Nanostructured carbon-based thin films: prediction and design

Cecilia Goyenola

Department of Physics, Chemistry, and Biology (IFM)
Linköping University, SE-581 83 Linköping, Sweden

Linköping 2015

ISBN 978-91-7685-976-6
ISSN 0345-7524

Printed by LiU-Tryck, Linköping 2015

A mis abuelos

Abstract

Carbon-based thin films are a vast group of materials of great technological importance. Thanks to the different bonding options for carbon, a large variety of structures (from amorphous to nanostructured) can be achieved in the process of film synthesis. The structural diversity increases even more if carbon is combined with relatively small quantities of atoms of other elements. This results in a set of materials with many different interesting properties for a wide range of technological applications.

This doctoral thesis is about *nanostructured* carbon-based thin films. In particular, the focus is set on theoretical modeling, prediction of structural features and design of sulfocarbide (CS_x) and carbon fluoride (CF_x) thin films.

The theoretical approach follows the synthetic growth concept (SGC) which is based on the density functional theory. The SGC departure point is the fact that the nanostructured films of interest can be modeled as assemblies of low dimensional units (e.g., finite graphene-like model systems), similarly to modeling graphite as stacks of graphene sheets. Moreover, the SGC includes a description of the groups of atoms that act as building blocks (i.e., precursor species) during film deposition, as well as their interaction with the growing film.

This thesis consists of two main parts:

Prediction: In this work, I show that nanostructured CS_x thin films can be expected for sulfur contents up to 20 atomic % with structural characteristics that go from graphite-like to fullerene-like (FL). In the case of CF_x thin films, I found that a diversity of structures can be formed depending on the fluorine concentration. Short-range ordered structures, such as FL structure, can be expected for low concentrations (up to 5 atomic %). For increasing fluorine concentration, diamond-like and polymeric structures should predominate. As a special case, I also studied the ternary system CS_xF_y . The calculations show that CS_xF_y thin films with nanostructured features should be possible to synthesize at low sulfur and fluorine ($[\text{S} + \text{F}] < 10 \text{ at.}\%$) concentrations and the structural characteristics can be described and explained in terms of the binaries CS_x and CF_x .

Design: The carbon-based thin films predicted in this thesis were synthesized by reactive magnetron sputtering. My modeling results regarding structure, composition, and analysis of precursor species (availability and role during deposition process) were successfully combined with the experimental techniques in the quest for thin films with desired structural features. They were used as guidance for the depositions and to understand the properties of the resulting thin films.

Populärvetenskaplig sammanfattning

Materialvetenskap är ett stort tvärvetenskapligt forskningsfält som handlar om att upptäcka och konstruera nya material såväl som att förbättra befintliga. Allting vi använder i vårt dagliga liv, från kläder till tekniska apparater, är skapat för att tillgodose vissa krav och är ett resultat av att många människor har investerat sin tid och sina pengar på att studera varje aspekt av dem för att göra dem *bättre* (billigare, mer hållbara, mindre, större, etc.).

Ta en persondator som ett exempel. De senaste decennierna har vi sett hur datorer har blivit mindre och mindre, men samtidigt kraftfullare: processorer är snabbare, lagringskapacitet av information är större, batterier har längre livslängd, skärmar är tunnare och har högre upplösning, etc. Hur är detta möjligt? Ofantligt mycket pengar har investerats för att anställa forskare och ingenjörer som i sin tur spenderat årtal med att förbättra varje enskild komponent i datorn. Detta arbete har i mångt och mycket inneburit utveckling och förbättring av de material som komponenterna är tillverkade av, vilket lett till ökad prestanda och minskad komponentstorlek.

Tunna filmer är väldigt viktiga för många komponenter i en dator. En tunn film är ett väldigt tunt lager av ett material med en tjocklek från ett par atomskikt till några mikrometer. Ett speciellt intressant exempel som är relaterat till denna avhandling är tunna kolnitridfilmer (CN_x) som används som beläggning i hårddiskar för att skydda mot slitage och korrosion. För att uppnå högre lagringsdensitet i en hårddisk så måste avståndet mellan läshuvudet och skivan minskas, vilket betyder att det finns väldigt lite utrymme för en skyddande beläggning (i storleksordningen nanometer). Därför är tunna filmer nödvändiga.

Tunna kolnitridfilmer har en unik kombination av hårdhet och elasticitet, samtidigt som de är väldigt resistent mot slitage. Det är dessa egenskaper som gör dem lämpliga att använda som fasta smörjmedel i hårddiskar. Efter över tjugo år av studier så är det välkänt att deras egenskaper är direkt relaterade till förekomsten av kväve i en amorf kolmatris.

En fråga som man då kan ställa sig är följande: kan vi hitta andra kolbaserade material som har liknande mekaniska egenskaper, men som är uppblandade med andra grundämnen än kväve och kanske har andra egenskaper som möjliggör användning i andra applikationer? Svar till denna fråga kan hittas om vi kom-

binerar modellerna och teorierna som har utvecklats inom teoretisk fysik och kemi (dvs. *modelleringsarbete*) med avancerade syntes- och karakteriseringstekniker (dvs. *experimentellt arbete*).

Denna avhandling behandlar frågan som ställdes ovan genom att använda svavel och fluor istället för kväve. Min forskning har bestått av modelleringsarbete för att studera och föreslå nya material bestående av svavelkarbid (CS_x) och kolfluorid (CF_x). Genom att ha ett nära samarbete med en experimentell grupp så har vi dessutom lyckats syntetisera och förstå egenskaperna hos dessa nya filmer och bildat oss en förståelse för själva syntesprocessen.

Preface

This dissertation is the result of my doctoral studies carried out between March, 2010 and October, 2015 in the Thin Films Physics Division and the Theoretical Chemistry Division at the Department of Physics, Chemistry and Biology (IFM), Linköping University.

My research has been focused on the theoretical study of nanostructured carbon-based thin films, and in particular the compounds sulfocarbide CS_x and carbon fluoride CF_x . While I have spent most of the time on theoretical calculations and modeling, I had a brief experience in the lab during the initial stages of the CS_x thin films deposition and characterization process. Large part of the results have been published as research papers in scientific journals and are appended to this thesis. The theoretical part of the results that have not been published yet are appended in the form of a paper manuscript.

My doctoral project was carried out with financial support from FunMat, VINN Excellence Center in Functional Nanoscale Materials financed by the Swedish Governmental Agency for Innovation Systems (VINNOVA), and from Linköping Linneaus Initiative on Novel Materials financed by the Swedish Research Council (VR).

All the theoretical calculations were performed at the National Supercomputer Center (NSC) at Linköping University.

Acknowledgements

I would like to start by mentioning the people that have been directly involved in the research that resulted in my thesis.

First of all, I would like to thank my supervisor *Gueorgui K. Gueorguiev*. Thanks for trusting and encouraging me through all these years.

I would also like to thank my co-supervisors *Lars Hultman* and *Sven Stafström*. No matter whether you were here or far away, I could always count on you.

Almost since the beginning of my doctorate I had the pleasure to collaborate and work together with *Susann Schmidt*. Thanks for all the discussions, I have learned a lot! I am looking forward to continuing working together!

During the last couple of years, my work has been enriched by the collaboration of *Chung-Chuan Lai*, *Hans Högberg* and *Johanna Rosén*. Special thanks to *Mark Tucker* for being my mentor in *real* thin film depositions.

I would also like to thank all my coauthors, we have obtained really nice results.

At this point I would like to acknowledge the place where everything began: la *Cátedra de Física, Facultad de Química, Universidad de la República*. I especially want to thank Ricardito and Luciana for their friendship and encouragement.

Fortunately, my years in Sweden have not only been about the thesis.

I want to thank my friends and colleagues in the *Thin Films Physics* and the *Theoretical Physics Divisions* for lunches, fikor, short conversations or just saying hi in the corridor.

Big thanks to the *Theoretical Chemistry Division* (ex-Computational Physics). You made me feel welcome from the very beginning. I have really enjoyed all our talks and social activities. I especially want to mention *Jonas S.*, *Patrick*, *Mathieu*, *Joanna*, *Paulo* and *Thomas*.

Being away from my family and friends has not been easy, and from time to time it has been really hard. However, I was fortunate to find new friends and family that helped me to keep going on: *Hanna*, *Amie*, *Bo*, *Jonas*, *Abeni*, *Zhafira*, *Lía*, *Leyre*, and our little family in Linköping, *Davide*, *Elinor* and *Ruben*. Thanks!

My Swedish family *Lotta*, *Lasse*, *Jenny*, *Peter*, *Izabel*, *Julia*, *Jonatan* and *Emma*. Thanks for taking me in, I am extremely lucky to have you!

This thesis and my life in Sweden would not have been possible without the support and love I receive from Uruguay.

Mamá, Papá, Pati, Juan and Memo. No matter the distance and no matter what happens I am grateful to know that we are all there for each other. Thanks for everything!

The rest of our big family, *abuelos, tías, tíos, primos* and *Isa*, and my dearest friends *Ceci, Fer* and *Vero*. Thanks for being there and showing me every year that I can always come back to you!

Finally, *Mattias* and *Milo*, you are the real blessing from my Swedish adventure. Thanks for our life together! And thanks for the continuous support, specially these last few months.

A handwritten signature in black ink, reading 'Cecilia Goyenola'. The signature is fluid and cursive, with a large loop at the end of the last name.

