separate graphene from graphite powder using adhesive tape repeatedly, and through consecutive peelings until a single carbon layer was obtained [53]. The exfoliation process is feasible due to the graphite structure, that it is formed from multiple vertical stacked graphene layers bound by weak Van der Waals forces [70]. Related methods, such as scotch tape, ultrasonication, electric field and transfer printing techniques, have all been used in the exfoliation method [70]. The quality of graphene by this method is high and it can be used for the study of its properties. However large-scale production using this technique is still challenging [53,70].

1.3.1.2 Electrochemical exfoliation

Electrochemical exfoliation is conducted by a graphite electrode (such as graphite foils, plates, rods, and graphite powders) immersed in an electrolyte and by applying electrical current, carbon is deposited on another electrode [12,53]. According to the type of reaction, anodic oxidation or cathodic reduction, the graphene production has different characteristics. In anodic oxidation, high-quality few layers graphene is obtained while cathodic reduction produces multi graphene layers. This method represents a good choice in terms of operation facility and process time (minutes/hours) leading to a good process for scaling up the production of graphene. The main disadvantage of this method is the high cost of ionic liquids and the wrinkled morphology of the synthesized graphene, limiting its properties and applications [12,53].

1.3.1.3 Chemical synthesis

Chemical synthesis methods are based on an electrochemical reduction process, where graphene is obtained from the chemical reduction of graphene oxide [12]. Parameters such as solvent, the reducing agent and the surfactant play an important role to maintain a stable suspension. Another crucial aspect is the complete elimination of oxygen because this may influence the properties of the graphene. For this reason, this approach to obtain reduced graphene oxide is not considered high-quality, because some intrinsic (edges or deformations) and extrinsic (O- and H- groups) defects are inevitably present [12]. The incorporation of environmentally friendly chemicals in recent years has facilitated the approach to graphene production with more solvent options to allow a relatively easy scale-up [12].

1.3.2 Bottom-up method

The most common Bottom-up method to grow graphene is chemical vapor deposition. Epitaxial growth on silicon carbide is also described.

1.3.2.1 Epitaxial growth on silicon carbide

The epitaxial growth of graphene on silicon carbide is a well-known and popular technique to obtain this carbon material. This method consists in the sublimation of silicon atoms at high temperature allowing the exposition of carbon atoms on the surface to form a graphene layer [53,70]. In this method, the atmosphere (vacuum, argon, or carbon source), pressure and temperature are key factors for graphene quality. In the search to adjust the growth parameters, one study used a nickel coating on the SiC substrate and reduced the temperature to 750 °C to obtain continuous graphene at the millimeter (mm) scale [53,71]. Some studies have incorporated gases such as H₂, Ar and Si to reduce the Si sublimation rate and improve the graphene quality. A main advantage of the epitaxial growth technique is the production of large-scale graphene on SiC, suitable for industrial applications. The direct deposition eliminates the use of a transfer process that could led to contamination impairing the graphene quality [70,72]. The excellent results of graphene growth on SiC substrates are advantageous for applications in transistors and circuits [71,72]. Nevertheless, this technique must be performed at high temperature (1500 °C to 2000 °C)

and is limited to applications on SiC because of the complexity to transfer graphene onto other substrates [72].

1.3.2.2 Chemical Vapor Deposition (CVD)

The chemical vapor deposition technique is the best known and considered as the most efficient method to obtain graphene [26,55]. CVD consists of a substrate exposed to a mixture of gases in a reactor chamber at a specific temperature, pressure, and gas flow rate to produce the film deposition [53]. There are different types of CVD: Thermal chemical vapor deposition (TCVD) [70,73,74], plasma-enhanced CVD (PECVD) [75,76] and hot filament chemical vapor deposition (HFCVD) [72,77].

1.3.2.2.1 Thermal Chemical Vapor Deposition (TCVD)

Thermal Chemical Vapor Deposition is the most common CVD method used in graphene synthesis, mainly composed of a quartz tube inside a furnace, forming the reactor chamber. The substrate is placed inside the quartz tube part that is inside the furnace, as can be seen in Figure 1.5. The carbon source and carrier gases have a laminar flow longitudinally with respect to the quartz tube [53]. The graphene synthesis is determined by the growth parameters such as temperature, pressure, and gas flow, where the precursor undergoes thermal decomposition due to heat of the furnace, depositing carbon on the surface of the substrate. Typical substrates are copper and nickel, which can be both catalytic for the carbon precursor dehydrogenation, and as a platform for graphene deposition. Other transition metals such as cobalt, palladium, ruthenium, and iridium are also used in graphene growth [70]. The substrate function can be explained in two stages. First it assists in the carbon separation from the precursor gas, second, the graphene layer is formed on the metal surface by the carbon bond with itself. Some parameters in the CVD experiments can be modified to achieve better graphene quality. The graphene growth can be performed at low or

atmospheric pressures, and the carbon sources can be in liquid (methanol, ethanol, and propanol), solid (polymers, graphite) and/or gaseous (methane, ethylene and propane) states. An annealing process can be used to improve the quality, roughness and remove the oxygen from the surface of the substrate [77]. Recent studies have proposed to grow graphene on nonmetallic substrates such as silicon oxide, silicon, quartz, silicon fused, and sapphire to avoid the complex transfer process [11,53,70,78]. This will be discussed in detail in chapter 3.



Figure 1.5 Schematic illustration of a Thermal Chemical Vapor Deposition (TCVD).

1.3.2.3.2 Plasma-Enhanced Chemical Vapor Deposition (PECVD)

In the PECVD method, a plasma is generated in a vacuum chamber to decompose of carbon precursor that will interact with the substrate surface leading to graphene film formation [53,70]. The plasma is produced using a variety of gases (H_2 , CH_4 , Ar) ionized by direct current (DC), microwave, inductive coupling or radio frequency (RF) (Figure 1.6). An important aspect of the PECVD technique is that the deposition can be performed at low pressure and temperature and does not require a catalytic substrate for graphene formation. This technique had allowed the direct growth of mono and few layer graphene on Si, SiO₂, Al₂O₃, Mo, Zr, Ti, Hf, Nb, W, Ta, Cu, and 304 stainless steels. The PECVD technique is a good candidate for large scale fabrication of graphene for industrial application [70]. Nevertheless, the use of gas-phase precursors makes it an expensive technique that limits its implementation.



Figure 1.6 Schematic illustration of Plasma-Enhanced Chemical Vapor Deposition (PECVD).

1.3.2.3.3 Hot Filament Chemical Vapor Deposition (HFCVD)

In the HFCVD technique, the decomposition of the carbon precursor is facilitated by an array of hot filaments placed above the substrate (Figure 1.7). The filaments are generally made of rhenium or tungsten and can reach a temperature of 2200 °C. The substrate is placed in a temperature controlled heater allowing more precise control of the deposition process. This CVD method has been widely used for the growth of diamond and nanotubes, but less so for graphene. [72, 77]. The hot filament allows the dissociation of the hydrogen and methane to produce active radicals and carbon atoms, where hydrogen reduces the amorphous carbon formation (Figure 1.7). The turbulent flow produced by the vertical introduction of the gases in the HFCVD provides better mixing compared with the laminar flow of a tube furnace CVD [77]. High quality graphene
on copper has been obtained by HFCVD and recent studies have reported graphene growth on SiO₂/Si by HFCVD with good quality [77].



Figure 1.7 Schematic of hot filament chemical vapor deposition (HFCVD) reactor.

1.4 Transfer process

CVD has been shown to be an efficient growth technique, that allows the production of large-area and high-quality graphene on metal substrates. Nevertheless, the vast majority of graphene applications require the deposition on dielectric substrates such as SiO₂, SiC and others. For this reason, the implementation of a transfer process to obtain the graphene film in the desired material is necessary [78]. Many transfer techniques had been proposed; however all processes require expensive chemicals and long process time. In this section, the characteristics of the wet and dry graphene transfer methods will be discussed.

1.4.1 Wet chemical methods

The wet transfer method is generally performed using a coating as protective layer made of polymeric polydimethylsiloxane (PDMS) or Poly (methyl methacrylate) (PMMA) over the graphene. The catalytic substrate is then etched with different solvents. The most common chemicals to remove the metal substrate are iron chloride (FeCl₃), hydrochloric acid (HCl), nitric acid (HNO₃), iron nitrate (Fe (NO₃)₃) and copper chloride (CuCl₂). After dissolving the metal substrate, the polymer is removed by heat and submerged in acetone for more than 10 hours [72,78].

1.4.2 Dry chemical methods

The dry transfer method does not use a solution as PMMA for graphene protection during its transport process. A thermal release tape is used as a support layer for the graphene. The graphene transfer procedure from the copper to the desired substrate starts by attaching the thermal tape to the graphene/copper sample at high pressure. This assembly is submitted to an etchant solution to remove the copper, after is then rinsed with deionized water and dried with nitrogen gas. The thermal tape and graphene are placed on the target substrate, then the tape is removed by a thermal treatment [72].

1.5 Motivation of the work/statement of the problem

The special 2D structure of graphene makes it a material with exceptional electrical, thermal, optical and mechanical properties with innumerable applications. The most common and efficient method for graphene synthesis is the thermal CVD technique, allowing it to grow on transition metals. The high quality and film size of graphene grown on copper makes the thermal CVD a promising technique for large scale production. However, many applications of graphene require a transfer process to the desired material, where wrinkles and chemical contamination degrade its properties [72]. Some research groups have proposed the direct growth of graphene on dielectric substrates such as SiO₂, quartz, silicon fused, sapphire and others using a metal catalyzed method. In this technique, a thin layer of a catalytic metal (copper or nickel) is deposited on the substrate allowing the production of atomic carbon. The catalytic metal is subsequently evaporated during or after the graphene growth. Other researchers have proposed metal free methods using a

CVD, although with some limitations on the controllability of the graphene growth parameters. HFCVD is a method with good controllability of the growth conditions that can be scaled up for industrial production of graphene. In comparison with the TCVD technique, the gas flow in the HFCVD is turbulent, while the gases in the TCVD flow in a laminar way. This characteristic enhances the gas mixing and heat transfer properties in the HFCVD process [77]. Studies have been reported that obtain high quality graphene on copper by HFCVD with excellent properties [72]. Although excellent results had been obtained with this technique in the graphene growth on copper, the transfer process onto target substrates remains a crucial issue in the quality of this material and its cost efficiency. In this present work, propose the direct growth of graphene on SiO₂/Si substrates by HFCVD avoiding the transfer process and with the prospect to produce it at industrial scale.

In addition to the potential applications of graphene on SiO₂/ Si substrates, the deposition of this carbon material on SiC has been the object of several studies because of its outstanding qualities. SiC is a promising material with a lot of applications due to its excellent properties, such as superior hardness, high thermal stability, high elastic modulus and extreme chemical stability [79,80]. The characteristics of this SiC are improved with graphene incorporation, and it can be used as a platform to grow graphene. The first studies to obtain graphene on SiC were carried out by the Si sublimation method at high temperature (2180 °C) in a vacuum environment [81]. Later experiments showed that the quality of graphene was impaired by the high sublimation rate of Si [9]. This fact led to the exploration of other methodologies to maintain the properties of graphene on SiC. These studies incorporated gases such as Ar, Si and H₂ in the growth step to reduce the Si sublimation rate and improve the graphene quality [82-84]. A few studies have used the combination of Si sublimation method during the annealing step and the carbon deposition assisted with methane as a carbon source using TCVD. Many unknowns remain about the process to grow graphene on SiC and further development is still needed. This work reports a method to obtain graphene on SiC using methane as a carbon source by HFCVD system, with the possibility to adjust the growth parameters to obtain different characteristics of this material on SiC.

Ti6Al4V (Ti64) alloy is a widely known material for its applications in aerospace, biomedical and automotive areas, due to its excellent properties, such as hardness, low density, high resistance to corrosion and fatigue compared with other metals. This alloy is considered as an excellent candidate for orthopedic implants due to its similar mechanical properties to human bone [85-87]. Nonetheless, Ti64 alloy has shown some biocompatibility mismatch for orthopedic implants, i.e., poor wear resistance and corrosion in extreme environments [88,89]. Because of this, some studies have proposed the incorporation of carbon-based materials such as graphene, carbon nanotubes and graphene oxide to improve the weaknesses of Ti64. Specifically, research has focused on the study of biocompatibility and corrosion resistance of this metal for biomedical applications. One of them found that a nanocoating of graphene on Ti64 inhibited the corrosion, while maintaining its structural integrity [90]. Another study incorporated reduced graphene oxide nanosheets on Ti, making possible a modification of the surface that promoted and accelerated the osteogenic differentiation in the early stage of dental implants [91]. Some studies have developed a hybrid multilayer system with graphene, Ti64 and niobium pentoxide [92], where the graphene/Ti64 samples showed the best corrosion resistance among the combinations that were evaluated [92]. Few studies have confirmed the incorporation of carbon materials on Ti and Ti64 using different methods such as TCVD on Cu, chemical reduction and micro-arc oxidation coating. CVD remains as the most common method for graphene deposition, nevertheless it requires a transfer process to incorporate this carbon film onto Ti and its alloy. In fact, there are no studies

that describe the direct incorporation of graphene on Ti64 alloy by TCVD or HFCVD. This work reports a method for direct deposition of graphene on Ti64 alloy by HFCVD for future biomedical applications.

1.6 Objectives

1.6.1 General Objectives

Analysis of graphene synthesis on SiO₂/Si, SiC, and Ti6Al4V substrates by hot filament chemical vapor deposition (HFCVD).

1.6.2 Specific Objectives

- Grow graphene directly on SiO₂/Si by HFCVD and analyze the structural, chemical, and morphological characteristics using Raman, SEM, EDS and XPS techniques.
- Evaluate the graphene quality and crystal size on SiO₂/Si using Raman spectroscopy and SEM images.
- Grow graphene on silicon carbide by HFCVD and identify the structural, chemical, and morphological qualities at different growth conditions using Raman, SEM, EDS and XPS techniques.
- Evaluate the graphene quality and crystal size on SiC using Raman spectroscopy and SEM images.
- Deposit graphene on Ti6Al4V alloy by HFCVD, analyze the carbon presence through a structural, chemical, and morphological study using Raman, SEM, EDS and XPS techniques.
- ▶ Propose a growth mechanism of graphene on SiO₂/Si, SiC and Ti6Al4V alloy.