Cecilia Goyenola
Linköping, September 2015

Contents

1	Introduction	1
1.1	Order in materials	2
1.2	Nanostructured materials	3
1.3	Thin films	5
1.4	Modeling materials	6
2	Carbon-based compounds	7
2.1	Carbon and its ordered allotropes	8
2.2	Carbon-based thin films	11
2.3	Fullerene-like carbon-based thin films	14
2.4	Introducing sulfur and fluorine	17
3	Synthetic growth concept	21
3.1	Overview of the method	22
3.2	Application to fullerene-like carbon-based materials	26
4	Density functional theory	37
4.1	Theoretical background	37
4.2	The basis of DFT: Hohenberg and Kohn theorems	39
4.3	Kohn-Sham ansatz	40
4.4	Exchange-correlation functionals	43
4.5	Wave function expansion: basis sets	44
5	Overview of experimental techniques	47
5.1	Thin film deposition	47
5.1.1	The sputter deposition process	48
5.1.2	Plasma characterization: Mass spectrometry	51
5.2	Thin film characterization	52
5.2.1	Structural characterization	52
5.2.2	Thin film composition and chemical bonding	54
5.2.3	Mechanical characterization	56

6 Summary and conclusions	59
A Short-range order in CF_x thin films	61
Bibliography	63
List of included Publications	77
My contribution to the papers	78
Related, not included Publications	79
Paper I	81
<i>Fullerene-like CS_x: A first-principles study of synthetic growth</i>	
Paper II	89
<i>Structural patterns arising during synthetic growth of fullerene-like sulfocarbide</i>	
Paper III	99
<i>CF_x: A first-principles study of structural patterns arising during synthetic growth</i>	
Paper IV	107
<i>CF_x thin solid films deposited by high power impulse magnetron sputtering: Synthesis and characterization</i>	
Paper V	117
<i>Reactive high power impulse magnetron sputtering of CF_x thin films in mixed Ar/CF_4 and Ar/C_4F_8 discharges</i>	
Paper VI	129
<i>Carbon fluoride, CF_x: structural diversity as predicted by first principles</i>	
Paper VII	139
<i>Theoretical prediction and synthesis of CS_xF_y thin films</i>	

Chapter 1

Introduction

Materials science is a large interdisciplinary field within the natural sciences area of knowledge, which is dedicated to the discovery and design of new materials as well as the improvement of existing ones. The increasing demand for comfort in our lives, the need for improved medical applications, the desire to explore the limits of the universe, and the pursuit of environmentally friendly technologies are all examples that benefit from a rapid technological development. Frequently, this advancement is limited by the lack of suitable existing materials and the need for new and improved ones has propelled the growth and importance of materials science.

This thesis belongs to the field of materials science and, more specifically, it is about the prediction and design of inherently nanostructured carbon-based thin films using theoretical modeling tools. The formulation of this overall goal, reflected in the title of the thesis, can be further understood by explaining the different concepts that it contains.

The work described herein is concerned with the study of a certain type of material, *the carbon-based materials*. In particular, the main focus is set on the sulfocarbide (CS_x) and the carbon fluoride (CF_x) compounds, which are carbon-based materials that incorporate relatively low amounts of sulfur and fluorine, respectively. Furthermore, the study is about *thin films* of these compounds, which are very thin layers of material with a thickness that can range from a few atomic layers to some micrometers.

The initial question that gave rise to this thesis is whether CS_x and CF_x could be obtained as *inherently nanostructured* materials. This means not only that their properties are defined by structural characteristics arising in the nanometer scale, but also that the nanostructured quality is developed during the synthesis of the material. Driven by the exciting properties shown by the fullerene-like carbon nitride and fullerene-like phosphorus-carbide compounds, a special interest was dedicated to the fullerene-like kind of nanostructure.

The research was performed from a *theoretical point of view*, using models that allow us to understand how atoms interact and, as a result, help us determine

whether a material can exist, what type of structure it should adopt, and which properties it may exhibit. This process constitutes the *prediction* of the material.

The prediction is accompanied by a study of the synthesis process and the resulting properties of the material. For this, the theoretical and experimental efforts take part of a feedback loop using each others results as input. The goal is to gain a broader understanding of the features of carbon-based compounds, how the structure is related to the properties, and how these two are affected by the synthesis process in order to obtain a material with tuneable properties that may serve a variety of applications. This constitutes the *design*¹ of the material.

The outline of the thesis is as follows: details of carbon-based thin films are described in Chapter 2 – *Carbon-based compounds*, including highlights of my main results. Chapter 3 – *Synthetic growth concept* and Chapter 4 – *Density functional theory* describe the theoretical tools used in the modeling of the compounds. Chapter 5 – *Overview of experimental techniques* covers the experimental techniques used to synthesize and characterize the thin films. Finally, Chapter 6 – *Summary and conclusions* closes the thesis. The purpose of the remaining part of *this* chapter is to present the key concepts that form the basis for the work done in this thesis.

1.1 Order in materials

To satisfy the technological demands mentioned in the introduction to this chapter, the diversity and number of materials that is known today is enormous. They can be classified in many different ways, for example according to their composition, structure, their properties, or applications. Relevant to this thesis is the classification according to the arrangement of the atoms in the material structure. From this point of view, materials can be divided in two groups: ordered materials and disordered materials.

In an ordered or crystalline material, the atoms are arranged in a three-dimensional periodic array - a lattice. Their structure exhibits long-range order, characterized by translational symmetry of a basic unit (a *unit cell*). This unit contains all the necessary information about the atomic species and their spatial positions to reproduce the complete solid by applying translation operations on the unit cell in all three dimensions [2].

On the opposite side, disordered or amorphous materials do not exhibit any long-range order. There is no compact way to represent the position of the atoms, e.g., by replication of a simple unit cell, and if the entire system is to be defined then a complete list of all the atomic coordinates has to be given. Nevertheless, the atoms are not randomly distributed. As in the case of crystalline materials, disordered materials present a high degree of short-range order [3].

Fig. 1.1 is a schematic representation of two two-dimensional networks featuring the two types of atomic arrangements. Fig. 1.1 a) represents an ordered network, where each atom (dot) has three nearest neighbors and the distance to them is

¹ *Design* is defined by the Oxford dictionary as *do or plan (something) with a specific purpose in mind* [1].

Figure 1.1. Schematic representation of a) an ordered material and b) a disordered material. The dots represent the equilibrium position of the atoms [3].

exactly the same. Considering the lines between the atoms as bonds, the bond angles are also exactly the same. Fig. 1.1 b) represents a disordered network in which all of the atoms also have three nearest neighbors, but the distance to them and the bond angles are not equal although similar.

The lack of long-range order in amorphous materials implies randomness at large separations in the sense that the knowledge of the position of a few atoms is not enough for locating the position of distant atoms. However, the atomic structure is not random for a few interatomic distances about any given atom. The presence of short-range order facilitates the study and the understanding of the local structure and the properties that may originate from it.

The carbon-based materials that are the topic of this thesis, fall in the group of disordered materials. While the position of the carbon atoms and atoms of other elements (referred to as *heteroatoms*) cannot be easily determined, the chemistry that governs the atoms' interaction prevails. Therefore, carbon atoms are usually found resembling the bonding conditions in one of the carbon allotropes (e.g., graphite and diamond) [4]. The same reasoning applies to the heteroatoms present in the compound.

A particular case arises in one of the types of materials studied – the fullerene-like carbon-based compounds. They contain regions which show short-range order at a scale beyond the atomic-scale, and more specifically, in the nanometer range. This type of materials can be cataloged as inherently nanostructured materials.

1.2 Nanostructured materials

Most properties of solids depend on the microstructure of the material, which is related to its chemical composition, its atomic structure, and its dimensions (e.g., grain size, length, and thickness). In particular, when the dimensions of a material are continuously reduced in any direction, a point is reached where some of the properties it exhibits differ from those exhibited by the corresponding bulk material. This limit can be found in the nanometer-range². The change in

²A commonly used value for this upper limit is 100 nanometers, but it should not be taken as a rigid limit [5, 6].

properties occurs because the dimensions of the material become comparable with the critical length scales of certain physical phenomena, e.g., the mean free path of the electrons or phonons. On such a length scale, phenomena that are classically explained mix with those that follow the rules of quantum mechanics, giving rise to new material properties [5, 7, 8].

A very clear example can be found in gold. The surface of bulk gold is well-known for being chemically inert. However, excellent catalytic properties for reactions like the decomposition of organic compounds appear in the surface of gold when its sample size is brought to the nanometer scale. Moreover, the catalytic nature (e.g., sensitivity and selectivity) can be tuned by controlling the size of the gold nanoparticles and choosing appropriate support materials [9].

Those materials whose physical and chemical properties are determined by structural features in the nanometer range and represent a noticeable difference from the properties found in the corresponding bulk material are called *nanos-structured materials*³ or nanomaterials. There are three types of nanostructured materials [7]:

- materials with three, two, or one dimension in the nanometer range such as particles, thin wires, or thin films, respectively, which can be unbound, embedded in a material matrix or supported by a substrate,
- materials exhibiting a microstructure with nanometer-sized features that are limited to a thin surface region in the bulk, such as coatings, and
- bulk solids with nanometer scale microstructural characteristics, such as polycrystalline solids or nanometer-sized ordered clusters that are mixed with non-crystalline regions that might differ in atomic structure and/or chemical composition.

When developing novel nanomaterials, decisions about which nanostructures are of interest must be made and the questions i) how can they be synthesized and ii) how can they be practically introduced in a material or a device, must be answered. Alongside this, there is the question of what is the relationship between the structure and the composition of a nanomaterial, and, if the nanostructures are embedded in a matrix or bound in some way, how the interaction with their matrices and interfaces control the properties of the material [5]. All these questions and the increasing interest in nanostructured materials have given rise to two growing interdisciplinary fields: *nanoscience* and *nanotechnology*. The field of nanoscience is in charge of understanding the fundamental physics behind the relation between size and properties. Perhaps the more famous field, nanotechnology, focuses on the development of products and processes based on controlling the nanostructure of the materials. Today, nanomaterials are used in a large and increasing number of applications, from aerospace components to tissue engineering; from beauty products to energy production devices. They are responsible for reducing the size-to-power (perceived as functionality) ratio of computers and cell-phones and many other applications at home, at work, and everywhere [8, 10, 11].

³Sometimes the term *nanostructured* is also used to refer to the fact that these nanostructures can be synthesized and partly organized by design.

The carbon-based materials⁴ studied in this thesis can be synthesized as nanostructured materials of different types. The most relevant to this work are the inherently nanostructured carbon-based fullerene-like compounds, which belong to the third category of nanomaterials according to the classification introduced above. While the issues addressed herein are mostly of relevance in nanoscience, the findings reported have an impact on the applications of these materials, thus making my results relevant to the corresponding nanotechnology.

1.3 Thin films

Thin films can be defined as layers of material with thicknesses that can range from a few atomic layers to several micrometers. Nowadays, they have an essential technological role in many industries. Thin films are formed on top of surfaces by depositing layers of atoms and/or molecules with the objective of improving the properties of the underlying material or providing new functionality [12]. A large variety of thin films have been discovered and widely applied. To cite some examples, i) titanium nitride and titanium nitride-based thin films have been widely used as protective hard coatings for cutting tools [13, 14], ii) uniform semiconductor thin films (e.g., SnSe_2 , SnS_2) are used as active components in thin-film transistors [15], and iii) thin films such as amorphous silicon have been employed as the light absorbing material in solar cells [16].