1.7 Reference

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Chapter 2. Experimental and Analytical Techniques

2.1 Overview

Carbon-based materials have played a key role in human development leading to many applications in electronics, energy technology (semiconductors, batteries, solar cells), environmental (water and air filtration), and biomedical areas (biosensors, tissue engineering and biological agents). These materials have been classified according to their historical progress into classic carbons, new carbons, and nanocarbons [1,2]. The first group of materials were developed before the 1960s and are comprised of graphite blocks (used as electrodes), carbon black (tires and inks), and activated carbon (water purification). In the 1960s the second group of "new carbon" materials, i.e. carbon fibers (automotive and aerospace industry), pyrolytic carbon (mechanical heart valves), glass-like carbon (electrode), and diamond-like carbon (coatings), were developed [1,2]. The third classification began to be developed in the 1990s, also known as the nanotechnology era. During this period, various fullerenes with closed-shell structures, carbon nanotubes with nanometer diameters, and graphene flakes with atomic thickness were discovered. Furthermore, the functionalization of carbon materials allows additional advantages due to the manipulation of the surface reactivity to tailor electrochemical properties. These functionalized carbon materials have broad applications in catalysis, batteries, supercapacitors, fuel cells, and organic photovoltaics [3,4]. The functionalization also modifies the optical and luminescent properties of these carbon-based nanostructures [3,4]. In summary, the well-known exceptional properties of graphene have allowed the extension of this material in diverse fields as a promising candidate to solve current technological limitations.

In this thesis a graphene synthesis procedure on different substrates (SiO₂/Si, SiC, Ti6Al4V) is reported. The sample pre-treatment and the HFCVD experimental conditions are

explained and analyzed in detail. The common graphene characterizations techniques such as Raman spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Optical Microscopy (OM), Energy-dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and X-Ray Diffraction (XRD) are presented.

2.2 Hot filament chemical vapor deposition (HFCVD)

2.2.1 System description

The versatility of the HFCVD system allows control and measurement of the temperature, gas flow and pressure with a high degree of confidence. A commercial HFCVD instrument (BWS-HFCVD1000, Blue Wave) was used for the graphene deposition. The setup is divided into three main parts: the reactor chamber, the control panel and the external connections (gas lines, mechanical pump, and cooling system) (Figure 2.1). The reactor of the HFCVD system consists of a spherical chamber with three filaments made of rhenium or tungsten located above the heater where the substrate is positioned (Figure 2.2). The number of filaments (1 up to 6) can be varied to suit the substrate size (1 cm x 1 cm), in this study three filaments were used. The system also has a thermocouple and a pyrometer to measure the heater and surface substrate temperatures, respectively. The chamber pressure is controlled and measured over a range of 2×10^{-2} to 135 Torr. The control panel the consists of multiple displays to register the temperature, pressure, and gas flow. The mass flow controllers (MKS Instruments and Alicat Scientific) can regulate the gas flow rate from 0.1 to 100 sccm. The filament temperature can reach up to 2500 °C and is regulated by a separate control. The third part of the CVD consist of the gas lines, the water line (cooling) and two mechanical pumps (PFEIFFER Vacuum), all connected to the CVD panel. The gases enter the chamber from the top as a shower-like turbulent flow. The spherical reactor is made of a double walled stainless steel chamber with a volume of ~ 20 liter, where the water flow pass through the

steel walls to control the system temperature while the experiments are running. In addition, three fans outside and above the chamber are used to control the temperature.

An important advantage of the HFCVD technique is the systematic adjustment of the growth parameters e.g., pressure, gas flow rates, deposition time, substrate-to-filament distance (5–15 mm) and substrate and filament temperature. This versatility allows the efficient production of large scale graphene compared with a tube furnace TCVD [5,6]. This study is a continuation of a previous work of graphene growth on copper [7], extending the procedure to deposit this carbon material on different substrates by HFCVD.



Figure 2.1 Schematic of HFCVD, three main parts: reactor chamber, control panel and the gases/cooler system.



Figure 2.2 Filaments and heater images of the HFCVD system.

2.2.2 Sample pre-treatment

The graphene growth experiments of this study were conducted on three different substrates SiO₂/Si, SiC and Ti6Al4V(Ti64). SiO₂/Si and SiC substrates were exposed to different cleaning pretreatments with chemicals such as acetone, isopropanol and H₂SO₄. The TiAl64V substrate was not cleaned with chemicals, because it is composed of a compressed powder pellet with nanoporous structure. The SiO₂/Si and SiC substrates were cut into 2×2 cm and 1×1 cm pieces, respectively. The thickness of both substrates is 0.55 mm. In the case of TiAl64V alloy, these substrates were prepared from a powder and pressed into a pellet with a diameter of 13 mm and a thickness of 2.6 mm.

In preliminary experiments, copper substrates were used as controls for the growth of graphene at different conditions. These substrates were cleaned with acetic acid, deionized water, acetone, and isopropanol to remove the copper oxide formed on the surface. The SiO₂/Si substrates were cleaned with deionized water, trichlorethylene, acetone (histology grade), and isopropanol (histology grade); the last three reagents were obtained from Fisher Scientific. To further clean the substrate, a mixture of sulfuric acid (H₂SO₄ purity range of 95–98%) and hydrogen peroxide (H₂O₂ solution at 30% w/w in H₂O) was prepared (both provided by Sigma Aldrich). A thin copper-strip

(3 mm width) was deposited in the middle of the SiO₂/Si substrate by sputtering (AMNPS-1 plasma-therm, Varian) with a deposition time of 1 minute. The copper target (99.99% pure) used for the deposition was obtained from the CERAC company. The thickness of the deposited copper layer was between 100–150 nm and was measured using an Ambios Technology XP-200 profilometer. The SiC substrates were subjected to the same procedure as SiO₂/Si. Additionally some of the samples were cleaned with hydrofluoric (HF) acid to study the effect of this treatment on the impurities and oxygen reduction of the surface. The Ti6Al4V pellets were prepared from powder (Advanced powders & coating), these were compacted at a pressure of 24 MPa using a Carmer pressure machine. The pellets were sintered in a CVD tube at 950 °C for 2 hours within an argon flow rate of 200 sccm. Figure 2.3 shows the schematic for the formation of pellets starting from Ti6Al4V powder. The titanium alloy pellets were not exposed to a chemical pretreatment.



Sintering using CVD tube furnace

Figure 2.3 Schematic of the Ti6Al4V alloy pellets preparation, from powder to solid compact.

2.2.3 Graphene Deposition

The experimental stages to grow graphene on different substrates were similar, but the growth parameters were modified to different characteristics of this carbon material for each type

of substrate. This was possible with the HFCVD system that allows systematic adjustment conditions (gas flow rates, deposition time, etc.).

As described previously, graphene on copper experiments were done as a control, because this is well established work with excellent results in our laboratory [7]. In general, the current work follows the stages of the graphene on Cu work, where the process is divided into the annealing, growth and cooling steps as shown in the schematic in Figure 2.4. In the first stage, the substrate is positioned over the heater and directly below the three filaments. Before initiating the annealing process, the chamber is evacuated to a pressure of 20 mTorr. H₂ and Ar gases are injected into the chamber with a flow rate of 80 sccm and 20 sccm, respectively. The temperature of the heater was fixed at 950 °C for 40 minutes to clean and improve the surface quality of the substrate. In the growth step, Ar gas was turned off, the H₂ flow is reduced (0 to 50 sccm) and the CH₄ gas is incorporated with a flow rate of 1 - 10 sccm. At the same time, the filament is turned on with a temperature of 1800 °C to 2000 °C for different times from 30 to 300 minutes. The hot filaments dissociate the CH₄ gas into reactive carbon species for graphene formation. Finally, the heater and filaments are turned off and the system is cooled down, maintaining the H₂ and CH₄ gases until it reaches a temperature of 100 °C. The gases are then evacuated, and the sample can be removed from the reactor. The graphene growth process on SiO₂/Si and SiC are similar to the copper substrates, but with adjustments in temperature and growth times to obtain different characteristics of graphene such as of number of layers and crystal size. For the graphene grown on Ti6Al4V pellets, these experiments were conducted without an annealing process and during the growth step, the H_2 gas was turned off after the heater reached the desired temperature. Table 4.1 summarizes the substrate preparation and the graphene growth parameters for each substrate.



Figure 2.4 Schematic of the main steps to growth graphene by HFCVD.

Table 2.1 Graphene growth parameters for different substrates.

Substrate	Substrate preparation	Annealing	Graphene growth
SiO ₂ /Si	Cu thin film in the	H ₂ (80 sccm),	H ₂ (0-50 sccm), CH ₄ (1–10 sccm)
	middle	Ar(20sccm)	950 °C
		950 °C	
SiC	Chemical treatment	H ₂ (80 sccm),	H ₂ (0-50 sccm), CH ₄ (1–10 sccm)
	(HF)	Ar (20 sccm)	950 °C
		950 °C	
Ti6Al4V	Pellet	NO	H ₂ (0-50 sccm), CH ₄ (10 sccm)
	formation/Sintering	INU	950 °C

2.3 Graphene Characterization

The graphene characterization was conducted by the standard techniques to understand the carbon film properties such as grain size, quality, morphology, defects, and number of deposited layers. The group of techniques used are the Raman spectroscopy (the most important), SEM, AFM, Optical images, XPS, EDS, and XRD.

2.3.1 Raman spectroscopy

Raman spectroscopy is the most common and versatile method to identify the growth of graphene and its respective characteristics. It has been considered as the fundamental method to study this carbon material. Raman spectroscopy is a versatile, non-destructive technique used for quality control at the mass production scale [8,9] and for academic research purposes. This allows the identification of unwanted by-products, structural damage, functional groups, and chemical modifications introduced during the preparation. Since the behavior of the delocalized electrons can influence the scattering of phonons, this technique can identify defect disorders [11-17], edges [12, 18-22], doping [23-29] and/or magnetic fields [30-37]. In addition, Raman spectra gives information about disordered amorphous carbons, fullerenes, nanotubes, diamonds, carbon chains and poly conjugated molecules [8,10].

The Raman technique consists of the interaction of photons with the molecule or crystal lattice in the system in a vibrational mode producing inelastic (Stokes and Anti-Stokes) or elastic scattering (Rayleigh scattering) of the incident photon. To obtain an active Raman signal, the molecule must undergo a change in its polarizability during the vibrational transition [7]. Most of the scattered light will be of the same wavelength as the monochromatic light source (UV-visible region), while a small quantity of the light will disperse inelastically to produce the Raman effect. The two types of inelastic scattering, Anti-Stokes and Stokes, happen when the scattered photons show a higher ($v_0 + v_m$) and lower ($v_0 - v_m$) frequency than the incident photon, respectively. The v_0 and v_m correspond to the incident monochromatic light source and the vibrational frequency of the molecule, respectively. The energy diagram of the different photons scattered (Rayleigh, Stokes, and anti-Stokes) are shown in Figure 2.5. The biggest contribution to the Raman spectra is typically due to the Stokes effect because in order to obtain photons at higher energy than the

monochromatic light source the molecules in the material should be initially vibrational excited by other means [7].



Figure 2.5 Schematic of the diagram of the energy for Rayleigh (elastic), Stokes and Anti-Stokes (inelastic) scattering.

Graphene characterization by the Raman technique allows determination of the quality and morphology of the film, as well as the number and orientation of the deposited graphene layers. It also allows the study of the effects of external perturbations in graphene, such as electric and magnetic fields, strain, doping, disorder, and functional groups. This information can be obtained by the pattern of the Raman signal, i.e. the position, width, and intensity of the peaks [8]. The characteristic Raman spectra of graphene shows two main peaks, the G peak (1580 cm⁻¹) that is sensitive to sp² carbon atoms and the 2D peak (2700 cm⁻¹) that appears in response to a two-phonon vibrational process. A third peak, the D (1350 cm⁻¹), is activated by the edges or defects

in graphene [38,39]. The G and 2D peaks characteristically correspond to the signal for graphitic materials [18]. In addition to the D peak, a peak at 1620 cm^{-1} known as D' [40,41], is also observed in defective graphene structures, as shown in Figure 2.6.



Figure 2.6 Raman spectra of graphene growth on SiO₂/Si by HFCVD. The D, D', G and 2D peaks are marked.

2.3.1.1 Particle size and defect calculations from Raman measurements

To obtain morphological information about the graphene films, Tuinstra [42] and Cancado [43] used the ratio of the D and G intensity peaks to estimate the particle size. Initially, Tuinstra suggested a relation using this ratio (D/G) from the Raman spectra using an excitation light source of 514.5 nm [44]. To establish a relation for any excitation laser wavelength, Cancado et al. introduced a relation (Equation (2.1)) between excitation laser wavelength (λ_l) [43] and particle

size (L_{α}). The value 2.4 x 10⁻¹⁰ is a proportionality constant, and I_D/I_G is the D/G intensity ratio.

$$L_{\alpha} = (2.4 \times 10^{-10}) \lambda_l^4 (I_D / I_G)^{-1}$$
(2.1)

Defects in the graphene films can be calculated from their Raman spectra using the Equation (2.2) [44,45], where L_D represents the inter-defect distance, E_L is the excitation energy, and the defect concentration corresponds to $1/L_D^2$ [44].

$$L_D^2 (nm^2) = \frac{3600}{E_1^4} (I_D / I_G)^{-1}$$
(2.2)

The number of graphene layers can be estimated by the ratio of the intensities of the 2D and G peaks. The full width at half maximum (FWHM) of the 2D peak can give information about the quality of graphene crystallites. However, the doping level in the carbon material is a potential aspect that can influence the 2D/G intensity value, and may lead to an incorrect estimation of the number of layers [45]. The pre-treatment for substrates and the growth conditions are crucial steps to avoid the incorporation of unexpected elements in this carbon material and allow the correct description of its properties.