Thin films can be compared to the same material in bulk form in terms of the properties they exhibit. Frequently, thin film properties diverge from the properties of the corresponding bulk material and, in many cases, they have turned out to be better from the point of view of applications. To find out if a large change in a certain property should be expected while going from bulk to thin film, the same reasoning used above for nanostructured materials applies: determine what the origin of the property is and how the typical length scale for the phenomena compares to the film thickness⁵.

A few important aspects can be considered when discussing the properties of thin films [17]. Since thin films are in fact thin, surface effects become increasingly important. This can lead to certain properties becoming size-dependent (e.g., resistivity) and, at very small dimensions, defined by quantum effects. The structure of thin films also depends on the film thickness. While thick films may be polycrystalline, thinner depositions may result in amorphous structures. Finally, all film properties and structural features are highly dependent on the deposition process. The conditions of non-equilibrium during film synthesis can lead to a material with a specific structure that only exists as a thin film and not in bulk.

⁴Carbon-based materials and subcategories are further explained in Chapter 2 – *Carbon-based compounds*.

⁵It is trivial to conclude that many thin films are nanostructured materials by definition.

1.4 Modeling materials

Material properties are defined by phenomena that occur in a large range of spatial scales that can go from angstroms to millimeters. To gain a deeper understanding of the behavior of a material, theoretical approaches that examine the structure of the material on the appropriate length scale and incorporate dynamic processes that occur on different time scales are needed [18].

Material modeling refers to the action of finding a representation or model, in particular a mathematical one, whose behavior resembles that of the *real* material. Depending on the particular properties to be studied, different types of models have been developed. Some are based on continuum mechanics, where the material is approximated as a smooth infinitely-divisible medium. Others use an atomistic representation, where the material is modeled as a collection of interacting particles and may even separate nuclei from electrons [18,19]. Multiscale approaches that combine the different levels of modeling are commonly used today to understand the relationship between phenomena observed at different scales.

When the interest is focused on properties that arise from the microstructure of the material, atomistic models are by far the methods of choice. Depending on the specific question, one could employ electronic structure methods, which take into account the atoms that constitute the material and their electrons; force field methods, which considers the atoms or molecules as rigid balls which can interact through springs of different stiffnesses; or a combination of them [20].

Regardless of the chosen method, by studying the atomic positions and the interaction between atoms, one can obtain the set of possible structures for the compound under consideration and calculate, estimate, and predict its properties. However, all these methods include different types of approximations that make the results deviate from the experimental observation and this should be borne in mind when these two are compared.

In the case of this thesis, the interest is in the structure of carbon-based compounds which can be represented by relatively small model systems. The modeling procedure follows an algorithm established by the synthetic growth concept⁶ and relies on simulations performed using density functional theory⁷, which is an electronic structure method.

⁶See Chapter 3 – *Synthetic growth concept*.

⁷See Chapter 4 – *Density functional theory*.

Chapter 2

Carbon-based compounds

Solid carbon-based compounds comprise a large family of materials with a wide variety of structural characteristics and physical properties. The distinctive attributes of these compounds are: i) their main component is carbon, ii) carbon is forming a solid matrix (with itself and sometimes other elements) which may be crystalline or may lack long-range order, and iii) their main features are directly related to the chemical behavior of carbon. In this family, one can find a broad list of compounds that include the carbon allotropes, organic and inorganic molecules that can form molecular crystals, polymers, carbides, non-crystalline carbon-based compounds, and more.

Among the member of this family, this thesis deals with the group of non-crystalline carbon-based compounds which are synthesized in the form of thin films and are composed by carbon only or in combination with hydrogen and/or elements belonging to the p-block of the Periodic Table. Even though the values for the physical properties of each compound vary within the group, in general, they exhibit high hardness and elastic modulus, low friction coefficient, high wear resistance, and chemical inertness. Due to this, they are technologically relevant materials with a wide range of applications [21–23]. This group of compounds are usually referred to as carbon-based thin films and that is the terminology adopted in this thesis.

Since the main features of carbon-based thin films originate in the peculiarities of carbon chemistry, Section 2.1 provides an overview of carbon bonding features and a description of the main *ordered* carbon allotropes. Following this, the generalities of carbon-based thin films are discussed (Section 2.2) with an emphasis on fullerene-like carbon-based thin films (Section 2.3). Finally, an overview is given in Section 2.4 of the materials investigated in this thesis: sulfocarbide (CS_x), carbon fluoride (CF_x) and the ternary compound carbon sulfur fluoride (CS_xF_y), together with highlights of the results.

Figure 2.1. Carbon hybridization states: a) sp^3 , b) sp^2 , and c) sp .

2.1 Carbon and its ordered allotropes

Carbon provides the basis for life on Earth and, at the same time, it is the basic element in many technological applications. The reason for carbon's important roles is that it can be combined with itself and almost all other elements in a variety of ways.

According to valence bond theory, when a carbon atom¹ bonds to other atoms, its four valence electrons participate in one of three different hybridization states: sp^3 , sp^2 or sp . A carbon atom in sp^3 hybridization has its four valence electrons occupying four hybridized orbitals with directions pointing towards the vertices of a tetrahedron, as illustrated in Fig. 2.1 a). Each of these orbitals form strong directional covalent σ bonds with similar orbitals in neighboring atoms. Typical examples for sp^3 -hybridized carbon atoms are diamond and methane (CH_4).

In the sp^2 hybridization state, the carbon atom has its valence electrons distributed among three hybridized orbitals arranged in a trigonal fashion and a p orbital in the perpendicular direction (see Fig. 2.1 b)). While the sp^2 hybridized orbitals form σ bonds, the non-hybridized p orbital forms π bonds with other p orbitals in neighboring atoms, as is occurring in graphite or ethylene (C_2H_4).

As shown in Fig. 2.1 c), carbon atoms in sp hybridization have only two hybridized orbitals located along the x axis, and two p orbitals in the y and z orientation, respectively. Acetylene (C_2H_2) is an example of a compound with sp -hybridized carbon atoms.

Carbon allotropes

The first consequence of these three bonding options is that elemental carbon can exist in a variety of forms, with diamond and graphite topping the list of allotropes. *Diamond* [24] is an extended three-dimensional network of carbon atoms in sp^3 hybridization as illustrated in Fig. 2.2 a). The formation of strong σ bonds between each carbon atom and its four nearest neighbors results in a close-packed structure that makes diamond the material with highest known atom

¹Electron configuration of the carbon atom: $1s^2 2s^2 2p^2$.

Figure 2.2. a) Diamond's crystal structure (carbon atoms situated in the faces and corners of the cell are represented by filled dots, hollow dots represent carbon atoms inside the cell), b) a diamond stone, c) a graphite network, where the carbon atoms are represented by filled dots, and d) a graphite fragment. [Figures b) and d) are attributed to Rob Lavinsky, iRocks.com. The images are licensed under the Creative Commons Attribution-Share Alike 3.0 Unported.]

number density on Earth. As a consequence of this high density and the strong covalent bonds, diamond exhibits extreme properties such as the highest hardness and elastic modulus of any known material. It also has high thermal conductivity, low thermal expansion coefficient, and it is a wide band gap semiconductor with a band gap of 5.5 eV. Additionally, perfect diamond is transparent and colorless as seen in Fig. 2.2 b).

Graphite [25] on the other hand, is composed of sp^2 -hybridized carbon atoms arranged in parallel planar layers as depicted in Fig. 2.2 b). Each carbon atom is covalently bonded to three other carbon atoms by σ bonds in the plane of the layer forming a honeycomb network. The remaining p orbitals form an extended conjugated π system, which keep the parallel layers bound to each other through Van der Waals interactions. This structure leads to properties substantially different from those of diamond. The most evident difference appears in their optical properties: unlike diamond, graphite is opaque with colors that go from black to gray, as can be observed in Fig. 2.2 d). Even though graphite is stronger than diamond along the planes, the weak interaction between layers makes them easy to slide and separate and graphite is a soft material with low hardness. The anisotropy of the graphite structure defines its other properties as well, for example its conductivity. While electrons are relatively free to move along the planes in the delocalized π system, the conduction in the perpendicular direction is substantially lower.

Refined cleavage of graphite can lead to the separation of individual layers [26]. The two-dimensional form of carbon consisting of a single layer of graphite is called *graphene* (Fig. 2.3 a)). Graphene is one of the synthetic allotropes of carbon. Even though it has been theoretically studied since the 1940s, it was only in 2004 that it was experimentally observed [26]. This discovery earned K. Novoselov and A. Geim the Nobel Prize in physics in 2010. Graphene is of great scientific interest due to its electronic properties: a zero-gap semiconductor whose charge carriers can be described as massless Dirac fermions. By measuring graphene's electronic properties, quantum electrodynamic phenomena such as quantum hall effect can be probed [27]. Besides its unusual electronic properties, graphene shows extremely high stiffness together with elasticity and extremely high thermal

Figure 2.3. a) Graphene - “the mother of all the graphitic forms” [27], and its derivatives b) fullerenes, c) nanotubes and, d) graphite. [Adapted and reprinted with permission from Macmillan Publishers Ltd: Nature Materials, A. Geim *et al.*, Vol. 6(3) Pages No. 183-191, Copyright 2007.]

conductivity. This makes it suitable for many technological applications in the fields of nanoelectronics, transistors, supercapacitors, biosensors, drug delivery, and fuel cells, just to name a few. Since its experimental discovery, considerable research has been dedicated to graphene and many reviews on graphene, graphene-based materials and graphene functionalization can be found [27–31].

Other synthetic allotropes of carbon can be derived from graphene [27]. *Carbon nanotubes* [32] are rolled-up pieces of graphene sheets, as illustrated in Fig. 2.3 c). They can be prepared as single-wall or multi-wall nanotubes, where the latter consist of concentric single-wall nanotubes of increasing diameter. Due to their high aspect ratio they are considered one-dimensional (diameters are of a couple of nanometers while lengths can be up to a few millimeters). Extensive research dedicated to carbon nanotubes and their functionalization has lead to a great number of applications in fields such as electronics, health care and environmental science [4, 33–35].

Yet another example of the synthetic allotropes of carbon, particularly relevant to this thesis, are the *fullerenes*, which can be obtained by wrapping up pieces of graphene as in Fig. 2.3 b). These are large spherical, cylindrical or ellipsoid molecules formed by sp^2 -hybridized carbon atoms. Fullerenes can also exist as a few concentric spheres of increasing diameter, which are known as *nano-onions*. Due to their closed shape, they are considered the zero-dimensional form of carbon. The first fullerene discovered, by H. Kroto *et al.* in 1985, was C_{60} which has the form of a football, containing twenty hexagons and twelve pentagons. For this discovery, they were awarded the Nobel Prize in chemistry in 1996. Up to date,

different types of fullerenes have been discovered and considered for applications that can go from clean energy production to drug delivery [4, 34–36].