In the present study, Raman measurements were conducted with an excitation laser operating at 532 nm (Thermo Scientific DXR, Waltham, MA). The spectra were collected over a frequency range of 1100 to 3100 cm^{-1} with a spot size of 0.7 µm, using the objective microscopy of 50x and all spectra were recorded using a Thermo Scientific OMNIC software. In addition, Raman mappings were taken for graphene on SiO₂/Si and SiC samples over an area of $150 \times 100 \text{ µm}^2$ and a step size of 2 µm; the collecting time for each point in the Raman mappings was 20

seconds. For graphene on copper and Ti6Al4V alloy samples, a mapping study was not done because the uniformity was evaluated by optical microscopy.

2.3.2 Optical microscopy

Optical microscopy provides information about the morphology of the surface of the material at the micrometer level. With this technique it is possible to identify particle size, contamination, and uniformity in the samples with a certain resolution and without an advanced magnification [46]. Specifically, an optical microscope can describe the homogeneity of 2D materials such as graphene, where the crystal shapes and distribution of the film can be observed. The optical microscopy captures the image using a regular camera to generate a micrograph. Currently advances in these areas use complementary metal-oxide-semiconductor and charge-coupled device (CCD) cameras to capture digital images [47]. This digital microscopy has the versatility to examine the sample through the conventional eyepieces and directly on the computer screen [47]. In addition, sample preparations such as thermal treatment have been used to improve the contrast and image resolution. For example, in graphene on copper samples, an oxidation treatment of this metal allows a better observation of the carbon crystals directly and without a transfer process [48].

Two optical microscopes were used in this study, the first one corresponds to a Raman microscopy (Thermo Scientific DXR) with a magnification of 50x and a Nikon shuttle-pix (P400R) with magnifications of 20x up to 200x. This characterization allows identification of graphene deposition in areas on top and next to the copper strip on SiO₂/Si. In the graphene on SiC study, optical images were taken of the surface at different growth conditions and chemical treatments. In the Cu and Ti6Al4V samples wrinkles and pores were observed, respectively.

2.3.3 Scanning Electron Microscopy (SEM)

Electron microscopy (EM) techniques are considered as the most powerful methods to investigate nanomaterials, due to their capacity to analyze the size, shape, and aggregation state of the nanoparticles [46]. There are two types of EM, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [46]. The latter was used in this work. The conventional SEM technique gives information about the sample morphology. The chemical composition can be obtained with the incorporation of Energy-Dispersive X-Ray Spectroscopy (EDX). The crystalline structure and orientation of the material can be determined with the addition of Electron Backscatter Diffraction (EBSD) [49]. The principle of these techniques is based on the interaction of a high energy electron beam with the sample, and depending on this encounter, the incident electrons produce secondary electrons (inelastic interaction), backscattered electrons (elastic scattering), and X rays. These electrons can be transmitted and diffracted. The SEM image is obtained by detecting the secondary and backscattered electrons emitted from the sample. The diffracted electrons toward the beam can give information about the crystallographic characteristics [46]. The detection of the X-rays enables the elemental analysis of the material study. In summary, backscattered electrons and secondary electrons are converted into a signal that is interpreted by a computer to produce the SEM image. In our study an SEM (IT500HR, JEOL) at different magnifications (5000×, 25,000× and 140,000×) and an energy of 20kV was used to identify the morphology and estimate the nanocrystal size of graphene films on different substrates (SiO₂/Si, SiC and Ti6Al4V). In addition, this technique was used for the characterization of the porous morphology of Ti6Al4V pellets and the estimation of the pore size.

2.3.4 Atomic Force Microscopy (AFM)

AFM allows the characterization of many types of surfaces, such as polymers, ceramics,

composites, glass, and biological samples. This method is used to measure forces (adhesion strength, magnetic forces and mechanical properties), and create topographic images (morphology) of the s material under study. This technique is ideal for characterizing sample topography at the nanoscale level with high spatial resolution and easy sample preparation process. In addition, the electronic and chemical properties of the atoms and molecules can be obtained [46]. The technique consists of the mechanical interaction between a sharp tip and the sample surface obeying the Hooke's law. The tip is located at the end of a microcantilever with a radius range of a few angstroms (made of carbon nanotubes) to a few nanometers (made of silicon). The cantilever deflection generated by the tip on the sample allows the formation of the image. The changes in the cantilever are detected by the laser displacement and registered by a photodiode array. The tip size and the type (contact or tapping mode) of the scanning measure can be adjusted according to the material to be studied. In the AFM contact mode, the tip is in continuous interaction across the surface. This contact is registered by the cantilever deflection, or the signal received to maintain the cantilever fixed on the surface. Due to the constant position of the tip on the surface, cantilevers with low stiffness are used to obtain the best deflection signal. In contrast, the AFM tapping mode is performed by the oscillation (up and down) of the cantilever at a resonant frequency. This oscillation can reach an amplitude up to 200 nm, and this last parameter is used to control the height of the cantilever above the sample and depends on the interaction forces between the tip and the surface. [46]. The AFM allows the topographical characterization of synthetic and biological materials. This allows a surface revelation of the quality of the graphene films at the nanoscale level, where changes of the amplitude, phase, and frequency of the oscillations from the tip and sample interactions determine the surface properties of the sample [46].

In the present study, an atomic force microscope, AFM (Nanoscope V, Vecco) was used

in tapping mode. The images were taken in areas of $3 \times 3 \mu m$ to analyze the morphology of graphene on SiO₂/Si, SiC and identify the crystal size and the number of graphene layers.

2.3.5 Energy-dispersive X-ray analysis (EDX)

EDX spectroscopy an atomic composition technique that is coupled to SEM equipment to facilitate the analysis of near-surface elements up to $2 \mu m$ of depth. This method allows the quantification of elements in a point or in a selected area by the atomic percentage value (A%) [46]. The X-rays produced during the SEM characterization allows an estimate of the composition of the material. Since these X-rays are generated from a depth of 2 µm, EDX is not an ideal technique to surface analysis. In the EDX spectra, the positions and intensity of the peaks indicate the type of element and its concentration, respectively. The measurement error in the concentration for elements heavier than fluorine is lower than 5%, while for lighter elements the error increases. There are different X-ray techniques for nanomaterials characterization. e.g. X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), small-angle X-ray scattering (SAXS), and X-ray diffraction (XRD). To obtain the best compositional characterization, techniques such as X-ray absorption spectroscopy (XAS), X-ray absorption fine structure (EXAFS), XPS, X-ray absorption near-edge structure (XANES), EDX, and X-ray fluorescence spectroscopy (XRF) are useful [46]. To stimulate the X-ray emission of the different elements of the sample, the beam can use different excited particles such as electrons, protons, or X-rays.

In this study, an EDX (DRYSD30, JEOL) spectrometer was used to identify chemical composition of the graphene on different substrates (SiO₂/Si, SiC, Ti6Al4V). The EDX spectra for SiO₂/Si and SiC were taken at 25000x of magnification. In the case of graphene on porous Ti6Al4V pellets, the EDX analysis were taken at 3000x of magnification. The excitation energy value for all EDX measurements was about of 20 kV.

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2.3.6 X-ray photoelectron spectroscopy (XPS)

The XPS technique can provide analytical characterization of the surface composition of the sample. This method can be used in many applications such as the identification of surface contaminants, surface defects, stains, and discolorations. In addition, it is possible to identify the elements in plasma-modified polymer materials and measure the thickness of coatings and oxide films [50]. The technique is based on the photoelectric effect. The sample is bombarded with X-rays, and the kinetic energy of the electrons removed from the material is analyzed to determine the elemental composition. The XPS spectra is formed measuring the binding energy of each emitted electron, calculated by the photoelectric effect in Equation 2.3, where the photon energy corresponds to the incident X-ray and the kinetic energy is measured by the analyzer [50,51]. Because the energy spectrum is different for each element, it is possible to identify the composition of the sample surface to a depth of approximately 1-5 nm.

Kinetic energy (KE) = Photon energy (hv) – Binding energy (BE)
$$(2.3)$$

Typical X-ray sources used are MgK α at 1253.6 eV and AlK α at 1486.6 eV. This radiation can penetrate up to a few micrometers in the sample. However, the detector can only receive reliable information from photoelectrons emitted closer to the surface (1 to 5 nm), because the deeper ones undergo inelastic collisions with other atoms and lose their energies to escape from the surface. A typical XPS spectrometer consists of an X-ray source, electron energy analyzer, and detection system. The chamber must be under ultra-high vacuum conditions, typically 1 × 10⁻⁷ mbar (7.5 × 10⁻⁸ torr) or lower, to reduce the collisions between the photoelectrons and atoms or molecules, while increasing the possibility of reaching the analyzer and detector [50,51]. This technique works well to detect chemical composition on the surface; however, what is most relevant is its ability to provide information on the chemical state of the emitting atoms. In terms of sample preparation for XPS measurements, solid samples are the most compatible form (require little or no preparation) but powders can be mounted on tape, and liquid samples can be deposited on a substrate such as silicon after a dry process [50].

In this study, X-ray photoelectron spectroscopy, XPS (PHI 5600 Physical Electronics), with an energy range of 0 a 1200 eV was used to identify the carbon element in all samples (SiO₂/Si, SiC and Ti6Al4V). It also was used to identify metals, like copper in areas on top of the strip for graphene on SiO₂/Si samples. Furthermore, the XPS method was used to confirm the absence of contaminants that could have an influence on the surface properties.

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Chapter 3. Graphene Growth Directly on SiO₂/Si by Hot Filament Chemical Vapor Deposition

3.1 Introduction

Microexfoliation of graphite by Novoselov and Geim in 2004 to obtain graphene opened a window on 2D materials technology [1]. This carbon material has been regarded as a promising material due to its excellent properties and potential applications [2–7]. Graphene with its high electron mobility, high conductivity, and optical transparency has become a candidate for highspeed electronics such as ultrathin transistors, photodetectors, and optical modulators [2,3]. These attributes contribute to the advancement of circuit boards, display panels, and solar cell technology [2,3]. Furthermore, its high internal surface area, electrochemical reactivities and mechanical (high stiffness and low density) properties allow greater efficiency in supercapacitors, electrochemical systems, and strain sensors, respectively [3-5]. In search to find the best method to obtain graphene, many studies have proposed a wide variety of process [8–11]. The best-known methodologies correspond to the microexfoliation of graphite [1], graphene oxide reduction [12], epitaxial growth on SiC [13,14] and chemical vapor deposition (CVD) on different substrates [15,16]. This last method is the most appropriate because it allows the manipulation of growth parameters to control the structural characteristics of graphene and the number of the deposited layers (monolayer, bilayer, few layers, and multilayers) [17,18]. Graphene growth by CVD on metallic substrates has been used extensively, because the catalytic properties of the substrate result in a large area of high-quality graphene [19–21]. To scale this technology to industrial production, hot filament chemical vapor deposition (HFCVD) promises to be one of the leading potential techniques. This method obtains large area, high quality graphene on copper substrates with controllable growth parameters [18,22–24]. The hot filament dissociates the hydrogen and methane, producing active radicals that reduce the amorphous carbon to improve the quality of the

graphene film [24] and the turbulent flow into the chamber conducts a better mixed of gases.

Nevertheless, for electronic applications, current chemical vapor deposition methods require a transfer process of the graphene film from the metal substrate to the dielectric, which has several drawbacks, i.e., residual chemical contamination and the risk of wrinkling or breakage of the graphene film [25]. To avoid this complex transfer procedure, researchers have sought to develop new methodologies to deposit graphene directly onto non-metallic substrates such as SiO₂/Si, quartz, fused silica, and others [26]. To date, there are no reports in the literature of the direct deposition of graphene on SiO₂/Si by HFCVD, although several attempts by tube furnace TCVD have been published. Table 3.1 presents a variety of methods for graphene deposition on SiO₂/Si by other types of CVD. These methodologies are under two classifications: Catalyst-free and metal catalyzed direct growth CVD, where both TCVD and plasma enhanced CVD (PECVD) are used [26].

In the first methodology (catalyst-free), most of the graphene growth experiments on nonmetallic substrates are conducted at high temperatures (1060–1100 °C) over a long deposition time [26]. Liu et al. obtained high-quality monolayer, bilayer and few-layer graphene without any catalyst over a temperature range of 1060–1100 °C at atmospheric pressure and using methane as the carbon source [27]. Sun et al. were able to grow continuous nanocrystalline graphene at 1000 °C with good electrical properties, such as sheet resistance and Hall mobility [28]. Medina and coworkers reported that the PECVD catalyst-free growth temperature can be reduced by directly growing a nanographene film on SiO₂ at low temperatures (400 °C) by using the electron cyclotron resonance CVD (ECR-CVD) method [29].

Method	CVD Type	Substrate	Pre-Growth Step	Carbon Source/ Temperature	Reference
	Tube Furnace	SiO ₂ (0, 90, 300, 500 nm)/Si	H ₂ (70–160 sccm)/1060–1100 ° C	CH ₄ (30 sccm)/1060–1100 ° C	[27]
Catalyst-free		SiO ₂ (300 nm)/Si	H ₂ (50 sccm) and Ar (1000 sccm)/1000 ° C	CH ₄ (300 sccm)/1000 ° C	[28]
	ECR plasma	SiO ₂ /Si, quartz, and glass	Ar (5sccm)/400 ° C	C ₂ H ₄ (0.12 sccm) and Ar (0.12 sccm)/400 ° C	[29]
	Tube Furnace d	Ni layer/silicon	H ₂ or He (400sccm)/ 900 ° C	CH ₄ or C ₂ H ₂ (50sccm) and H ₂ (50sccm)/900 \degree C	[30]
		Cu layer (60 nm)/SiO ₂ (300 nm)/Si	H ₂ (35 sccm)/1000 ° C	CH ₄ (30 sccm) and H ₂ (20 sccm)/960 ° C	[31]
Metal-catalyzed		Cu layer (450 to 100 nm)/quartz, sapphire, SiO ₂ (300 nm)/Si, and fused silica	H ₂ (35sccm)/1000 ° C	CH ₄ (35 sccm) and H ₂ (2 sccm)/1000 ° C	[32]
	Rapid heating plasma	Ni film (55 nm)/SiO ₂ (300 nm)/Si	CH ₄ :H ₂ (9:1)/600– 975 ° C	CH ₄ :H ₂ (9:1)/950 ° C	[33]

Table 3.1 Methodologies to grow graphene on non-metallic substrates by CVD. Some growth parameters such as gas flow, temperature and carbon source are presented.