A large number of ordered carbon structures have been envisaged by combining carbon atoms in different hybridization states to form a large diversity of geometries [4, 35]. Some of them have been synthesized, while others have only been theoretically predicted. This vast range of natural and synthetic carbon allotropes is an indication of the variety of structural features that carbon and carbon-based materials can exhibit. This variety becomes even larger if one takes into account that for each ordered structure there exists a large number of analogous amorphous ones, including nanomaterials.

2.2 Carbon-based thin films

In non-crystalline carbon-based thin films, carbon atoms in the three different hybridization states coexist forming a disordered matrix. As amorphous materials², they exhibit short-range atomic order with a characteristic length of ~ 10 Å [37]. The particular attributes of these films are defined to a large extent by the relative content of sp^3 - and sp^2 -hybridized carbon atoms, with a negligible contribution of the sp hybridization state [37, 38]. Consequently, they possess a variety of properties ranging from those close to graphite to those similar to diamond.

To achieve certain control over their structural features, carbon-based thin films are frequently deposited by vapor phase deposition techniques with a thorough control of the growth environment [12, 38]. Some of the most commonly used deposition methods are ion beam, sputtering, cathodic arc and pulsed laser deposition. For these methods, the carbon sources, the presence of hydrogen during deposition, and the energy of the deposited species are determining factors for the structure and the properties of the films [37]. In addition, the incorporation of different p-elements, such as nitrogen [38–42], phosphorus [43–47], silicon [48, 49], sulfur [50–53], fluorine [54–58], and chlorine [59, 60], allows for further adjustment of the film's structure, expanding the range of possible properties and applications.

Given the large diversity of carbon-based thin films, they have been classified according to similarities in their structural features. For this purpose, phase diagrams for amorphous carbon, as the one shown in Fig. 2.4, are constructed using the content of sp^3 and sp^2 carbon atoms together with the hydrogen concentration in the film as independent parameters [37].

Among the different classes of amorphous carbon, *diamond-like carbon* (DLC) gets the majority of the attention due to the vast range of its technological applications³. DLC thin films are characterized by a relatively high content of sp^3 -hybridized carbon atoms (over 40 at.%) and hydrogen concentrations lower than 40 at.%. They are wide band gap semiconductors to insulators that usually exhibit high hardness and elastic modulus, low friction coefficients and high wear resistance [62, 63], chemical inertness, and optical transparency [37, 38, 64]. These

²See Chapter 1 – *Introduction*, Section 1.1 – *Order in materials*.

³The global market for diamond and diamond-like coatings has been estimated in USD to 1.7 billion for the year 2015 [61].

Figure 2.4. Phase diagram for amorphous carbon thin films [37]. [Reprinted from Materials Science and Engineering: R: Reports, Vol. 37, J. Robertson, “Diamond-like amorphous carbon”, Pages No. 129-281, Copyright (2002), with permission from Elsevier.]

properties are directly related to the fraction of sp^3 carbon atoms and the hydrogen content in the film [12, 37, 38].

The outstanding tuneable physical properties that can be achieved in DLC thin films, together with a relatively low cost of production, makes them suitable for many technological applications. Some examples are:

- DLC films are excellent wear resistant coating materials. Due to this, they are widely used in the automotive sector where low friction and wear resistant surfaces are needed, e.g., piston top rings (see Fig. 2.5 a)) [21, 22].
- DLC films are also used in the edge of razor blades, where they are deposited on the steel blade with the objective of keeping it sharp (see Fig. 2.5 b)) [22, 64, 65].
- Due to the high density that can be achieved with featureless DLC films, they are used as protective coatings against corrosion and wear on magnetic storage disks and their read heads (see Fig. 2.5 c)) [21, 22, 66].
- High density and optical transparency are the reason for the use of hydrogenated DLC thin films in polyethylene terephthalate (PET) bottles containing beer to prevent carbon dioxide loss [22, 66] (see Fig. 2.5 d)).
- DLC thin films are also potential materials for biomedical applications thanks to their mechanical properties and chemical inertness. This can be useful in orthopedics, DLC coated stents and implants in oral cavities, among others [67, 68].

Figure 2.5. Examples of applications of DLC thin films: a) piston top ring with DLC coating [69], b) transmission electron microscopy image of a diamond-like carbon coated razor blade [22], c) schematic of a hard disk indicating the carbon coatings [66], and d) PET bottle with hydrogenated DLC coating on the inside wall to minimize the permeation of CO₂, O₂, and H₂O [66]. [Figure b): reprinted from *physica status solidi (a) applications and materials science*, Vol. 205, J. Robertson, “Comparison of diamond-like carbon to diamond for applications”, Pages No. 2233-2244, Copyright (2008), with permission from John Wiley and Sons. Figures c) and d): adapted and reprinted from *Materials Today*, Vol. 10, C. Casiraghi *et al.*, “Diamond-like carbon for data and beer storage”, Pages No. 44-53, Copyright (2007), with permission from Elsevier.]

2.3 Fullerene-like carbon-based thin films

Fullerene-like carbon-based thin films [40,70,71] are a lesser known category within the carbon-based materials. In contrast to DLC, the fullerene-like compounds are characterized by a higher content of sp^2 -hybridized carbon atoms than sp^3 . While being hydrogen-free, they are usually deposited as compound films combining carbon with other p-elements of the Periodic Table, e.g., nitrogen [40,70,71] or phosphorus [45], but they have also been deposited as pure carbon thin films [71–73]. Moreover, these films are inherently nanostructured and they show short-range order with a characteristic length of a few nanometers, considerably larger than the usual ~ 10 Å expected for most of the carbon-based thin films.

Structurally, fullerene-like compounds can be described as an assembly of nano-clusters composed by parallel curved graphene fragments packed in different orientations [70,71]. This type of structure is shown in Fig. 2.6, which is a plan-view high resolution transmission electron microscope image of a fullerene-like carbon nitride (FL-CN_x) thin film. The formation of spherical nanostructures (or *dome-shaped* features) that intersect each other resembles an array of nano-onion fragments as the model depicted in Fig. 2.7. Cross-sectional images of this type of films usually look like *finger-prints* as shown in Fig. 2.8 [74].

Even though a high concentration of carbon atoms in sp^2 hybridization had previously been associated with soft films, e.g., glassy carbon [37,38], the fullerene-like compounds show hardness values comparable to those of DLC thin films. This is accompanied by a extremely high elastic recovery [40]. The reason is that regardless of the fact that most of the carbon atoms are incorporated into the sp^2 hybridized graphene-like sheets, the curvature and cross-linking of the graphene fragments combined with the exceptional in-plane strength provided by the directional σ bonds extend the extraordinary strength of the sp^2 network in three dimensions [70,75,76].

Figure 2.6. Plan-view high resolution transmission electron microscope image of a FL-CN_x (CN_{0.12}) thin film at a fracture edge. The observed microstructure resembles an array of intersecting nano-onions [74]. [Reprinted with permission from Applied Physics Letters, Vol. 79, Zs. Czigány *et al.*, Pages No. 2639-2641. Copyright 2001, AIP Publishing LLC.]

Figure 2.7. Model for the formation of dome-shaped features in fullerene-like carbon-based compounds. Potential cross-linkage sites are indicated by dots at the intersections of the curved lines [40, 74].

Figure 2.8. Cross-sectional high resolution transmission electron microscope image of a FL- CN_x ($\text{CN}_{0.12}$) thin film representing the typical microstructure for fullerene-like CN_x thin films [74]. [Reprinted with permission from Applied Physics Letters, Vol. 79, Zs. Czigány *et al.*, Pages No. 2639-2641. Copyright 2001, AIP Publishing LLC.]

A bit of history

The first fullerene-like carbon-based compound was discovered by Sjöström *et al.* in 1995 at Linköping University when they were depositing carbon nitride thin films by reactive magnetron sputtering in the pursuit of the elusive but theoretically predicted super-hard crystalline phase $\beta\text{-C}_3\text{N}_4$ [77, 78]. The resulting carbon nitride thin films (CN_x , $0 < x < 0.3$) did not turn out to be $\beta\text{-C}_3\text{N}_4$, but they showed an unusual combination of high hardness and high elastic recovery [70, 79]. The high elasticity and the low tendency to plastic deformation of these films indicated a resilient nature that was described as “superhard rubber” [40].

The curvature in the graphene planes is attributed to the incorporation of rings different from hexagons, such as pentagons, in an hexagonal network, i.e., *ring defects* [70]. Theoretical calculations using the semi-empirical Hartree-Fock-

based AM1 method [80], whose results were later confirmed by density functional theory calculations [81, 82], showed that the presence of nitrogen atoms in the graphene network reduces the energy cost for creating a pentagon defect [70]. It was also shown experimentally and theoretically that the degree of curvature in CN_x thin films depends on the nitrogen content [40, 44, 76, 79, 83].

X-ray photoelectron spectroscopy of these CN_x thin films showed the presence of sp^3 carbon atoms bonded to nitrogen atoms [70, 76]. At the same time, theoretical calculations showed that the incorporation of nitrogen in a graphene network increases the reactivity of the surrounding carbon atoms and it can induce a change in hybridization from sp^2 to sp^3 [70, 81]. These results point to the possible existence in CN_x of graphene planes interlocked by covalent bonds, which prevents the sheets from gliding between each other with inter-sheet distances shorter than in graphite [70, 76, 81].

Experimental and theoretical results indicated that the incorporation of ring-defects and the formation of cross-linkage sites is facilitated by the nitrogen atoms incorporated in the sp^2 network [40, 70, 74, 75]. Therefore, the remarkable mechanical properties of the FL- CN_x thin films are to a great extent a consequence of nitrogen incorporation in the carbon matrix, which can be optimized and controlled using different deposition techniques and by adjusting the deposition parameters [57, 75, 76, 84].

Another option for tuning the structural features and mechanical properties of this kind of thin films is changing nitrogen for other elements belonging to the p-block of the periodic table. In this context, phosphorus was chosen by Furlan *et al.* to achieve fullerene-like phosphorus-carbide (FL- CP_x) [85]. Phosphorus' larger atomic radius, low electronegativity, and tendency to tetrahedral coordination brings bonding characteristics different from nitrogen. It was anticipated that the CP_x thin films would show a larger density of cross-linkage than CN_x and a larger deformation of the graphene-planes, leading to even higher values of hardness.