In the metal-catalyzed direct growth method, many experiments have used a sacrificial metal layer to stimulate graphene growth. McNerny et al. deposited a nickel layer on SiO₂/Si wafers as a catalyst, which was subsequently delaminated using adhesive tape, leaving behind the graphene layer on the substrate [30]. They obtained a continuous (>90% coverage) graphene film on the centimeter scale, consisting of micrometer order domains and ranging from monolayer to multilayer [30]. Dong et al. deposited a copper layer on SiO₂/Si substrate to synthesize graphene using a CVD tube furnace [31]. They concluded that the copper evaporation occurred after the graphene deposition, but they observed some defects and residual copper in the graphene layer, which they removed by using an FeCl₃ solution [31]. Similarly, Ismach et al. deposited a copper layer on a variety of substrates (quartz, sapphire, fused silica, and SiO₂/Si) to promote graphene

growth [32]. They found that the copper layer was dewed and evaporated during or after graphene deposition producing areas free of copper, but residues remained all over the substrate [32]. Kato et al. combined the metal catalytic method with rapid heating plasma CVD to obtain graphene on SiO₂/Si [33]. They deposited a nickel film on the substrate and using a growth temperature ranging from 600–950 °C, obtained high-quality single-layer graphene sheets with hexagonal domains, suitable for the fabrication of a graphene-based field effect transistor [33].

This chapter presents a novel method suitable for industrial scale-up production to directly grow high-quality graphene on SiO₂/Si substrates by HFCVD. A metal-catalyzed method is used in a limited manner to graphene deposition over the entire substrate. To reach that a thin copperstrip was deposited on the middle of the SiO₂/Si substrate to increase the methane dehydrogenation and the carbon absorption and leaving the rest of the surface free of metal. Structural, morphological, and compositional analyses were made on the graphene grown on the SiO₂/Si and a growth mechanism is presented. This research targets SiO₂/Si substrates due to their ubiquity in graphene applications, such as photodetectors, gas sensors, solar energy, and others [3]. In addition, we use a HFCVD system that has unique advantages in terms of scalability for deposition over large area substrates [34].

3.2 Experimental Details

3.2.1. Substrate Preparation

Nanocrystalline graphene films were grown on p-type SiO₂/Si wafers with a top oxide layer of 285 nm and a thickness of $500 \pm 25 \,\mu$ m manufactured by Graphene Supermarket. These wafers were cut into 2×2 cm pieces and cleaned with: deionized water, trichlorethylene, acetone, and isopropanol; the last three reagents were obtained from Fisher Scientific. They also exposed to a mixture of sulfuric acid (H₂SO₄ purity range of 95–98%) and hydrogen peroxide (H₂O₂ solution

at 30% w/w in H₂O), for a further cleaning, both chemicals were provided by Sigma Aldrich. A thin copper-strip (3 mm width) was deposited in the middle of the SiO₂/Si substrate by sputtering (AMNPS-1 plasma-therm, Varian) with a deposition time of 1 minute (cf. Figure 3.1). In the next, "on top of the copper strip" will used for areas inside the metal. For areas outside the metal, we will use "next to the copper strip" (Figure 3.1). The copper target (99.99% pure) used for the deposition was obtained from the CERAC company. The thickness of the deposited copper layer was between 100–150 nm, this was measured by an Ambios Technology XP-200 profilometer.

3.2.2. Graphene Synthesis

A commercial HFCVD instrument (BWS-HFCVD1000, Blue Wave) was used for the graphene deposition. The reactor consists of a heated substrate holder that is positioned below three heated filaments of rhenium as explained in detail in chapter 2 (cf. Figure 3.1). The SiO₂/Si substrates (4 cm²) with the thin copper-strip (0.3 cm \times 2.0 cm) were submitted to the graphene synthesis procedure at different growth parameters. First the substrate was placed in the HFCVD chamber as shown in Figure 3.1 with the copper strip perpendicular with respect to the filament orientation. The substrate-to-filament distance was in a range of 5 to 15 mm and the chamber is evacuated until reach a pressure of 1x10⁻³ Torr. The pressure and heating rate were fixed at 35 Torr and 35 °C/min, respectively, for the complete process (annealing and growth steps). During the annealing stage, the substrate was kept at 975 °C with 80 sccm of hydrogen and 20 sccm of argon for 30 min. For the growth stage, the substrate temperature was reduced to 900 °C, and the filaments were turned on at a temperature range of 1800 °C–2300 °C in an atmosphere of methane (1–10 sccm) and hydrogen (10–50 sccm) for 30 to 120 min.



Figure 3.1 Hot filament chemical vapor deposition (HFCVD) reactor schematic and the SiO₂/Si substrate with the deposited copper-strip.

Finally, the samples were cooled by spontaneous convection to room temperature. As a control study, SiO₂/Si substrates without a copper-strip were also submitted to the graphene growth procedure.

3.2.3. Characterization Techniques

The structural characterization of graphene was conducted by Raman spectroscopy. The spectra were collected over a frequency range of 1100 to 3100 cm⁻¹ and Raman mappings were taken over an area of $150 \times 100 \ \mu\text{m}^2$ and a step size of 2 μ m. A morphological study of the synthesized graphene was done using a SEM at different magnifications (5000×, 25,000× and 140,000×) and an atomic force microscope in tapping mode over an area of $3 \times 3 \ \mu\text{m}$ was used. Compositional analyses of the graphene samples were done by energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The equipment details are presented in the chapter 2.
3.3 Results and Discussion

3.3.1 Raman Analysis

All three graphene peaks D, G and 2D were observed in the Raman spectra (cf. Figure 3.2) [35], both on top of and next to the copper-strip areas on SiO₂/Si substrate. For the control samples without a copper strip, these graphene peaks were not observed, indicating that the copper metal is necessary for the growth of graphene under our experimental conditions. Figure 3.2a, b shows the Raman spectra on top of and next to the copper-strip area deposited on SiO₂/Si substrate, respectively. The red and green spectra show two different signals next to the copper strip (Figure 3.2a) and the blue and black represent the same, but on top of the metal strip (Figure 3.2b). The insets show the optical images of both areas, respectively.

The G peak at 1579 cm⁻¹, the 2D peak at 2692 cm⁻¹ and a high D peak at 1348 cm⁻¹ were observed in the Raman spectra for both areas. The G and 2D peaks characteristically correspond to the signal for graphitic materials [18], where the intensity of these peaks was higher on top of the copper-strip areas than next to this film. In addition, a peak at 1620 cm⁻¹ known as D' was found, which is related to the defects in the graphene film structure [36,37]. The D' peak was bigger in the graphene grown on top of the copper-strip than the next to the metal film, where the peak was almost indistinguishable. This suggests that the graphene film grown on top of the copper strip has more defects. The high intensity of the D peak in both areas indicates that the carbon films are composed of nanometer-scale crystallites [36]. This effect could be explained as consequence of strong scattering in the edges of the particles [36]. In addition, the manifestation of this peak (D) could also be associated with defects in the crystallite structure [18,36,37,38]. However, other parameters like FWHM of the Raman peak give additional information about the graphene quality.



Figure 3.2 Raman spectra of graphene on SiO₂/Si substrates and its respective peaks (D, G and 2D): (a) Next to the copper-strip areas and (b) On top of the copper-strip areas.

3.3.2 Estimation of grain size and defect level

Furthermore, the Raman peaks provides information about the morphological characteristics of the graphene films [39-44]. In specific, the average intensity ratio between the D and G peaks ($I_{D/G}$) yields an estimate of the graphene grain size [39,40] and the level of the defective crystallites [36,37,41,42]. In next to the copper strip samples, $I_{D/G}$ values were between 0.30 ± 0.04 and 0.80 ± 0.03 . while, the higher $I_{D/G}$ values, 0.45 ± 0.07 and 0.87 ± 0.03 , were found on top of the metal strip. Although, the Raman spectra shows a significant observed D peak, the average of the full width at half maximum (FWHM) of the D, G and 2D peaks indicates good quality crystallites [36]. The FWHM of these peaks on top of the copper strip were 35 ± 1 cm⁻¹, 25 ± 1 cm⁻¹, and 56 ± 3 cm⁻¹, respectively and in areas next to the copper strip were: 38 ± 2 cm⁻¹, 29 ± 1 cm⁻¹ and 52 ± 2 cm⁻¹.

In addition, the $I_{D/G}$ values were used to calculate the crystal size by the Cancado equation

(Equation (2.1)), that is written below for convenience [38]. The calculations shown that the L α on top of and next to the copper strip was in the range of 24.03 to 64.07 nm and 22.11 to 42.72 nm, respectively. These values agreed with the D peak characteristics associated to the nanocrystals, but different from the grain size measured by SEM that it was in a range of 35 to 140 nm.

$$L_{\alpha} = (2.4 \times 10^{-10}) \lambda_l^4 (I_D / I_G)^{-1}$$
(2.1)

According to our knowledge, the difference in the particle size estimates is likely due to the multiple phonon dispersion produced by defects inside of the graphene crystallites [37,43]. These imperfections in the crystal affect the intensity ratio between the D and G peaks in the Raman spectra, resulting in false behavior of smaller grains [37,43]. To estimate the contribution of these defects, we use Equation (2.2), showed in the next for convenience [44,45]. The results show that the average L_D in areas next to and on top of copper strip were 18 nm and 10 nm, respectively. In addition, a calculation of the defect concentration for both areas, next to and on top of copper strip presented values of $3 \times 10^{-3}/\text{nm}^2$ and $7 \times 10^{-3}/\text{nm}^2$, respectively. These results confirm that some point defects are present in the nanocrystals and contribute to the I_D/I_G ratio intensity. Nevertheless, higher concentration of defective crystals was present on top of the copper strip versus next to this metal film.

$$L_{\rm D}^2 \,({\rm nm}^2) = \frac{_{3600}}{_{\rm E_{\rm L}^4}} ({\rm I_{\rm D}}/{\rm I_{\rm G}})^{-1} \tag{2.2}$$

The graphene disorder can be classified by two types, the first, it is known as graphite to nanocrystalline graphene and the second correspond to nanocrystalline graphene to low sp3 amorphous carbon. The apparition of the D, D' peaks in the Raman signal, the broadening of the peaks and the increment of $I_{D/G}$, correspond to some characteristics of the first classification. In

the second type, the G peak position is reduced (1600 cm⁻¹ to 1510 cm⁻¹) and the $I_{D/G}$ tent to cero. According to this previous analysis, the nanocrystal graphene obtained in this research correspond to the first classification, because a D peak was observed and very small D' was noticed in some samples [43]. Further morphological study was done by Raman mapping (cf. Figure 3.3) to understand the uniformity of graphene layers on the SiO₂/Si substrate and to estimate the number of graphene layers through the intensity ratio of the 2D/G peaks [18,39]. A visual image of the graphene growth next to and on top of the copper-strip for a selected mapping area of 150×100 μ m² are showed in Figure 3.3a, b. It was possible to identify a general uniformity of the graphene growth throughout the mapped areas (Figure 3.3a), while the presence of the copper particles is clearly observed in Figure 3.3b. Figure 3.3c, d show the Raman mapping of the intensity ratio of 2D/G peaks, for the same areas next to and on top of the copper-strip shown in Figure 3.3a, b. The values for the average 2D/G ratio were 0.70 ± 0.05 and 0.50 ± 0.07 for next to and on top of the copper-strip samples, respectively. According to the value of the 2D/G intensity ratio, few layers of graphene were growth on SiO₂/Si for both areas (next to and on top of the copper-strip) [18,32,35]. However, other aspects such as the doping levels in the graphene layer can influence this value (2D/G intensity), leading to an incorrect estimate of the number of layers [45].

	Raman peaks (cm ⁻¹)			FWHM (cm ⁻¹)			I _{D/G}	I _{2D/G}	La	L _D	$1/L_D^2$
	D	G	2D	D	G	2D	2,0		(nm)	(nm)	(1/nm²)
Next to the copper	1348	1579	2692	38 ± 2	29 ± 1	52± 2	$\begin{array}{c} 0.30 \pm 0.04 \\ 0.80 \pm 0.03 \end{array}$	0.70±0.05	22.11 to 42.72	18	3 × 10 ⁻³
On top of the copper	1346	1582	2697	35 ± 1	25 ± 1	56 ± 3	$\begin{array}{c} 0.45 \pm 0.07 \\ 0.87 \pm 0.03 \end{array}$	0.50 ± 0.07	24.03 to 64.07	10	7 × 10 ⁻³

Table 3.2 Raman parameters of graphene growth on SiO₂/Si.



Figure 3.3 Raman mapping for graphene growth on SiO₂/Si substrate. Where (a) and (b) represent the optical images of the selected mapping area $(150 \times 100 \ \mu m^2)$ next to and on top of the copperstrip, respectively. (c) and (d) show the ratio between the intensity of 2D/G peaks in the same areas as in (a) and (b).

3.3.2 SEM analysis

The SEM images taken in two areas next to the copper strip with a magnification of $140,000 \times$ are shown in Figure 3.4a, b. Figure 3.4a shows an area 8 mm from the copper film, while Figure 3.4b is an area closer (4 mm) to the copper strip. Similarly, Figure 3.4c, d show two different areas on top of the copper strip, upper and middle.

From the SEM images, it was possible to estimate the size of the graphene crystals from the scale bar to ca.100 nm. By measuring many crystals, we obtained an average size of 120 nm and a range of 100 to 140 nm for particles next to the copper strip, and smaller particles (35-120 nm; average size = 74 nm) on top of the copper-strip. At lower magnification ($5000\times$), no copper particles were observed next to the copper film.



Figure 3.4 SEM measurements of the graphene growth on SiO₂/Si substrate: (a) and (b) show the SEM image taken in two areas next to the copper-strip at 140,000×. Similarly, (c) and (d) show two areas on top of the copper strip at the same magnification. In all cases, crossed arrows represent the position relative to the copper strip where the image was taken.

3.3.3 AFM analysis

Figure 3.5 shows the AFM measurements for graphene growth on SiO₂/Si substrate for both next to (cf. Figure 3.5a) and on top of (cf. Figure 3.5b) the copper-strip area, respectively.

The copper grains were identified with an average height of 50 nm (Figure 3.5b) and uniform graphene layers were observed next to the copper strip with an average height of 5 nm (Figure 3.5a) corresponding to 6–12 graphene layers [18,46–48], supporting our calculations obtained from the Raman spectra.

A nanocrystalline pattern was expected to be found, [36] however this was not identified because the deposited carbon material was composed of more than one layer of graphene. Nevertheless, two different morphologies were observed between areas on top of and next to the copper-strip.



Figure 3.5 AFM measurements of the graphene growth on SiO₂/Si substrate: (**a**) and (**b**) show the AFM images taken next to and on top of the copper-strip, respectively.

3.3.4 EDS analysis

A compositional analysis of graphene on SiO₂/Si samples was done by EDS. In areas next to the copper strip (cf. Figure 3.6a), the following elements were identified (with their respective atomic concentrations): silicon (77.28 \pm 0.04%), oxygen (19.37 \pm 0.03%) and carbon (3.34 \pm 0.12%). In the EDS spectra on top of the copper-strip, the following elements were observed,

silicon (57.02 \pm 0.05%), oxygen (11.89 \pm 0.07%), copper (20.08 \pm 0.03%) and carbon (11.01 \pm 0.12%) (cf. Figure 3.6b). There are no other elements found in both areas (next to the and on top of the copper strip).

These atomic concentrations are consistent with the 2D/G intensity ratio in the Raman mapping experiment, where the lower values were found on top of the copper strip areas, indicating that more carbon atoms were deposited [35]. Although a higher carbon concentration was presented on top of the copper strip, a considerable percentage next to the metal film was identified. Additionally, no trace of copper was found next to the copper strip area, showing that there is graphene growth in metal-free areas.



Figure 3.6 EDS spectrum of graphene on SiO₂/Si substrate (a) and (b) shows the EDS spectrum next to and on top of the copper-strip, respectively.

3.3.5 XPS analysis

The compositional analysis of graphene grown on SiO₂/Si was done by XPS measurements, where it was possible to obtain information about the elements involved in the reaction as the understanding of the chemical/electronic behavior of each element with their environment [38]. In our case, the carbon and copper peaks were the central elements of this study

because the first determine the graphene deposition and the absence of the second peak in areas next to copper strip, confirm the efficiency of the method present in this study.

XPS spectra were taken both next to and on top of the copper-strip. Figure 3.7a, d show the elements found in both areas, respectively. The carbon 1s (C1s) peak was observed in both areas (Figure 3.7b, e). The raw data is shown on the dotted line and the solid lines represent the contribution of all the peaks after deconvolution. Contribution peaks were observed at 284.6 eV, 285.9 eV and 290.0 eV, corresponding to C-C, C-O and O-C=O respectively [38,50]. The presence of oxygen is confirmed in both areas in the XPS spectra (Figure 3.7a, d). The incorporation of oxygen most likely occurred after the graphene growth following exposure to air. As observed by Yang et al that founded a peak at 286.6 and related to C-O bond they suggest that this result of edge passivation or the contamination on the surface [36].

The copper peaks (Cu $2p_{3/2}$: 930–937 eV and Cu $2p_{1/2}$: –954 eV) were observed on top of the copper-strip (Figure 3.7f), as expected. However, this metal shows a very small signal next to the copper-strip area (Figure 3.7c) and peaks corresponding to Cu 3s (119.5 to 124.7 eV) were neglected in both areas [38]. Signals from other metals such as Fe (Fe $2p_{3/2}$: 706.7–710.9 eV), Co (Co $2p_{3/2}$: 778.1–780.2 eV) and Ni (Ni $2p_{3/2}$: 852.5–854.4 eV) were not observed on areas next to and on top of the copper-strip. The absence of other metals demonstrates that the graphene growth was either catalyst free or catalyzed by copper [25]. (Figure 3.7a, d).



Figure 3.7 XPS measurements of the graphene growth on SiO₂/Si substrate: (a) shows the XPS full composition spectra, (b) carbon peak after deconvolution and (c) the copper peaks taken next to the copper-strip. Then (d–f) represent the same but on top of the copper-strip.

3.4 Graphene growth mechanism

The growth mechanism most likely begins with dehydrogenation of methane by the hot filament [18]. In the absence of copper, no graphene is observed, and therefore the growth must be catalyzed by the metal. This raises the question of whether the graphene is catalyzed on the metal film and migrates across the surface to cover the substrate (Figure 3.8a), or if the catalysis occurs due to vapor phase copper species above the surface (Figure 3.8b) [18,32,51–53]. If the vapor phase metal-catalyzed mechanism is operative, the expectation is that copper should be present across the substrate. While we do not see abundant amounts of copper next to the copper

film, we cannot conclusively rule out the mechanism shown in Figure 8b because of the small signal observed in our XPS data. According to the growth distribution of graphene on the substrate we suggest that some crystals grew as migration from the copper-strip (Figure 3.8a), but some of the crystals next to the metal film were formed by the copper vapor catalyst effect (Figure 3.8b) [51,52] that is evaporated during the growth stage [31,51–53], leaving a small residual amount consistent with our XPS data.



Figure 3.8 Schematic of the graphene growth mechanism on SiO₂/Si substrate. (a) graphene migration from the copper-strip film and (b) the catalytic effect of the copper vapor to form graphene. In both figures, CH_4/H_2 molecules pass through the hot filaments prior to deposition. For more detail on the mechanism, see text.

3.5 Conclusions

This study presents an approach to directly grow graphene on SiO₂/Si by HFCVD, using the metal catalyzed method in a limited manner. A structural (Raman), morphological (SEM and AFM) and compositional (EDS and XPS) study of the graphene on SiO₂/Si characteristics was done. This graphitic material grew over all areas of the SiO₂ substrate at the nanocrystalline scale with good quality. The calculated grain size from Raman measurements was between 24.03 to 64.07 nm (next to the copper-strip); however, defects in the crystal due to phonon scattering may lead to an error in this estimate. These defects inside of the graphene nanocrystal were corroborated by the calculation of the inter-distance defect. The real size was confirmed through the images taken by the SEM technique where the particle size was in a range of 35 to 140 nm with an average of 120 nm (next to the copper-strip). EDS and XPS measurements confirmed the graphene presence and the absence of the other metals in next to the copper areas. A graphene growth mechanism on SiO₂/Si was presented. This work demonstrates that the thin copper-strip deposited on the middle of the SiO₂/Si enables the graphene growth over all the substrates. By eliminating the need for a mechanical transfer step in the device fabrication process, this accomplishment launches the possibility of integrating graphene with currently available silicon device technologies.

Further research, needed to continuously improve the quality of the graphene deposition. One approach is the reduction of the nucleation density [15,54–56] by modifying the methane and hydrogen gas flow rates that will allow an increment in the graphene crystal size and reduction of the point defects [55,56]. This study allows the possibility of growing graphene directly on dielectrics without a transfer process and the opportunity to produce it on an industrial scale.

3.6 References

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Chapter 4. Graphene Growth Directly on Silicon carbide by Hot Filament Chemical Vapor Deposition

4.1 Introduction

In the search to discover new technologies, such as those that emerged during the silicon (Si) era, considerable research has been focused on exploring similar materials that contribute to electronic innovations. Graphene, a two-dimensional structure, looks like a promising material for the next generation of electronic devices, due to its favourable properties, e.g., high electron mobility of 200,000 cm²V⁻¹s⁻¹ and a carrier concentration of 10^{12} cm⁻² [1]. There are many techniques to obtain graphene, including microexfoliation [2], graphene oxide reduction [3], epitaxial growth on SiC [4,5], and chemical vapor deposition (CVD) [4,6,7]. This CVD methodology is the most widely used and efficient method to grow graphene [8,9] and can be further subdivided into thermal chemical vapor deposition (TCVD) [10,11], hot chemical vapor deposition (HFCVD) [12,13,14] and plasma-Enhanced CVD (PECVD) [15,16]. Among these, the HFCVD method has been shown to be a systematic and easier way to control the growth parameters. This technique allows two thermal points (holder temperature and filament) to be set independently, resulting in a temperature gradient on the sample [12,13,14]. To take advantage of its excellent electrical properties, graphene must be deposited on particular substrates, i.e., dielectrics, such as silicon carbide (SiC). Therefore, many studies have focused on finding the best method to grow graphene on semiconducting materials [17,18,19]. Specifically, SiC appears to be a remarkable material for electronic applications due to its wide bandgap, high thermal conductivity, excellent thermal/chemical stability, and other properties that make this material a good candidate for high-temperature and high-power applications [20,21,22]. There are ~ 170 polytypes of SiC with different interesting properties formed under ambient conditions [20,23]. According to the stacking sequence, SiC can form three different structures: cubic, hexagonal, and

rhombohedral [23]. However, the most prevalent types correspond to hexagonal (4H, 6H or α) and cubic (3C or β) structures. The combination of these two exceptional materials, graphene and SiC, has attracted a lot of interest because they mutually improve their shared electrical properties, such as the reduction of sheet resistance in this system compared to normal SiC [24,25].

The first approach to grow graphene on SiC was carried out by Badami in 1965 on a hexagonal substrate at 2180 °C in a vacuum environment [26]. In 1975, Bommel et al. were able to form a graphite monolayer on hexagonal SiC for the Si and C faces at 800 °C in ultra-high vacuum (UHV) [27]. Based on these experiments, researchers used this thermal decomposition method to obtain graphene on SiC [25,28,29,30,31,32] under different conditions. In 2004, Berger et al. recorded the first transport measurements of multilayer graphene on SiC obtained in UHV [33] and found that the electron mobility was ca. $1100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Since then, many researchers have focused on improving the quality of graphene on SiC. For example, Rollings et al. obtained graphene at 1200 °C in UHV [31], while Boeckl's group followed up their experiments in a vacuum environment, but at a higher temperature [34]. However, the high sublimation rate of Si in thermal decomposition experiments impairs the quality of graphene [4], which led to the exploration of methodologies involving gas flows e.g. argon, to maintain the excellent properties of this carbon material. Emtsev et al. grew graphene on 6H-SiC in an argon environment (900 mbar) at 1650 °C [35], and their results confirmed an improvement in the graphene quality according to Raman and Hall Effect measurements. Similar experiments were conducted in hydrogen [36] and Si [37] environments to optimize the films' properties. New methodologies, such as the application of a confinement-controlled sublimation system to reduce the Si evaporation rate [38] and the nickel film deposition on SiC to induce the graphitization at lower temperatures [24], were implemented. Several studies have shown that reducing the sublimation rate of Si improves the quality of graphene [39,40,41,42]. Consequently, some works have proposed the incorporation of the external carbon source, such as propane and methane [39,40,41,42] to reduce the Si sublimation effect. As observed in the study conducted by Dagher et al., where graphene growth experiments were carried out at different mixture of gases (Ar, H₂ and CH₄), temperatures and pressures [39]. They concluded through experimental processes and thermodynamic simulations that in experiments carried out in an atmosphere of Ar/H₂ gases, the effect of Si sublimation is reduced due to the presence of H_2 , inhibiting the carbon layer formation. Therefore, graphene growth on SiC was only possible including the CH₄ gas as external carbon source [39]. Similarly, Liu et al. proposed a graphene growth method using methane as a carbon source. Their experiments were divided into three steps: hydrogen etching, nucleation, and growth [41]. In the first step, uniform flat terraces were obtained on the substrate, and in the second step using an argon atmosphere, carbon nuclei were formed from the SiC substrate. Finally, the graphene growth was completed with the flow of methane [41]. These results demonstrate that the use of the CVD method with an external carbon source provides a clear advantage i.e., the reduction of the Si sublimation effect, avoiding the influence of the substrate, which could incorporate defects into the graphene film. In contrast to other methods relying only on the Si sublimation process, the CVD technique with an external carbon source has delivered the highest quality graphene. In this chapter, we present here a method to grow high quality graphene on 6H/SiC, C- terminated face by HFCVD, using methane as the carbon source. The experiments were conducted at low temperature (950 °C) and high pressure (35 Torr) compared to other methods. The graphene films are characterized by Raman, SEM, AFM, EDS and XPS measurements.

4.2 Experimental details

4.2.1 Substrate preparation

The silicon carbide substrates (1cm x 1cm) correspond to the C-terminated α -SiC (6H) hexagonal structures from Valley Design Corp. with a thickness of 508 ± 50 µm. The substrates were cleaned sequentially by two processes on the first one with trichlorethylene (TCE), acetone, deionized water, and isopropanol, followed by a H₂SO₄:H₂O₂ mixture to eliminate organic residues. In some cases, a 50% hydrofluoric acid (HF) treatment was used as extra cleaning to remove the oxide on the SiC surface [40] and to analyze the effect on the graphene quality. Two groups of substrates were prepared, one with 10 min of HF treatment, and one without HF acid treatment. Other HF treatment exposure times (from 0 to 360 minutes) were tried, but no difference was found. All reagents listed above were obtained from Fisher Scientific.

4.2.2 Graphene synthesis

The SiC substrates were introduced into the HFCVD equipment (BWS-HFCVD1000, Blue Wave, Baltimore, MD, USA) [14], and the chamber was evacuated to $1x10^{-3}$ Torr. The graphene deposition procedure was then carried out in two steps: (1) annealing; and (2) growth. In the annealing process, the SiC substrates were heated at 950 °C and exposed to a mixture of 80 sccm of hydrogen and 20 sccm of argon for 30 minutes. For the growth process, the argon gas flow was stopped, and filaments were turned on, over a temperature range of 1800 to 2300 °C. Methane gas (1- 10 sccm), and H₂ gas (0-50 sccm) were flowed, and the graphene growth process was done for different time periods (30-300 minutes) and different experimental flow conditions. Following the growth process, the filament and heater were turned off, and the sample was allowed to cool to ambient conditions (see figure 4.1b). All experiments leading to graphene deposition (annealing and growth) were conducted at a constant pressure of 35 Torr.



Figure 4.1 Hot filament chemical vapor deposition (HFCVD) reactor and graphene growth process, a) scheme and b) Graphene growth steps on the SiC.