The CP_x compound was first theoretically addressed by the synthetic growth concept⁴. The main results showed that besides pentagons, tetragon rings are also feasible resulting in strongly bent graphene planes [86]. Moreover, phosphorus atoms promote the formation of cross-linking sites between parallel graphene sheets and inter-linking between intersecting ones [44]. Finally, it was prescribed how FL- CP_x thin films could be synthesized by magnetron sputtering for phosphorus concentrations between 5 at.% and 15 at.% [44].

The theoretical findings were later confirmed experimentally when CP_x thin films were successfully deposited by magnetron sputtering [45, 47]. Films with phosphorus concentration of 10 at.% deposited at a substrate temperature of 300°C exhibited fullerene-like structural characteristics less pronounced than in FL- CN_x , with similar elastic recovery but a higher hardness. Increasing the phosphorus concentration leads to a structural transition towards amorphization [47].

⁴Refer to Chapter 3 – *Synthetic growth concept* for a description of the method.

2.4 Introducing sulfur and fluorine

The extensive research dedicated to FL-CN_x and FL-CP_x made it clear that the incorporation of atoms of p-elements constitutes a key approach to manipulate the nanostructure and properties of fullerene-like carbon-based thin films. Enlarging this class of materials by considering new elements to be incorporated in the carbon matrix provides the opportunity to obtain thin films with enhanced mechanical properties, i.e., higher hardness and higher elastic recovery, as well as a combination of different optical, electrical and thermal properties. Furthermore, this approach can be used to tune the chemical nature of the thin film's surface, affecting, for example, its surface energy, which is relevant for many applications of thin films.

The original idea for this thesis was the consideration of sulfur and fluorine as candidates to combine with carbon in order to obtain new fullerene-like compounds. This demanded the understanding, from a theoretical point of view, of how sulfur and fluorine interact with carbon, what structural and bonding features to expect, and how this knowledge can be translated to direct experimental efforts for synthesizing them.

Sulfocarbide, CS_x

Even though sulfur incorporation in porous carbon for energy and environmental applications has been attracting growing attention during the last years [87–89], the incorporation of sulfur in carbon-based thin films remains largely unexplored. Only a few reports can be found on sulfur-containing DLC or amorphous carbon thin films. In some of them, sulfur was incorporated during deposition [50, 51, 90–92], while in others, the sulfur was incorporated into the amorphous carbon matrix after deposition using sulfur powder and heat treatments [53, 93–95] or ion implantation [52]. The only conclusion that all these works have in common is that the presence of sulfur affects the size or number of sp² clusters in the films, but depending on the deposition method, this quantity is directly or inversely related to the sulfur concentration in the film. Besides, there was little information on the final concentration of sulfur in such films or on the structural role played by the sulfur atoms.

Nevertheless, the effects of sulfur incorporation on the physical properties of amorphous carbon, as well as on other carbon systems, makes this element a promising candidate in the quest for new carbon-based materials with unique properties. Some of the exciting properties found in sulfur/carbon systems are: i) sulfur constitutes an n-type dopant in diamond [96, 97] and DLC [50] thin films, improving their optoelectronic properties; and ii) sulfur-doped graphite [98], and amorphous carbon thin films [53, 93–95] have shown indications of superconductivity at approximately 35 K.

Regarding the effects of sulfur on the carbon nanostructures, both experimental and theoretical studies have shown that when a sulfur atom is incorporated in an sp² carbon network, e.g., graphene or nanotubes, the corresponding planar or cylindrical shape is perturbed and local deviation from the pristine network

surrounding the sulfur site occurs [99,100]. It was also observed that the incorporation of sulfur atoms favors the formation of pentagons and heptagons, thus enhancing the curvature of the network [101]. Comparing these results with the structural effects of nitrogen and phosphorus in FL-CN_x and FL-CP_x, respectively, it is clear that sulfur has the potential to induce the formation of FL-CS_x.

For these reasons, I explored the feasibility of FL-CS_x from a theoretical point of view using the synthetic growth concept. The complete set of results have been published in scientific journals [102,103] and are appended to the thesis as **Paper I** and **Paper II**. Highlights of these results include:

- sulfur atoms can take the place of carbon atoms in graphene-like networks inducing smooth local curvature and ring-defects;
- FL-CS_x is expected at sulfur concentrations between 10 and 15 at.%;
- the structural features and the related mechanical properties of FL-CS_x occupy an intermediate position between FL-CN_x and FL-CP_x;
- the main structural features that make FL-CS_x unique are parallel graphene-like sheets with a reduced impact of cross-linking as well as cage-like systems without tetragons.

These modeling results are being tested by reactive magnetron sputtering deposition of CS_x thin films using a graphite target and carbon disulfide (CS₂) as reactive gas and their subsequent characterization currently taking place in our lab.

Carbon fluoride, CF_x

Fluorine incorporation in a carbon matrix is a clearly different case from nitrogen, phosphorus, and sulfur. Due to their electronic configuration, fluorine atoms can form only one single bond. Moreover, fluorine is the most electronegative element and has low polarizability. These substantial differences from carbon have considerable effects on the structural features and properties of CF_x compounds [54].

Fluorinated carbon-based thin films⁵ have been largely studied in the last fifteen years due to their low dielectric constant and low refractive index [104–106], moderate hardness [55, 56, 107], low surface energy, high wear resistance and low friction coefficient [107, 108], chemical inertness, and biocompatibility [55]. These films have been synthesized by different vapor phase deposition methods with resulting structures of amorphous nature (e.g., DLC and polymer-like) [54–57, 104–107, 109–111]. Another line of research dedicated to CF_x compounds is related to the substantial interest in Teflon[®]-like materials with improved thermal resistance [112, 113].

Despite the extensive research surrounding CF_x thin films, the prospects of obtaining FL-CF_x was not evaluated before the work described below. In this thesis, I considered the carbon/fluorine system following the principles of the synthetic growth concept. All the modeling results have been published in scientific

⁵See reference [58] for an updated review on fluorinated carbon-based thin films.

journals [56, 114–116], and are appended to the thesis as **Paper III**, **Paper IV**, **Paper V**, and **Paper VI**. Highlights of these results are:

- the ring defects typical for most of the other fullerene-like compounds (i.e., tetragons, pentagons and heptagons) are not feasible in CF_x ;
- instead, the incorporation of fluorine in graphene-like networks results in the formation of large rings of eight to twelve members and network disruptions by branching mechanisms;
- CF_x compounds are characterized by a variety of structures depending on the fluorine concentration, with a tendency to become more disordered as fluorine concentration increases;
- CF_x compounds with fullerene-like characteristics could be achieved for fluorine concentrations up to 10 at.%

In **Paper IV** and **Paper V** the modeling outcome was combined with results obtained from synthesis and characterization of CF_x thin films. The main conclusions are: i) the predicted structural trends of DLC and polymer-like features for fluorine concentrations over 15 at.% were confirmed, and ii) the modeling of precursor species together with the analysis of the bonding properties of the films and the characterization of the plasma resulted in a deeper understanding of the deposition process.

For a few years, the prediction of FL- CF_x for low fluorine concentration was longing for experimental results to confirm it. Fortunately, recent results from S. Schmidt *et al.* on synthesis and characterization of CF_x thin films grown by reactive high power impulse magnetron sputtering have shown that it is possible to obtain CF_x with short-range order characteristics. A summary of the experimental details and a discussion of the preliminary results are included in Appendix A.

Carbon sulfur fluoride, CS_xF_y

With the knowledge acquired about the binary compounds CS_x and CF_x and the opportunity to deposit thin films using an in-house built magnetron deposition system from a graphite target and sulfur hexafluoride (SF_6) as reactive gas, the CS_xF_y compound was next to be addressed. The corresponding modeling results are described in the manuscript appended to the thesis as **Paper VII**. The highlights are:

- the structural behavior of CS_xF_y can be explained in terms of the structural characteristics of the CS_x and CF_x binaries;
- for low sulfur and fluorine concentrations ($[\text{S} + \text{F}] = 10$ at.%), the structural distortions produced by sulfur and fluorine atoms in the hexagonal network appear independently of each other and the resulting structure is a superposition of the structural characteristics of CS_x and CF_x ;

- for higher concentrations, sulfur and fluorine structural distortions interact enhancing each other and resulting in increasingly disordered structures;
- fullerene-like features are expected for combined sulfur and fluorine concentrations below 10 at.%;
- the structural trends described above are supported by initial experimental results on synthesis and characterization of CS_xF_y thin films and are included in **Paper VII**.

Chapter 3

Synthetic growth concept

The synthetic growth concept (SGC) is a methodological approach developed by G. K. Gueorguiev *et al.* to study and model inherently nanostructured materials synthesized by vapor phase deposition processes. As explained in Chapter 1 – *Introduction*, this type of materials do not show periodic order as in crystalline solids. Instead, repetitive structural patterns with short range order can be identified within the material. Such ordered nano-sized structural formations may be seen as clusters of atoms, i.e., *nano-clusters*, which can be bound together or embedded in an amorphous matrix.

To model an amorphous nanostructured material, one must avoid the immense task of describing the entire solid atom by atom. Instead, the material can be treated as an assembly of the nano-clusters mentioned above, which may be studied individually as well as interacting with each other. For example, the structure of fullerene-like carbon-based compounds can be seen as stacks of graphene pieces containing defects¹.

With this idea as departure point, the objectives of the SGC are to understand the structural features of the material of interest and to link this structure to the process of its synthesis. This is necessary in order to understand how the structure and synthesis conditions determine the material's properties.

This chapter is dedicated to explaining the steps taken in the SGC modeling approach through its application to fullerene-like carbon-based thin films. Other examples are the exploration of silicon-transition metal cage-like molecules (MSi_{12} [117, 118]) as building blocks for cluster-assembled materials [119, 120] and the study of properties and gas phase chemistry during growth of III-nitrides [121–123].

¹See Chapter 2 – *Carbon-based compounds*, Section 2.3 – *Fullerene-like carbon-based thin films* for an extended description.

Figure 3.1. Diagram of the SGC scheme.

3.1 Overview of the method

The SGC establishes a modeling scheme for nanomaterials obtained by vapor phase deposition. Such scheme, illustrated in Fig. 3.1, consists in three main steps: i) identification of nanoclusters, ii) construction of model systems, and iii) simulation of the material’s structure formation (e.g., film growth simulation). This section provides a general description of each step, while in the next section the details of the application of the SGC to fullerene-like carbon-based materials is discussed together with the particular example of CS_x .