4.2.3 Graphene characterization

The graphene confirmation on SiC and its characteristics were evaluated using multiple morphological, structural, and compositional techniques. Raman spectroscopy was performed by a spectral range of 1100 - 3100 cm⁻¹, using a focused spot size of 0.7 μ m. Raman measurements made it possible to estimate the characteristics of graphene, such as the number of graphene layers and the crystal size. In addition, Raman mappings were taken in areas of 150 × 110 μ m² with a step size of 2 μ m; the collection time for each point was 20 seconds. A SEM and an AFM were used to study the morphological characteristics of graphene crystals, as well as their size and distribution. The compositional analysis was performed by EDS and XPS spectroscopy. The specifications of techniques used in this work are described in the chapter 2.

4.3 Results and discussion

Graphene growth on 6H-SiC samples under different conditions was characterized using the Raman technique to estimate the number of deposited layers and defects in the films. SEM and AFM allowed a deeper study about the morphology, and EDS and XPS were used to identify the presence of expected elements (carbon, silicon) and rule out the presence of contaminating or unwanted elements in the graphene films.

4.3.1 Raman analysis

The graphene growth on SiC substrates (treated with and without HF acid) was characterized by the D, G, 2D, and SiC peaks of the Raman spectra. Figure 4.2a, b show the signal obtained in samples at 10 sccm and 1 sccm of methane flow, respectively, that were previously cleaned with HF. Figure 4.2c, d shows the same but for samples prepared with untreated (No HF) substrates. The growth conditions of all experiments are summarized in table 4.1. The D, G and 2D peaks were observed at ~1349 cm⁻¹, ~1580 cm⁻¹ and at ~2694 cm⁻¹, respectively (cf. Figure 4.2). SiC peaks were observed at 1526 cm⁻¹ and 1715 cm⁻¹, showing that few layers of graphene were grown, and that the Raman signal of the substrate is not eliminated by the carbon deposition [13,34]. However, in experiments with higher methane fluxes or longer growth times, the intensity of SiC peaks is reduced. Nevertheless, multilayer graphene was obtained on substrates that were previously cleaned with HF and in experiments at longer growth time and with a flow of 1 sccm (cf. table 4.1). The characteristics of the D and G peaks provide information about the graphene quality [13,43,44] and the crystal size [45,46,47], where the D peak is related to the defect and disorder of the sp² carbon network [13,24,43,44]. The D/G intensity ratio is used to obtain information about the defect level in the films, where high values are associated to a more defective structure [24].



Figure 4.2 Raman spectrum of graphene on SiC substrate. a) and b) represent the samples cleaned with HF acid and exposed to 10 and 1 sccm of CH₄ flow, respectively, and c) and d) correspond to samples at the same gas flow but without the HF acid cleaning process, respectively.

Our results show that the D/G intensity ratio for a few layers (cleaned and uncleaned substrates) is between 0.20 ± 0.03 and 0.80 ± 0.03 which indicates a low defective crystal structure [24], while in multilayer samples (cleaned substrates) this value was between 1.70 ± 0.02 and 1.90 ± 0.03 .

Condition		Graphene			
	CH ₄ (sccm)	H ₂ (sccm)	Time (min)	Temperature (°C)	films characteristics
Cleaned	10	50	120	950	Few layers
with HF	10	50	60	950	Few layers*
aciu	1	-	300	950	Multilayers
	1	-	120	950	Few layers
	1	-	60	950	No growth
	10	50	120	950	Few layers
Not cleaned	10	50	60	950	Few layers*
with HF	1	-	300	950	Few layers
acid	1	-	120	950	Few layers*
	1	-	60	950	No growth

Table 4.1 Graphene on SiC – Growth conditions and Raman analysis

We established that the presence of this peak (D) could be related to the nanometric particle size of the carbon crystals [48], and to the strong scattering caused by defects in the crystal structure [13,50,51].

In addition, the full width at half maximum (FWHM) values of the graphene peaks gives us more information about the crystallinity and quality of this carbon material [13,49]. The results show that the D, G and 2D FWHM values correspond to 30 cm⁻¹, 30 cm⁻¹ and 60 cm⁻¹ for few layer films grown on cleaned and uncleaned surfaces with HF and 48 cm⁻¹, 60 cm⁻¹ and 90 cm⁻¹ in multilayers samples prepared on cleaned surfaces. Although we obtained the FWHM of the 2D peak in a range of 60 to 90 cm⁻¹, indicating low crystallinity, these results are compared with the single layer (60 cm⁻¹) and bilayer (90 cm⁻¹) epitaxial graphene obtained in Ni's work [29].

The D/G intensity ratio was used for the estimation of the particle size of graphene [44,46] that is substituted in the Cancado relation (Equation (2.1)), where L α represents the particle size,

as showed in chapter 2. The equation 2.1 is written below by convenience.

$$L_{\alpha} = (2.4 \times 10^{-10}) \,\lambda_l^4 \, \left(\frac{I_D}{I_G}\right)^{-1}$$
(2.1)

According to Cancado's relation, the nanometric crystallites were around 23.50 nm to 90.00 nm for few layers samples and 8 nm to 12 nm in multilayer films. Although these results were close to the particle size estimated by SEM in the few layers (30 to 100 nm) and multilayer samples (10 nm), some discrepancies were observed. To understand these discrepancies, Equation 2.2 was employed to calculate the crystal's defect, where L_D is the inter-defect distance and $1/L_D$ is the defect concentration [52]. Details of the Equation 2.2 are presented in the chapter 2, and this is showed below by convenience. These calculations result in L_D values of 24 nm and 8 nm for few layer and multilayer films, respectively, and defect concentrations of 1.30 x 10^{-3} /nm² and 1.55 x 10^{-2} /nm² correspondingly.

$$L_D^2 (nm^2) = \frac{3600}{E_L^4} (I_D / I_G)^{-1}$$
(2.2)

To obtain information about the number of graphene layers and the uniformity of these films on SiC, a Raman map was taken in areas of 150 x 110 μ m². These measurements were derived from the intensity ratio of the 2D/G peaks [13,46]. Figure 4.3a shows the image of the selected mapping area of the 2D/G intensity ratio for a few layers (cleaned and uncleaned substrates) of graphene, where the blue and red colors correspond to the lowest and highest values, respectively. These values were in the range of 0.5 ± 0.03 and 0.6 ± 0.03, confirming that a few layers were deposited [45,49,53]. Similarly, Figure 4.3b shows the image corresponding to the intensity ratio of the 2D and G peaks of the mapped area in the multilayer (cleaned substrates) graphene samples. In this case, the values (2D/G) were in the range of 0.3 ± 0.05 to 0.4 ± 0.05, but with less uniformity than in the few layer samples. While the 2D/G intensity ratio provides an

estimate of the number of graphene layers [13,17,29], other aspects, e.g., the level of doping in graphene films, should also be considered because they can an influence in this ratio (2D/G), as well [54].



Figure 4.3 Raman mapping of graphene on SiC substrate. Where a) and b) represents the mapping image of the 2D/G intensity ratio for few layers and multilayers samples, respectively.

According to our results the best graphene quality and uniformity were achieved using two methods: (1) the substrates (without HF treatment) were exposed to a methane flux of 1 sccm for 300 minutes at 950 °C; and (2) the SiC substrates were cleaned with HF, then heated at 950 °C in an atmosphere of 10 sccm of methane and 50 sccm of hydrogen for 60 or 120 minutes.

A significant observation is that graphene grew on cleaned and uncleaned SiC substrates. Nevertheless, the results demonstrated that more graphene layers were deposited on substrates cleaned with HF than in the untreated substrates. This outcome is consistent with the HF removing the oxygen on the surface and allowing better carbon incorporation [40]. However, Dhar et al. reported that an oxygen monolayer with an OH termination was still present on the SiC surface after the exposition to HF acid [55]. Therefore, it is possible to find residual oxygen after the HF treatment which will have an effect in the growth of graphene. For this reason, we always perform an annealing process. In summary, it was possible to grow few layers graphene on both treated and untreated SiC substrates, but Raman spectra show that multilayer graphene was obtained only on HF cleaned substrates for longer growth times. SEM, AFM, EDS and XPS characterization show that the morphology and composition of the graphene layers were indistinguishable between clean and uncleaned substrates. For this reason, the following analysis will be limited to the graphene grown on SiC substrates cleaned with HF.

4.3.2 SEM analysis

The SEM images of graphene on SiC for few layers and multilayers samples, respectively, at 140,000x magnification are shown in Figure 4.4a and 4.4b. Figures 4.4c and 4.4d show the images of the same samples but at 25,000x magnification. We observed, in both images, the nanometer scale particles over all samples with an average grain-size of 30 to 100 nm in few layer samples. However, in the multilayer films, fiber-like particles, 10 nm in size, were evenly distributed throughout the SiC surface. The graphene particle size obtained by SEM, are in reasonable agreement with the estimates calculated by the Cancado equation [46] (D/G peaks) above.

4.3.3 AFM Analysis

The morphology of graphene on SiC was further characterized by AFM measurements taken in an area of $3 \ \mu m \ x \ 3 \ \mu m$. Figure 4.5a shows the nanometer-scale crystal with a height of 20 nm and a diameter of around 100 nm, corresponding to few layers of graphene [35]. The AFM results of the graphene morphology are consistent with the SEM images, confirming that the graphene nanocrystals were grown on SiC. Figure 4.5b corresponds to the AFM image of the SiC substrate where it was possible to observe some lines and scratches from the manufacturing.

process.



Figure 4.4 SEM measurements of the graphene growth on SiC substrate: (a,b) show the SEM image taken in few layers and multilayers samples at $140,000 \times$ magnification. Similarly, (c,d) show the same but at $25,000 \times$ magnification.



Figure 4.5 AFM measurements: (a) and (b) show the AFM images taken in graphene growth on

SiC and on the SiC substrate, respectively.

According to some works the annealing process improves imperfections (like scratches) of the substrate surfaces [42] and remove the oxygen deposition. To analyze the influence of the annealing process in the surface improved, two groups of substrates (cleaned and uncleaned with HF acid) were exposed at different time of annealing (30, 60 and 120 min). All annealing experiments were conducted in argon (20 sccm) and hydrogen (80 sccm) gases at 950 °C with a total pressure of the 35 Torr. The surface characterization of the SiC substrates was carried out by AFM technique. In Figure 4.6 is possible to observe the surfaces images of the substrate at different conditions. The results shown that the surface has neglected changes respect to the original substrate, and it was also unchanged between all treatments, where scratches are still observed. In addition, experiments at higher temperature (2100 °C) were done but the surface resulted invariant. Furthermore, Raman measurements confirmed the absence of graphene films on SiC substrates after this annealing study. These results are according to Dagher experiments, where they concluded that a carbon source is necessary to reach the graphene deposition in a hydrogen atmosphere using a CVD reactor [39].

Futures annealing experiments at different conditions such as pressure and gas flow must be directed, in the search to achieve the best initial surface of the substrate to improve the graphene quality, reducing the defect in the films.



Figure 4.6 AFM measurements of SiC substrates cleaned and uncleaned at different annealing time (30, 60and 120 minutes).

4.3.4 EDS analysis

As expected, elemental carbon and silicon were identified as the major components on the EDS spectra. The few layers graphene samples show an atomic concentration of $60.41 \pm 0.17\%$ of carbon, $37.73 \pm 0.04\%$ of silicon and $1.86 \pm 0.02\%$ of oxygen (Figure 4.7a). For multilayers samples, the percentage was $69.47 \pm 0.13\%$, $29.90 \pm 0.07\%$ and $0.63 \pm 0.04\%$ to carbon, silicon, and oxygen, respectively (Figure 4.7b). By comparation, SiC substrates showed a percentage of $49.09 \pm 0.07\%$, $50.68 \pm 0.08\%$, $0.32 \pm 0.03\%$ for carbon, silicon and oxygen, respectively. No other elements were found in the samples, e.g., copper, nickel, or rhenium (filament) that could

modify the mechanism of the growth reactions.



Figure 4.7 EDS spectrum of graphene on SiC in few layers (a) and multilayer (b) samples, respectively.

4.3.5 XPS analysis

XPS measurements were done before and after graphene deposition on the SiC substrate. Figures 4.8a,b show the full spectrum and carbon peak for few layers of graphene growth on SiC, respectively. Similarly, the XPS spectrum of the bare SiC substrate and C peak are shown in Figures 4.8c,d. As expected for both samples (before and after graphene growth), elemental carbon, silicon, and oxygen were present in the spectra. No trace metals were found on the surface, consistent with the EDS measurements. After deconvolution of the C1s peak of graphene on SiC samples, two peaks, 283 and 285 eV corresponding to SiC and graphene, can be resolved [24,41,56]. These peaks correspond to the characteristic signal of graphene grown on the carbon-terminated face of SiC [57]. The deconvolution of the C1s peak of the bare SiC substrate showed a peak at 283 eV corresponding to the SiC bond. A second peak (X) at 285.7 eV and a third peak (Y) at 287.6 eV were found, that are generally associated with a C-O and C=O bonding on the



surface [41,58]. In addition, we observed the reduced intensity of the SiC peak, after the growth of graphene (Figure 4.8b) [59].



Figure 4.8 XPS measurements of full composition spectra (a) and carbon peak (b) after deconvolution of graphene on SiC, respectively. (c, d) correspond to the same but for the bare SiC substrate prior to deposition of graphene.

4.4 Graphene growth Mechanism

In the present work, nanographene films were grown on SiC substrate by HFCVD using methane as carbon source. We propose that the graphene growth mechanism occurs in two steps: (1) The dehydrogenation of methane by the hot filaments produces reactive carbon species, CHx and C (Figure 8-1); and (2) these reactive species deposit carbon atoms, stabilizing the SiC/C surface and forming the graphene film [34,60] (Figure 4.9-2). Annealing prior to the growth process was

conducted to clean the surface from contaminants [28] and oxygen [61,62] as well as to promote flat terrace on SiC [63,64]. We discarded the graphene growth by Si sublimation [25] during the annealing, given that the gas mixing (Ar/H₂), the pressure (35 torr) and temperature (950 $^{\circ}$ C) were not the correct conditions for this process [39]. This was confirmed by Raman measurements, where the graphene signal was not observed for SiC substrates with just the annealing. For this reason, the graphene growth experiments on SiC at the above mentioned conditions were conducted with methane as an external carbon source. The addition of H_2 works as a carrier gas and reduce the formation of defects as it promotes better uniformity in the graphene film [42]. The SiC substrates cleaned with HF showed more graphene layers, at the same growth conditions. The HF helps to remove the oxide layer at the SiC surface allowing better carbon incorporation at the graphene growth step. The growth time also has an effect in the number of deposited layers, i.e., longer growth time results in more graphene layers. In summary, the deposition of graphene on SiC is possible independently of the HF treatment. Nevertheless, the type of treatment and the growth time has an influence in the number of graphene layers. These results open the possibility of obtaining graphene on SiC using HFCVD at relatively low temperature and high pressure (not UHV) compared to other methods, which allows easier incorporation for mass production.

4.5 Conclusion

Graphene growth on 6H-SiC was done by HFCVD at 950 °C and high pressure (not UHV), using methane as the external carbon source. Raman, SEM, AFM, EDS and XPS measurements confirmed that few layers of graphene were deposited at nanometer size. The surface morphology analysis indicated that high quality graphene was obtained and further cleaning with HF acid increased the number of carbon layers. A comparative analysis of the AFM measurements of SiC substrates with and without HF treatment showed no differences in surface quality. This work establishes a method for graphene growth on SiC with controllable parameters under different conditions to adjust the characteristics of graphene according to the application. Furthermore, these experiments open the possibility for graphene production by HFCVD method, which is suited for scaling in industrial applications.



Figure 4.9 Graphene growth mechanism on SiC. The process was divided into two steps, carbon production, and the graphene formation on SiC surface.

4.6 References

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Chapter 5. Graphene Growth Directly on Ti6Al4V alloy by Hot Filament Chemical Vapor Deposition

5.1 Introduction

Graphene, known for its numerous outstanding properties, has been widely considered as a potential material for novel electronic, mechanical, and biomedical applications [1-7]. The most common substrate used to grow graphene is copper, due to its low absorption rate of carbon atoms, low price, and reusability [3]. The integration of graphene with different materials requires a transfer process from the copper substrate where it was initially grown, to the new target (SiO₂/Si, quartz, and Ti alloys)) [8]. Studies have revealed that the transfer process influences the quality of the graphene, leading to drawbacks such as contamination, wrinkles and film breakage [9,10]. To avoid this, some studies have proposed the direct growth of graphene on the target substrate for the specific application [9-11]. Several groups have reported direct graphene growth on different substrates (SiO₂/Si, quartz, sapphire), using a thin layer of copper as a surface catalyst during Thermal Chemical Vapor Deposition (TCVD) and Hot Filament Chemical Vapor Deposition (HFCVD) [10,11]. Chen et al used an oxygen-assisted method to grow polycrystalline graphene directly on SiO_2 substrates without metal catalysis [12]. Titanium and its alloys are an excellent example of materials that can combine with graphene to improve their properties, enhancing their applications in different areas, e.g. biomedical and aerospace [13-17]. Among all the titanium alloys, Ti6Al4V (Ti64; 90% Titanium, 6% Aluminum and 4% Vanadium) is one of the most popular due to its superior performance: enhanced corrosion resistance, excellent mechanical properties and biocompatibility [18,19]. In the biomedical field, Ti64 is most widely used to manufacture orthopedic implants due to its biocompatibility, high strength, low weight, and similarity to Young's modulus of human bone compared with other metals [20-22].

Despite the excellent properties of Ti64, the biocompatibility, wear and corrosion resistance must be improved in joint implant applications. To improve the Ti64 weaknesses, some compounds such as hydroxyapatite, TiO_2 and carbon-based materials have been incorporated [18,23,26,27]. Nevertheless, carbon materials, e.g. graphene, are most commonly used to improve corrosion resistance [18,28,29,30,31], and to accelerate the bone regeneration and osseointegration [18,32,33,34] of Ti64. Kalisz et al analyzed the effect of niobium pentoxide and graphene coatings on the corrosion resistance of Ti6Al4V in acidic environments [28]. Two systems were prepared: niobium pentoxide/Ti6Al4V and graphene/Ti6Al4V by magnetron sputtering and TCVD methods, respectively, where the higher wear and corrosion resistance values were obtained with the graphene coating [28]. Malhotra et al, applied a nanocoating of graphene onto a Ti6Al4V alloy to study the corrosion protection of this carbon material in an acidic solution for 240 days [29]. In this case, the graphene was grown on a Cu foil by chemical vapor deposition (CVD) and film was removed from the copper and deposited on Ti64 via a polymer supported dry transfer method. They found that the graphene nanocoating was capable of inhibiting the corrosion of the Ti64 alloy in different aggressive environments, which would allow its application in dental implants and other biomedical fields [29]. Kewen et al deposited a graphene coating on another Ti alloy (Ti5Al1V1Sn1Zr0.8Mo) by a micro-arc oxidation method to improve the wear and corrosion resistance [31]. Several studies have focused on graphene incorporation into Ti and its alloys to improve their osteointegration properties [32-35]. Li et al. used CVD to grow graphene on copper and then transferred it to the Ti64 alloy to study the bioactivation of the surface of this material. They found that graphene promoted the acceleration of the osteogenesis and osteointegration at the implant-bone interface [32]. Lu et al. conducted a similar approach to improve the osteogenesis of dental implants made of titanium alloys [33]. They studied a graphene-coated titanium sheet,

where the carbon film was prepared by the chemical reduction of graphene oxidation (GO) obtained by the chemical oxidation and exfoliation of natural graphite. The reduced GO nanosheets were subsequently inserted on the titanium. The results showed that the titanium with the surface modification promoted and accelerated the osteogenic differentiation ability, thus providing a viable alternative to improve the osteogenesis of early stage dental implants [33]. Direct graphene growth on Ti was proposed by Zhang et al. via plasma enhanced CVD, (PECVD) using methane as carbon source [35]. They concluded that the corrosion resistance and hydrophobicity of Ti was improved, and that the composite material increased the antibacterial ability against Gram-positive Staphylococcus aureus (S. aureus) and Gram-negative Escherichia coli (E. coli) under nearinfrared light [35]. The cited works (vide supra) have incorporated graphene on Ti, and its alloys by different methods, such as thermal CVD on copper (using a transfer process) [28], chemical reduction of GO [33], micro arc-oxidation [31] and PECVD [35]. These procedures are effective for graphene incorporation, but some of them lead to undesirable side effects and several require expensive hardware. We conclude that studies of the direct graphene growth on titanium and its alloys, e.g. Ti64, are limited, and further research on the topic is merited.

This study proposes a method to grow graphene directly on Ti6Al4V pellets by HFCVD using methane as a carbon source at 950 °C and a pressure of 35 Torr. The Ti6Al4V samples were prepared from a powder of the alloy compacted into a pellet. The graphene on Ti64 alloy samples were characterized through structural, morphological, and compositional techniques. This research aims to enhance the properties of the Ti64 alloy to increase its use in biomedical and engineering areas. Furthermore, HFCVD is proposed as a new method for the incorporation of graphene in Ti64 that opens the possibility of being implemented in industrial production [11].

5.2. Experimental Details

5.2.1. Substrate Preparation

Ti6Al4V pellets, with a diameter of 13 mm and thickness of 2.24 mm, were formed from the metal alloy powder (spherical particles; 2 - 45 μ m) available from Advanced Powders & Coating, APC. The Ti alloy powder was compacted at 5.5 ton (24 MPa) using a press from the Carver Company. Polyvinyl alcohol (PVA) was mixed with the powder to improve the adhesion of the pellet but was removed in a tube furnace at 400 °C for 2 hours in a flowing Ar gas environment at atmospheric pressure. Finally, the Ti6Al4V pellets were sintered in a tube furnace at 980 °C for 5 hours and a controlled atmosphere of argon with a flow rate of 200 sccm, as shown in Figure 5.1.

5.2.2. Graphene Synthesis

For graphene deposition, a commercial HFCVD (BWS-HFCVD1000 Blue Wave, Baltimore, MD, USA) was used, where the Ti64 alloy in pellet form is placed in the position of the heater, below the filament, as shown in Figure 5.1. The gases are introduced in the chamber from the top with a shower-like turbulent flow, (cf. Figure 5.1). The HFCVD equipment permits the systematic adjustment of the growth parameters e.g., pressure, gas flow rates, deposition time, substrate-to-filament distance (5–15 mm), and substrate and filament temperature. The total pressure and heating rate were fixed at 35 Torr and 35 °C/min, respectively. The annealing step was omitted because the Ti64 pellets were sintered at high temperature. In the graphene growth step, the heater temperature is fixed at 900 °C, with a gas flow range of 1–10 sccm for CH₄ and 50 sccm for H₂. Once the heater temperature is reached, the filaments are turned on in the range of 1800 °C to 2300 °C, the H₂ is stopped, and the system is kept in this condition for 30 to 120 min.



The samples were cooled by natural convection.

Figure 5.1 Schematic of pellet formation of Ti64 alloy and the graphene deposition setup.

5.2.3. Characterization Techniques

The Raman spectroscopy was used for structural characterization of graphene on Ti64 alloy by a Thermo Scientific DXR (Waltham, MA) equipment, with an excitation laser of 532 nm. The spectra were collected over a frequency range of 1100 to 3100 cm⁻¹ with a spot size of 0.7 μ m. A Nikon model P300 microscope was used to identify the distribution and size of the spherical particles that constitute the Ti64 pellets, the images were taken at 10x, 50x and 400x magnification. To study the morphology of graphene, a scanning electron microscope, SEM (IT500HR, JEOL) was used at different magnifications, 100×, 1000×, 3000× and 50,000×. An energy-dispersive Xray spectroscopy, EDS (DRYSD30, JEOL) and X-ray photoelectron spectroscopy, XPS (PHI 5600 Physical Electronics) were used to analyze the elemental composition of the Ti64 alloy, the measurements were taken in an energy range over of 20kV and 0 to 1200 eV, correspondingly. More details about the techniques and instrumentation are presented in the chapter 2.

5.3 Results and Discussion

Graphene growth on Ti6Al4V pellets was characterized using the Raman technique to identify and estimate the number of deposited layers and defects. SEM images allowed a deeper study about the morphology and particle size of the graphene crystals. EDS and XPS were used to identify the elements present in the graphene on Ti6Al4V samples.

5.3.1 Raman Analysis

In the Raman spectra of graphene on Ti6Al4V pellets, we observed the characteristic peaks: the G peak arising from the presence of sp^2 carbon atoms; the 2D peak as consequence of two-phonon vibration; and the D peak that is activated by the edges or defects in the graphene films [36]. Figure 5.2 b. shown the Raman spectra for samples of graphene grown on Ti6Al4V pellet. Although some differences in the D peak intensity were found, in general all samples shown the same Raman spectra at similar peaks positions. These were found at 1344 cm^{-1} for the D peak, at 1580 cm⁻¹ for the G peak, and at 2691 cm⁻¹ for the 2D peak. In addition, a low intensity peak at 2450 cm⁻¹ was observed in almost all samples, commonly associated to the double resonance of Raman scattering [37]. The D' peak (an indicator of defects) at 1620 cm⁻¹ was small confirming that good quality crystals were obtained [37 - 39]. Figure 5.2 a show the Raman spectra of the Ti6Al4V alloy in powder form as received from the manufacturer (without carbon deposition). The spectra were taken over two wavenumber ranges, the first from 100 to 1000 cm^{-1} and the second from 1100 to 3100 cm⁻¹ (see inset of Figure 5.2 a). Ti6Al4V alloy peaks were observed at 141.52 cm⁻¹, 261.05 cm⁻¹, 402.35 cm⁻¹, 603.19 cm⁻¹, 797.60 cm⁻¹. These peaks confirmed the presence of anatase and rutile phases of Ti6Al4V [40]. Over the second range (1000 to 3100 cm^{-1}), a peak at 1580 cm⁻¹ was identified, and attributed to amorphous carbon present on the Ti64 powder [41]. Figure 5.2 d shows the optical image of graphene deposited on Ti6Al4V pellet taken by the

Raman microscope at 50x of magnification. Figure 5.2 c represent the image of Ti6Al4V alloy in powder form (as received). It was possible to identify that Ti6Al4V spheres with graphene were opaquer and rougher (Figure 5.2 d) than observed in the Ti6Al4V powders (Figure 5.2 c). The features of the D, G and 2D peaks obtained by Raman spectra provide information about defects [42,43], crystallinity [43], particle size [44], morphology [45] and the number of graphene layers [8,45] deposited on Ti64 pellet.



Figure 5.2 Raman measurements of graphene deposited on Ti6Al4V pellet. a) Raman spectrum of graphene on Ti6Al4V pellet, a) Raman spectrum of Ti6Al4V in powder from 100 to 1000 cm⁻¹ and the inset shows the range from 1000 to 3100 cm⁻¹. c) and d) Raman microscope images taken in a) and b) areas with a magnification of 50x. (The spectra were taken with a 532nm laser).

According to the Cancado equation (Equation (1)) [44], it is possible to calculate the crystal size using the intensity values between the D and G peaks ($I_{D/G}$). The I_D/I_G values were around 0.60 ± 0.05 to 0.80 ± 0.03 and the particle size (L α) resulted in a range of 12.09 to 14.15 nm. These estimates show that the deposited material is composed of nanocrystals [46], however the spherical morphology of the particles that constitute the Ti6Al4V pellet could lead to inaccurate estimates.

$$L_{\alpha} = (2.4 \times 10^{-10}) \lambda_l^4 (I_D / I_G)^{-1}$$
(2.1)

Additional information about the morphology, uniformity, and the number of layers of this carbon material was evaluated from the intensity ratio of the 2D/G peaks [8,44]. The average 2D/G ratio value was 0.87 ± 0.05 , corresponding to few layers of graphene were grown on Ti6Al4V alloy [8,10,36].

Depending on the level of doping (involuntary) of this carbon material, it is also possible that the estimate of the graphene layers is incorrect again arising from spherical nature of the Ti6Al4V particles, and their influence on the 2D/G intensity value [47]. The full width at half maxima (FWHM) of the D, G and 2D peaks were calculated to obtain additional information about the morphology and crystal quality of the graphene layers on Ti6Al4V. The FWHM value of these peaks was 32 ± 1 cm⁻¹, 32 ± 1 cm⁻¹ and 58 ± 3 cm⁻¹, respectively. This result is consistent with good quality graphene [46] and supports the idea that the high intensity of the D peak arises from the graphene nanocrystals and the spherical edges of the particles that make up the Ti6Al4V pellet.