STEP 1 - Identification of nano-clusters

The first step is to find any identifiable characteristic nanocluster that compose the material by studying the experimental information about it or by considering theoretical and experimental results available for similar and better-known materials. In fact, this step provides a qualitative description of the nanoclusters that allows for making best guesses about their structural features.

STEP 2 - Construction of model systems

The second step consists in generating a number of model systems (or templates) based on the structural description of the nanoclusters from the previous step. These model systems are a first approximation to the real nanoclusters as featured in the compound. For example, regarding graphite clusters, one can study a graphene piece or a graphene bilayer as a first approximation. These generated model systems must be submitted to geometry optimization², in order to find realistic and stable structures that are then used to understand the structural features of the material at larger scale.

STEP 3 - Simulation of the material’s structure formation

Finally, the SGC models the chemical or physical processes taking place during vapor phase deposition with the aim of understanding it at the atomic level and finding properties characteristic of the material’s structure formation. In this type of deposition, solid, liquid or gas sources of the elements that compose the

² *Geometry optimization* is the process of finding the atomic arrangement of minimum energy.

Figure 3.2. Schematic representation of vapor phase deposition.

material are introduced in a chamber. During the deposition process, precursor species (atoms, molecules, radicals and/or clusters of atoms) enter, or are formed, in the gas phase. The growth of the material occurs by subsequent deposition of these precursor species (or building blocks) onto a substrate. Fig. 3.2 shows a schematic representation of this process³.

Depending on the material of interest and the corresponding deposition technique, STEP 3 can take different forms [44, 102, 103, 119, 121, 123]. In the case of thin films deposited by physical vapor deposition, as those ones relevant to this thesis, the structure formation of the material is addressed by directly simulating the film growth as it is explained below.

The general procedure for the film growth simulation is as follows: first, the precursor species which are relevant to the material and the deposition method are predicted; then, the possible interactions between them as well as with the growing material are studied by means of an iterative process in which precursor species are sequentially attached to a model system.

The precursor species present in the gas phase may be different types of chemical entities such as isomers of molecules, radicals, and small atomic clusters with different composition. The initial selection of viable precursors for a given compound and its corresponding deposition process is constrained to known molecules and radicals together with experimental data about precursor species availability in related deposition processes for similar materials. The precursor species initially selected are then submitted to geometry optimization to obtain the corresponding stable structures. Following this, a set of possible precursor species is chosen based on their relative stability. This set contains the building blocks for the film formation simulation.

To simulate the growth process of the film, the SGC follows an iterative procedure as illustrated in Fig. 3.3. The starting point is any of the model systems optimized in STEP 2 (i.e., the initial model system in Fig. 3.3). Then, a precursor species is randomly chosen from the previously established set and placed in the

³A more detailed description of the deposition techniques used for the thin films considered in this thesis can be found in Chapter 5 – *Overview of experimental techniques*.

vicinity of the template⁴. To obtain an energetically and structurally stable system, the template/precursor group is submitted to geometry optimization. Since the initial position and orientation of the precursor species with respect to the model system affect the final result, a series of different starting configurations should be considered. This results in a number of relaxed structures (i.e., final configurations in Fig. 3.3) from which the one that presents the optimal bonding location, most favorable energetics, or a configuration of particular interest is chosen to continue the growth simulation. Then, the chosen relaxed system becomes a new starting point.

Repetition of this procedure results in a sequence of N precursor species⁵ attaching to a growing model system. The number of times the procedure is repeated can go from only a few to a few dozens, depending on the scale of growth events one is interested in. It is important to emphasize that in order to obtain reliable information independent of the simulation procedure, many different starting points and precursor sequences, i.e., many different chains of growth events, should be simulated.

This iterative procedure results in the formation of structural features or patterns in the growing model systems (e.g., sheets, cages, and cross-linkages). Moreover, conclusions can be drawn about changes in the hybridization of atoms during growth, bonding characteristics between the same and different atomic species, and cases of segregation, to name just a few.

It should be noted that in this particular approach the role of the substrate, which is an unavoidable component of the film growth, is not studied. Instead, the interest is set on the steady state growth of the film, where the precursor species are being deposited on the surface of an already developed material.

⁴Placing a precursor species in the vicinity of a template implies that they should be close enough to be involved in an effective interaction between them during geometry optimization.

⁵The sequence of precursor species can be generated beforehand or as the growth simulation progresses by randomly choosing a precursor species before each iteration cycle.

Figure 3.3. SGC iterative process for synthetic film growth simulation.

3.2 Application to fullerene-like carbon-based materials

The purpose of this section is to explain the application of the SGC to the class of the fullerene-like carbon-based materials (FL-CA_x)⁶. To illustrate this, the concrete example of applying the SGC to FL-CS_x is provided here. The details given in this section are excerpts of **Papers I** and **II**, where the complete description of the results regarding the CS_x compound can be found.

STEP 1 - Identification of nanoclusters

According to the structural description of fullerene-like carbon-based materials given before⁷, the nanoclusters usually identified in these compounds are regions of short-range order formed by parallel stacks of curved graphene-like pieces in which both carbon atoms and atoms of the element *A* participate. The curvature in the graphene planes has been attributed to the presence of ring defects in the network, i.e., some rings are not hexagons. This, in turn, is attributed to the bonding diversity that the element *A* brings to the system [70, 82, 86].

STEP 2 - Construction of model systems

For a generic FL-CA_x compound, the model systems are generated from pieces of graphene-like networks, as those shown in Fig. 3.4. They are designated as *graphene-like* because they are two-dimensional (if curvature is not taken into account) and the atoms are mostly arranged in the vertices of a honeycomb network. These model systems are chosen in different sizes and containing different ring defects. A range of concentrations of the element *A* are simulated by substituting some of the carbon atoms in the model systems from Fig. 3.4 with *A* atoms.

The CA_x model systems are then submitted to geometry optimization⁸. The relaxed CA_x structures provide information on the stability of the different types of defects in carbon networks with different heteroatom concentrations. The relative stability of the relaxed model systems can be assessed by calculating their cohesive energy per atom, $E_{coh/at}$. $E_{coh/at}$ is defined as the energy required to break the system into isolated atoms normalized by the number of carbon and *A* atoms according to the equation:

$$E_{coh/at} = \left| \frac{E_{\text{system}} - n_H \times E_H - n_C \times E_C - n_A \times E_A}{n_C + n_A} \right|. \quad (3.1)$$

In Eq. 3.1, E_{system} is the total energy of the model system, n_H , n_C , and n_A are the number of hydrogen, carbon, and *A* atoms, and E_H , E_C , and E_A are the

⁶FL-CA_x is a fullerene-like compound whose chemical composition is carbon and another element *A* belonging to the p-block of the Periodic Table. In this thesis, atoms of the chemical species *A* are referred to as heteroatoms.

⁷See Section 2.3 – *Fullerene-like carbon-based thin films*, Chapter 2 – *Carbon-based compounds*.

⁸All the geometry optimizations performed in this thesis are based on density functional theory which is presented in Chapter 4 – *Density functional theory*.

Figure 3.4. Typical graphene-like model systems used in SGC: a), and b) pure hexagonal networks; c), and d) networks containing a single pentagon defect; e) a network containing a double pentagon defect; f) a network containing a Stone-Wales defect; and g) a network containing a tetragon defect.

energies of the corresponding free atoms in their ground states, respectively.

It is well known that the creation of a ring defect in graphene is energetically unfavorable. However, as it was proven for CN_x [82] ($A \equiv N$), the presence of an heteroatom in the ring defect or at a neighboring position can reduce the energy cost for the defect. The incorporation of a defect associated to an A atom can be conceived as a series of structural changes in the following way:

where Hex^C represents a pure carbon graphene network, Hex^A is a graphene network with one carbon atom substituted by an heteroatom A , and Def^A represents the CA_x model system with a non-hexagonal ring defect.

The energy cost (ΔE_T) for introducing a ring defect containing an A atom in an hexagonal pure carbon network is the total change in energy for the structural sequence in Eq. 3.2, which can be calculated using the $E_{coh/at}$ for the first and last model system in Eq. 3.2. The feasibility of the different defects can be compared by considering their ΔE_T value.

Example of application: FL-CS_x

In **Paper I**, I studied the substitution of one carbon atom by a sulfur atom in the model systems showed in Fig. 3.4, taking into account every possible substitution position. After geometry optimization, the relaxed model systems showed that all the tested defects (single and double pentagon, Stone-Wales defect and tetragon) as well as pure hexagonal networks are stable when sulfur is incorporated. Nevertheless, the sulfur atoms do not remain in the original carbon atoms' place. Instead, they stick out of the plane and induce local curvature in the system or enhance the previously existing one (e.g., the model systems containing single pentagons). Fig. 3.5 shows some of the relaxed CS_x model systems in which the substituted carbon atom is in one of the internal positions (i.e., not at the model system's periphery).

The feasibility of the different defects was compared by considering the energy cost (ΔE_T) for the incorporation of a ring defect associated with a sulfur atom in an hexagonal pure carbon network as explained above (Eq. 3.2). Tab. 3.1 shows the ΔE_T values obtained for the formation of the defects in Fig. 3.5. These results show that the most feasible defect (lowest energy cost) is the single pentagon, followed closely by the Stone-Wales defect. The double pentagon and the tetragon are not as likely and should play a less important role in the structural formation of FL-CS_x.

In conclusion, I found that sulfur atoms can be readily incorporated in hexagonal carbon networks, where they promote defect formation and local curvature without producing disruptions. This constituted the first indication of the feasibility of synthesizing FL-CS_x.

Following these results, in **Paper II**, I studied the structure and stability of different carbon networks for a range of sulfur concentrations (0–30 at.%). I used different patterns of sulfur substitution on a pure hexagonal network and two networks containing a single pentagon and a Stone-Wales defect^a. The model systems used are those presented in Fig. 3.4 b), d), and f), respectively.

Fig. 3.6 shows the $E_{coh/at}$ as a function of sulfur concentration for all the model systems studied. It can be seen that sulfur-containing hexagonal networks are energetically more favorable than the networks containing defects up to a sulfur concentration of 10 at.%. Above this concentration, all the systems have similar energies, meaning that they become equally feasible.

^aThe choice of defects for this follow up study - the single pentagon and the Stone-Wales defect - is based on the fact that, in **Paper I**, they were found to be the most feasible ones.

Figure 3.5. Front and side views of model systems after relaxation containing: a) a single pentagon; b) a double pentagon; c) a Stone-Wales defect; d) a tetragon; and f) a pure hexagonal network model system [102].

Defect	ΔE_T (eV/at)
Single pentagon	0.53
Stone-Wales defect	0.55
Double pentagon	0.64
Tetragon	0.82
Hexagonal	0.38

Table 3.1. Energy cost ΔE_T for incorporation of a sulfur-containing ring defect in a pure carbon hexagonal graphene-like sheet (Fig. 3.4 b)) for the CS_x model systems shown in Fig. 3.5 [102]. The results were obtained using the PW91 exchange and correlation functional [124], as implemented in Gaussian [125].

Figure 3.6. a) $E_{coh/at}$ as a function of sulfur concentration for three different substitution patterns (Hex1, Hex2, and Hex3) in a pure hexagonal network, b) $E_{coh/at}$ differences between the pentagon-containing network and Hex1 for three different substitution patterns (Pent1, Pent2, and Pent3), and c) $E_{coh/at}$ differences between the Stone-Wales defect-containing network and Hex1 for three different substitution patterns (SW1, SW2, and SW3) [103]. [Reprinted with permission from The Journal of Physical Chemistry C, Vol. 116, C. Goyenola *et al.*, “Structural patterns arising during synthetic growth of fullerene-like sulfocarbide”, Pages No. 21124-21131, Copyright 2012 American Chemical Society.]

Example of application: FL-CS_x - continuation

Fig. 3.7 shows some representative conformations obtained for different sulfur concentrations. When the concentration is below 10 at.%, the graphene-like planes show smooth bending without disruptions. For higher sulfur concentration, the curvature quickly increases along with the defect concentration, resulting in increasingly large network disruptions. There is a maximum sulfur concentration that a graphene-like network can accommodate without fully disrupting its structure and that maximum concentration is between 15 and 20 at.%.

The main conclusion from STEP 2 is that to obtain a well-structured FL-CS_x the sulfur content should be above 10 at.%, but definitely below 20 at.%. The resulting structures should combine bent graphene-like sheets containing an average concentration of defects with cross- and inter-linking sites. FL-CS_x thin films are expected to show valuable mechanical strength, boosted by sufficient intermixing of the sp³ bonding within the predominating sp² network [103].

Figure 3.7. Conformation of graphene-like model systems at different sulfur concentration (top and side views): (a) smooth bending at lower sulfur concentration (10 at.%), (b) heavy bending (17 at.%), and (c) and (d) partially disrupted graphene-like sheets (24 and 26 at.% of sulfur, respectively) [103]. [Reprinted with permission from The Journal of Physical Chemistry C, Vol. 116, C. Goyenola, *et al.*, “Structural patterns arising during synthetic growth of fullerene-like sulfocarbide”, Pages No. 21124-21131, Copyright 2012 American Chemical Society.

STEP 3 - Film growth simulation

As explained above, the final step is the simulation of the film growth. In the general case of a FL-CA_x material, the set of precursor species usually contains C_mA_n (m, n ≤ 4) species, while the initial model systems are chosen from the CA_x templates obtained in the previous step.

Example of application: FL-CS_x - continuation

The deposition process *imagined* for CS_x was magnetron sputtering using graphite and elemental sulfur (cyclo-octasulfur, S₈) as a combined solid target^{a, b}. Based on this choice, in **Paper I**, I considered a variety of structural isomers of precursor species C_mS_n (m, n ≤ 4). The choices were made taking into account the chemistry of sulfur and carbon interaction [126] and the experience previously obtained from CN_x [127, 128] and CP_x [45, 86] deposition processes. After relaxation and taking into account their relative stability (comparing $E_{coh/at}$, Eq. 3.1), the precursor species that were found of relevance for film growth are: C₂, CS, S₂, C₂S, CS₂, C₂S₂, S₃, and S₄. Their stable geometries are shown in Fig. 3.8.

To simulate the film growth, randomly selected precursor species C_mS_n were placed in the vicinity of the CS_x model systems from STEP 2 and submitted to relaxation. By this approach, I could identify the structural patterns that arise during growth as well as repeatedly occurring phenomena. The most important aspects of CS_x growth evolution are published in **Paper II** and selected cases are covered below.

I found that precursor species tend to bond to carbon atoms that are bonded to at least one sulfur atom in the network. It may be explained by the fact that sulfur atoms bring extra electrons to the network which are shared with the neighboring carbon atoms. These remain with an excess of negative charge that is prone to be shared with the incoming precursor species.

During the initial steps of growth evolution, the formation of cross-linkage sites are observed, but in many cases they are re-adsorbed (or assimilated) into the growing film after additional precursor species are attached. This phenomenon is visualized in Fig. 3.9. Consequently, it is expected that the cross-linkages sites that may form in CS_x act as seeds for the growth of other graphene-like planes intersecting the original one, but have a minor role in linking parallel ones.

^aThe deposition process was first *imagined* because at that time there were no reported experiments on CS_x thin film deposition and based on the experience with CP_x, a magnetron sputtering process from a solid mixed carbon/sulfur target presented a good alternative.

^bDetails on the magnetron sputtering deposition process can be found in Chapter 5 – *Overview of experimental techniques*.

Figure 3.8. Optimized structures for the C_mS_n precursor species most relevant to CS_x film deposition [102].

Figure 3.9. Chain of bonding events leading to the formation of a cross-linkage site and its subsequent assimilation into the growing planar network: a) the model system at the starting point of cross-linking formation, b) a cross-linking resulting from incorporation of a series of precursors $\{C_2S, CS \text{ and } C_2S\}$ and c) the assimilation of the cross-linking to the planar sheet after two additional precursors $\{C_2S_2 \text{ and } C_2S_2\}$ are incorporated [103]. [Reprinted with permission from The Journal of Physical Chemistry C, Vol. 116, C. Goyenola *et al.*, “Structural patterns arising during synthetic growth of fullerene-like sulfocarbide”, Pages No. 21124-21131, Copyright 2012 American Chemical Society.]

Figure 3.10. Structural patterns arising during large scale growth evolution of CS_x : (a) parallel growing planar graphene-like sheets; (b) intersecting planar graphene-like sheets; (c) a cage-like structure indicated by the shadowed area. In the insets, different views of the same systems are shown [103]. [Reprinted with permission from The Journal of Physical Chemistry C, Vol. 116, C. Goyenola *et al.*, “Structural patterns arising during synthetic growth of fullerene-like sulfocarbide”, Pages No. 21124-21131, Copyright 2012 American Chemical Society.]

Example of application: FL-CS_x - continuation

Finally, when a large number of precursor species have been attached (accounting for 30-50 atoms), two types of conformations frequently appear:

- quasi-planar graphene-like sheets, which can be parallel or intersecting as illustrated in Fig. 3.10 a) and b), respectively. These sheets are mainly graphene-like fragments containing a moderate number of pentagons, thus, they are not flat.
- cage-like conformations (represented in Fig. 3.10 c)). These networks include considerably more pentagons and heptagons than the previous category. They may also include tetragons. The incorporation of such quantity of defects in the graphene-like sheets leads to enough bending to close the sheet into itself.

The conclusion of this part of my study is that the structural features observed in the CS_x model systems and in the growth evolution simulation indicate that the FL-CS_x compound may be synthesized for moderate sulfur concentrations (10-15 at.%) and it would structurally be in an intermediate point between FL-CN_x and FL-CP_x.

Besides this detailed example of application of the SGC to the FL-CS_x compound, a few other concrete examples related to the papers included here can be cited:

- in **Paper V**, the theoretical study was focused on the first part of STEP 3 (Fig. 3.1): analysis of precursor species and their possible interactions. We used the corresponding results to understand the reasons why CF_x thin films deposited by reactive HiPIMS⁹ under the same conditions but using different reactive gases (i.e., CF₄ and C₄F₈) yield different structural features and properties;
- in **Paper VI**, the study was focused on STEP 2 (Fig. 3.1) to probe the stability and structural evolution of CF_x graphene-like model systems under different fluorine concentrations. With this, I obtained a relationship between the structural features and the fluorine concentration that can be used as a guideline for synthesis of CF_x films; and
- in **Paper VII**, the focus was also on STEP 2, but in this case the objective was to study the feasibility of the compound CS_xF_y. My results showed that a clear relationship regarding structural features can be established between the ternary CS_xF_y, and its binary predecessors CS_x and CF_x.

⁹See Section 5.1 – *Thin film deposition*, Chapter 5 – *Overview of experimental techniques*.

The examples cited above illustrate how the application of the SGC provides a systematic study of the physical mechanisms behind defect incorporation and structural pattern formation in an inherently nanostructured material.

Density functional theory

The application of the SGC described in the previous chapter requires geometry optimizations and energy calculations for different finite model systems. In this thesis, the method of choice for these calculations is density functional theory (DFT).

DFT is a widely used electronic structure method for calculating properties of matter. This chapter gives an overview of the machinery behind DFT following the formulation given in reference [129]. For a more thorough description of the method, a wide selection of literature exists, e.g., [20, 129–131].

4.1 Theoretical background

To construct the theory of DFT and its application scheme, one should start by looking at basic quantum mechanics. All issues related to the electronic structure of matter can be included in the time-dependent Schrödinger equation. Often, as in the case of this thesis, one is not interested in any time dependent property and the problem can be reduced to the time-independent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (4.1)$$

where $\hat{H}$ is the Hamiltonian of the system, E is the total energy and $\Psi(\mathbf{r})$ is the wave function which contains all the information about the system.

For an isolated interacting system of electrons and nuclei, one can write the following Hamiltonian¹:

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ze} + \hat{T}_Z + \hat{V}_{ZZ}, \quad (4.2)$$

where $\hat{T}_e$ is the kinetic energy operator for the electrons² given by

¹Relativistic effects, magnetic fields and quantum electrodynamics are not included here.

²Hartree atomic units are used throughout this chapter.

$$\hat{T}_e = \sum_i -\frac{1}{2} \nabla_i^2, \quad (4.3)$$

$\hat{V}_{ee}$ is the electron-electron interaction,

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4.4)$$

$\hat{V}_{Ze}$ is the potential acting on the electrons due to the nuclei,

$$\hat{V}_{Ze} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|), \quad (4.5)$$

$\hat{T}_Z$ is the kinetic energy operator of the nuclei,

$$\hat{T}_Z = \sum_I -\frac{1}{2M_I} \nabla_I^2, \quad (4.6)$$

and $\hat{V}_{ZZ}$ is the nucleus-nucleus interaction,

$$\hat{V}_{ZZ} = \frac{1}{2} \sum_{I \neq J} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (4.7)$$

In these equations, $\mathbf{r}_i$ and $\mathbf{r}_j$ are the coordinates of the electrons and $\mathbf{R}_I$ and $\mathbf{R}_J$ are the coordinates of the nuclei.