5.3.2 Optical microscopy images

Optical images (Nikon microscopy) of graphene on Ti6Al4V pellet were taken through the pellet preparation and graphene incorporation. These images correspond to: (1) compaction, (2) sintering and (3) graphene deposition by HFCVD, as showed in Figure 5.3. In the optical images was possible to observe the spherical particles over all pellets, keeping this form through all three processes. The images were taken with magnification of 400× and without extra light processing, it was not observed a considerable difference in the particle morphology between Ti6Al4V alloy samples with and without carbon deposition by optical microscope.



Figure 5.3 Optical microscopy images of graphene deposition on Ti6Al4V alloy steps from compaction to graphene synthesis.

5.3.3 SEM analysis

The SEM images taken of Ti6Al4V pellets without and with graphene deposition are shown in Figure 5. 3 a, b at 1000x, respectively. Figure 5.3b shows the image of the graphene on Ti6Al4V pellet, where the smaller spherical particles (1 to 14 μ m) look more granulated and amorphous than observed in pellets without carbon deposition (Figure 5.3 b). An increase in roughness was also observed in all spheres containing graphene. Some carbon agglomerations in

the graphene on Ti6Al4V samples were observed. In Figure 5.3 a, the Ti6Al4V pellets are shown before graphene deposition at 1000×. Spherical particles with a size of ~20 μ m were predominant, but smaller ones in a range of 2 -10 μ m were found.



Figure 5.4 SEM images of Ti6Al4V pellet with and without graphene deposition, where a) and b) represent the image of before and after graphene deposition on Ti6Al4V alloy at 1000x, respectively.

Figure 5.5a, b shows the graphene on Ti6Al4V pellet at 3000x and 50,000x respectively, these images are taken to have a better understanding of the nanoparticles size and morphology that are deposited on Ti6Al4V pellets. According to Figure 5.4b, polycrystal graphene is growth with a particle size in a range of 40 to 110 nm. These results have a discrepancy that obtained by Cancado equation (12.09 to 14.15 nm), that could associate to the nanocrystal size of the particles or defect inside of the graphene crystal. Other important aspect is related to the difficult estimation by SEM, because the crystals are very close to each other.



Figure 5.5 SEM images of graphene deposited on Ti6Al4V pellet, where a) and b) represent the graphene deposited on Ti alloy samples with a growth at 3000x and 50,000x, respectively.

5.3.4 EDS analysis

A compositional analysis of graphene on Ti6Al4V pellets was done by EDS as observed in Figure 5.6 a, where the following elements were identified (with their respective atomic concentrations): carbon (29.23 \pm 0.05%), oxygen (20.65 \pm 0.22%), titanium (44.88 \pm 0.05%), aluminum (3.81 \pm 0.01%) and vanadium (1.42 \pm 0.01%). In the EDS spectra on Ti64 pellets without carbon deposition, were also observed, carbon (7.56 \pm 0.03%), oxygen (5.15 \pm 0.20%), titanium (77.09 \pm 0.03%), aluminum (7.89 \pm 0.02%) and vanadium (2.30 \pm 0.02%), (cf. Figure 5.6 b).

Other metal elements were not observed indicating that the carbon deposition was not influenced by external conditions. In addition, the highest carbon atomic concentration was found in samples after graphene deposition [36], while the carbon percentage found in the Ti6Al4V pellets are related to trace of elements (~0.37 wt.%) from company [48] and residues from PVA.



Figure 5.6 EDS images of Ti6Al4V pellet without and with graphene deposition, where a) represent the Ti6Al4V pellet without graphene deposition and b) shows the graphene grown on Ti6Al4V pellet.

5.3.5 XPS analysis

XPS measurements were taken as a complimentary compositional analysis of the graphene grown on Ti6Al4V pellet. This chemical analysis allowed us to obtain more information about the surface of Ti alloy before and after graphene deposition to determine the elements involved in the growth mechanism [49]. Our first aim was to identify the elements that constitute the Ti6Al4V (Ti, Al, and V) material and the presence of the carbon, and to confirm the absence of other elements or contaminants in the samples. Figure 5.7 a, b shows the XPS spectra of Ti6Al4V pellets before and after graphene deposition, respectively. These spectra show the presence of titanium, aluminum, vanadium, carbon, and oxygen. The spectra of the Ti6Al4V pellet showed carbon at a lower intensity than on pellets with graphene deposited. These results are consistent with our EDS

measurements, and they can be correlated to traces and residues on the powder and from the binder (PVA), respectively. Figure 5.7 c, d shows the carbon peak after the deconvolution process for Ti6Al4V granules without and with graphene deposition, correspondingly. The carbon 1s (C1s) peak at 285 eV was found in both pellets, treated and untreated with carbon [49,50]. In both figures, the raw data is represented by the dotted line and the solid lines correspond to the contribution of all peaks after deconvolution process.



Figure 5.7 XPS measurements of Ti6Al4V pellet without and with graphene deposition, where a) and b) represent the XPS full composition spectra for samples before and after graphene deposition respectively. c) and d) shows the carbon peak after deconvolution for the same samples showed in a) and b).

The C1s for Ti6Al4V pellets with and without graphene was compose of peaks at 285.0 eV, 285.6 eV and 287.4 eV, relating to C-C, C-OH, and C=O respectively [49,50]. Furthermore, the oxygen identification in all XPS measurements is due to the incorporation of this element after the experiments, during air exposition. All graphene depositions on Ti6Al4V pellets were conducted in controlled environments, during heating and cooling with gases flow to minimize the presence of oxygen. Other metal elements such as Fe (Fe $2p_{3/2}$: 706.7–710.9 eV), Co (Co $2p_{3/2}$: 778.1–780.2 eV), Ni (Ni $2p_{3/2}$: 852.5–854.4 eV) and Cu (Cu $2p_{3/2}$: 930–937 eV and Cu $2p_{1/2}$: –954 eV) were not observed [51].

5.3.6 Graphene Growth Mechanism

In this study graphene was grown on Ti6Al4V alloy pellets using the HFCVD technique. Methane was used as carbon precursor and the hot filaments were used to promote the dehydrogenation of methane. The graphene formation mechanism on Ti6Al4V is divided in two parts, shown in Figure 5.8. First the methane is dehydrogenated in most part by the hot filaments producing free carbon atoms and methane radicals. Second, the free carbon atoms are absorbed on the Ti6Al4V surface and the remaining methane radicals are further dehydrogenated by the catalytic properties of titanium, leading to the graphene film formation The catalyst properties of titanium have been demonstrated in formal redox transformations (C-C, C-O and C-N) and hydrofunctionalization catalysis reactions [52]. Furthermore, the high affinity of titanium allows the reaction with CH₄ to form titanium carbide (TiC) [53]. Another aspect that can influence the growth of graphene in the Ti6Al4V pellets is the carbon residues of the binder used (PVA). Although hydrogen was used to reduce excess carbon and improve the quality of graphene, some agglomerations were found on the Ti6Al4V surface that are associated to secondary nucleation or renucleation process as observed in experiments of nanodiamond deposited on 3D titanium

substrates conducted by Braga [54].



Figure 5.8 Schematic of the graphene growth mechanism on Ti6Al4V pellets. (a) dehydrogenation of methane by the hot filaments (b) absorption of carbon on Ti6Al4V surface and graphene film formation.

5.4 Conclusions

The current research demonstrates a method to deposit graphene on Ti6Al4V alloy by HFCVD technique, without an extra catalytic material or transfer method. A structural analysis of graphene deposition was conducted by SEM, optical microscopy, and Raman measurements. The crystal size of graphene was estimated from Raman spectra, resulting in a range of 12.09 to 14.15 nm. The FWHM values of D, G and 2D peaks from Raman spectra shown that a good crystal quality was obtained. SEM images revealed that Ti64 alloy is composed of spherical particles in a range of 2 - 20 μ m. Unfortunately, the graphene crystals were not clearly identified by SEM images, due to nanocrystal size and the morphology of the Ti6Al4V alloy. Some agglomerations and surface changes were detected in the spherical particles of this alloy after graphene deposition. EDS and XPS measurements revealed the presence of C, Ti, Al, V, and O elements and the absence of external contaminants. The carbon reactive species produced by methane decomposition on the

hot filament and the titanium catalytic activity allows graphene formation on the surface. This approach to graphene deposition on Ti6Al4V by HFCVD has been successfully demonstrated here and opens new possibilities for the scale-up of graphene incorporation in titanium alloys.

5.5 References

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Chapter 6. Summary and Future Directions

6.1 Summary

This dissertation reports the growth of graphene on SiO₂/Si, SiC and Ti6Al4V by HFCVD. The relation between the growth parameters and the graphene films characteristics are presented. Three chapters of this thesis are dedicated to the analysis of graphene growth on each different substrate with their respective structural, morphological and compositional characterizations. For graphene growth on SiO₂/Si, we found a method to deposit polycrystalline graphene directly onto this substrate by HFCVD avoiding the complex graphene transfer process. As a catalyst, a thin copper-strip (0.3 cm \times 2.0 cm) was deposited in the middle of the 4 cm² substrates, leaving most of surface uncovered. The structural characterization by Raman spectroscopy (D/G and 2D/G intensities) confirmed that high quality graphene was obtained. The size of the graphene nanocrystals (100 to 140 nm) deposited on the SiO₂/Si substrates were determined from SEM images. A compositional study by EDS and XPS measurements, revealed the presence of carbon in all samples and the absence of copper in areas next to the metal-strip. The graphene growth mechanism begins with the dehydrogenation of methane by the hot filament and the catalytic effect of vaporized copper atoms, allowing the deposition of carbon atoms over the entire substrate. Graphene crystals grow at a faster rate on the substrate area where the copper strip was deposited, nevertheless graphene still grows on areas next to the copper strip. This work demonstrates that a thin copper-strip deposited on the middle of the SiO₂/Si substrate enables the growth of graphene over the entire substrate. This accomplishment enables the possibility to directly integrate graphene on current silicon devices avoiding the transfer process. In the graphene growth study on 6H-SiC, methane was used as the carbon source and Raman, SEM, AFM, EDS and XPS measurements confirmed that the nanographene films were deposited. The high quality of graphene was confirmed through surface morphology analysis by Raman and SEM. The graphene growth mechanism on 6H-SiC substrate occurs in two steps: first the dehydrogenation of methane by the hot filaments produces reactive carbon species, and second the carbon species are deposited on the SiC surface crystalizing as a graphene film. In addition, it was found that SiC substrates cleaned with HF acid showed more graphene layers, for the same growth conditions. The HF acid helps to remove the oxide layer at the SiC surface allowing better carbon incorporation. The growth time also has an effect in the number of deposited layers, i.e. longer growth time results in more graphene layers. The deposition of graphene on SiC is possible independently of the HF acid treatment. Nevertheless, the type of treatment and the growth time has an influence in the number of graphene layers.

The last material studied was the deposition of graphene on Ti6Al4V (Ti64) alloy, which is relevant for aerospace and biomedical applications. Graphene deposition on Ti6Al4V was confirmed by Raman, SEM, EDS and XPS measurements. No other metals, that could have an effect on the growth process, were observed. The graphene crystal size (12.09 to 14.15 nm) and the particle size of Ti64 alloy (2 -20 μ m) were calculated from their Raman spectra and SEM images, respectively. The proposed mechanism of the graphene formation on Ti64 was divided into two parts. First the methane dehydrogenation by the hot filaments, second the deposition of carbon species on the Ti64 surface and graphene film formation. The carbon incorporation on Ti64 surface may be due to the catalytic properties of the titanium and its high affinity to react with the CH₄ molecule. Other aspect that can have an influence in the growth process is the carbon residues from the binder (PVA), that was not eliminated in the sintering process.

6.2 Future Directions

This Ph.D. dissertation contributes to the understanding and production of the graphene growth on SiO₂/Si, SiC and Ti6Al4V by HFCVD method. Here is exposed the growth parameters and its relationship with the graphene quality on different substrates. Although a detailed study of graphene growth on different substrates is presented, this work suggests further analysis and future applications of these materials.

- a. High quality of graphene was obtained on the SiO₂/Si substrate; however some point defects were found in the crystal. The growth parameters can be modified to improve the characteristics of the films. One approach is the reduction of the nucleation density [1, 2–4] by modifying the methane and hydrogen gas flow rates that allows an increment in the graphene crystal size and reduction of the point defects [3,4]. Furthermore, a deeper analysis is needed regarding the doping levels in the graphene films and how this influences the ratio of the D/G and 2D/G peaks.
- b. Further compositional analysis needs to be employed to understand the influence of oxygen on the number of graphene layers in SiC [5]. Experiments under different annealing conditions, such as pressure and gas flow are also needed. These studies could improve the initial surface of the SiC substrate allowing better deposition of graphene and reducing the oxygen and defect in the films.
- c. In the graphene on Ti6Al4V alloy study, a better pellet must be fabricated. For this, the Ti64 powders must be mixed through a ball milling and filtered with a sieve to obtain a uniform particle size [6], then a higher compression force should be applied to create a rigid piece [7]. In the sintering process, the Ti64 pellets must be exposed to higher temperatures under argon flow at different times until the best mechanical properties

are achieved. The finished pellet will then undergo a polishing process to reduce surface roughness. Finally, the Ti64 pellets can be exposed to the carbon deposition by HFCVD and tested by mechanical measurements such as hardness, density, strain, and shear. In addition, 3D printed pieces of can be used as a base material for graphene incorporation.

d. Electrical and surface characterization using the Hall effect and contact angle measurements of the graphene films on SiO₂/Si and SiC substrates can be performed. Additionally, electronic devices can be fabricated using the techniques discussed in this work and subsequently performance tested. For graphene deposited on Ti64, biocompatibility tests with mesenchymal stem cells such as osteoblasts and fibroblasts and the study of their mechanical properties can be performed. A theoretical study using density functional theory can be conducted to obtain a deeper understanding of the crystallization mechanism of graphene on each substrate (SiO₂/Si, SiC and Ti64).

6.3 References

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