To study and predict different phenomena observed in matter, one needs to solve Eq. 4.1 using the particular Hamiltonian based on Eq. 4.2 constructed for the system of interest. Unfortunately, the exact analytic solution for this kind of problems can only be found for a very limited number of systems. Observing equations 4.1 to 4.7, it becomes evident that for a system of M nuclei and N electrons, the mathematical problem becomes increasingly complex with increasing M and N . Therefore, approximations and methods have been developed over the years to simplify the problem.

The first approximation that one can make is the Born–Oppenheimer approximation [132]. In this approximation, the mass of the nuclei is infinitely larger than the mass of the electrons. As a consequence, the kinetic energy of the nuclei can be set to zero. The problem can be reformulated as a system of N interacting electrons in the presence of an external potential $\hat{V}_{ext}$ given by the Coulomb interaction between the nuclei and the electrons $\hat{V}_{Ze}$. The energy of the electronic system differs from the total energy by a constant W equal to the Coulomb repulsion between the nuclei, $\hat{V}_{ZZ}$, and any other term that contributes to the energy of the system but does not affect the electronic problem. The new mathematical problem to be solved is expressed in terms of the new Hamiltonian for the electronic system:

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ext}. \quad (4.8)$$

Even though the degrees of freedom in this problem are substantially reduced, there are still $4N$ degrees of freedom since for each electron one has three spacial coordinates and one spin coordinate.

To further simplify the problem, the wave function $\Psi(\mathbf{r})$ and the associated Schrödinger equation can be replaced by a scalar electronic density $\rho(\mathbf{r})$ and a corresponding mathematical scheme [133, 134]. The advantage of such a model is that while the degrees of freedom of a wave function problem increases exponentially with the number of electrons, the electronic density only depends on three spatial coordinates and is independent of the number of electrons. However, it was not until Hohenberg and Kohn [135] formulated the density functional theory as an exact theory for many-body systems that these density methods became a valid tool to solve the electronic structure problems.

4.2 The basis of DFT: Hohenberg and Kohn theorems

In 1964, Hohenberg and Kohn proved that the ground state electronic energy is completely determined by the electronic density $\rho(\mathbf{r})$ [135]. In their paper, they postulated the following two theorems as the ground for DFT:

Theorem I: For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state density $\rho_0(\mathbf{r})$.

Theorem II: A universal functional for the energy $E[\rho]$ in terms of the density $\rho(\mathbf{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. For any particular $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $\rho(\mathbf{r})$ that minimizes the functional is the exact ground state density $\rho_0(\mathbf{r})$.

The consequence of Theorem I is that all properties of the system are completely determined by the ground state density $\rho_0(\mathbf{r})$, since the full Hamiltonian is determined by $\rho_0(\mathbf{r})$, except for a constant, and, therefore, all many-body wave functions for all states are also determined by $\rho_0(\mathbf{r})$.

The second theorem shows that if the functional $E[\rho]$ is known, then it is the only thing needed to determine the exact ground state energy E_0 and the corresponding density $\rho_0(\mathbf{r})$.

Since all properties are uniquely defined by the electronic density $\rho(\mathbf{r})$, then all properties can be seen as functionals of $\rho(\mathbf{r})$, including T_e and V_{ee} . Therefore, the total energy for the entire system (nuclei and electrons) can be written as:

$$\begin{aligned} E_{\text{HK}}[\rho] &= T_e[\rho] + V_{ee}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + W \\ &\equiv F_{\text{HK}}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + W. \end{aligned} \quad (4.9)$$

The functional $F_{\text{HK}}[\rho]$ includes the internal kinetic and potential energy of the electronic system, which depend *only* on the electronic density $\rho(\mathbf{r})$. This means that $F_{\text{HK}}[\rho]$ is a universal functional (for all electron systems) independent of the external potential $V_{\text{ext}}(\mathbf{r})$. It can be concluded that if the functional $F_{\text{HK}}[\rho]$ was known, by minimizing the total energy of the system with respect to the density $\rho(\mathbf{r})$, the exact ground state energy E_0 and density $\rho_0(\mathbf{r})$ would be found. Unfortunately, the most difficult part of DFT is actually finding the functional $F_{\text{HK}}[\rho]$, and a wave function-free (or orbital-free) density functional theory is still elusive.

4.3 Kohn-Sham ansatz

In 1965, Kohn and Sham presented a scheme to deal with the problem of the unknown functional $F_{\text{HK}}[\rho]$ [136]. Since the major problem in the use of DFT is the poor representation of the kinetic energy in terms of the electronic density $\rho(\mathbf{r})$, the idea proposed by Kohn and Sham was to introduce orbitals in a way that the kinetic energy can be split in two terms, one that can be calculated exactly and a small correction term.

Even though the reintroduction of orbitals increases the number of variables again (from 3 to $3N$), Kohn and Sham succeeded to make DFT a practical tool for rigorous electronic structure calculations by avoiding the inaccuracies that arise from trying to find functionals of the density.

The assumptions for the Kohn-Sham ansatz is that the ground state density $\rho_0(\mathbf{r})$ of the electronic interacting system can be represented by the ground state density $\rho_s(\mathbf{r})$ of an auxiliary system of non-interacting particles subject to an effective potential V_s . For the independent-particle auxiliary problem, one can write the following Schrödinger-like equation:

$$\left[-\frac{1}{2}\nabla^2 + V_s(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (4.10)$$

where the effective potential V_s is given by:

$$V_s(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{Hartree}}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \quad (4.11)$$

$$= V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \quad (4.12)$$

In the previous expression, E_{Hartree} represents the classical Coulomb interaction of the electron density with itself,

$$E_{\text{Hartree}} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (4.13)$$

and E_{xc} is the exchange-correlation energy which can be defined as the difference between the kinetic and the internal interaction energies of the true interacting electron system and the auxiliary non-interacting one. This definition becomes clear by comparing Eq. 4.9 and Eq. 4.14, where Eq. 4.14 results from rewriting

the Hohenberg-Kohn expression for the total energy functional in Eq. 4.9 within the Kohn-Sham approach:

$$E_{\text{KS}}[\rho] = T_{\text{s}}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{Hartree}}[\rho] + W + E_{\text{xc}}[\rho]. \quad (4.14)$$

Then, one obtains for the exchange-correlation energy:

$$E_{\text{xc}} = F_{\text{HK}} - (T_{\text{s}}[\rho] + E_{\text{Hartree}}[\rho]), \quad (4.15)$$

where the independent particle kinetic energy T_{s} is given by:

$$T_{\text{s}} = -\frac{1}{2} \sum_{i=1}^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle. \quad (4.16)$$

Finally, for a system of independent electrons obeying Eq. 4.10, the electrons are filling those orbitals $\varphi_i(\mathbf{r})$ with the lowest eigenvalues ε_i , and the density can be calculated as:

$$\rho_{\text{s}}(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2. \quad (4.17)$$

Equations 4.10, 4.12 and 4.17 are the main equations of the Kohn-Sham approach and are the ones that need to be solved to find the solution to the electronic problem. To solve this set of coupled equations one must employ a self consistent procedure as showed in Fig. 4.1.

The key in the Kohn-Sham method is to calculate the kinetic energy assuming non-interacting electrons. Since in reality the electrons are interacting, the value for the kinetic energy obtained by this procedure differs from the total kinetic energy, but this difference is small and goes into the exchange-correlation energy E_{xc} .

Once again, one is left with a functional (E_{xc}) that, if known, it would allow the calculation of the exact electron density and total energy. Unfortunately, for a realistic system of interest, this functional is, *a priori*, not known. Thus, an important task in the Kohn-Sham approach, that will be further explained in the next section, is to develop approximations to it.

It is worth mentioning that, regardless of the reintroduction of orbitals and the unknown exchange-correlation functional, the Kohn-Sham approach is still an improvement to the orbital-free models. In the latter, the task of deriving approximations to the kinetic, the exchange, and the correlation functionals represents a larger part of the problem than the E_{xc} in the Kohn-Sham approach.

Figure 4.1. Schematic representation of the self-consistent loop to solve the Kohn-Sham equations [129].

4.4 Exchange-correlation functionals

Even though the exchange-correlation functional is a unique universal functional of the density for all systems, its explicit analytic form is unknown, except for some special cases. Instead, approximations to this functional have to be developed, usually resulting in a mathematical form that takes different variables and contains parameters whose values need to be assigned. There are two ways for assigning these parameters: requiring that the functional fulfills a set of theoretical constraints [137] or fitting the parameters to experimental data or higher level *ab initio* calculations (such as Hartree-Fock or configuration interaction [138]). Either way, many useful approximations exist today which are far from being universal, but work extremely well for the set of problems they were developed for.

J. P. Perdew *et al.* proposed a system for classifying the exchange-correlation functionals according to the variables on which they depend - the *Jacob's Ladder* [139]. Climbing up the rungs of the ladder means increasing the level of complexity of the functionals and, correspondingly, higher computational costs. However, it does not necessarily mean that the obtained results are of better quality. This always comes down to the type of system under consideration and the constraints under which the particular functional was developed. In the following, a description is given of some of the approximations used in common exchange-correlation functionals.

The first rung of Jacob's ladder corresponds to the approximation given by Kohn and Sham in the same paper where they proposed their method [136]: the local density approximation (LDA). It is based on the fact that solids can often be considered close to the limit of the homogeneous electron gas where the effects of exchange and correlation are local. The mathematical form for the LDA exchange-correlation energy (Eq. 4.18) is given by an integral over all space in which the exchange-correlation energy density ϵ_{xc} in each point is assumed to be the same as the one for the homogeneous electron gas with the same electronic density $\rho(\mathbf{r})$ as in the real problem.

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{hom}(\rho). \quad (4.18)$$

The function $\epsilon_{xc}^{hom}(\rho)$ is the sum of two contributions: exchange $\epsilon_x^{hom}(\rho)$ and correlation $\epsilon_c^{hom}(\rho)$. While the exact analytic form for the exchange contribution $\epsilon_x^{hom}(\rho)$ is known [129], this is not the case for the correlation part $\epsilon_c^{hom}(\rho)$, but it has been calculated to great accuracy by Monte Carlo methods [129].

The LDA is applicable to systems with slowly-varying densities, but can not be formally justified for systems with highly inhomogeneous densities, like a single atom or molecule whose densities must go continuously to zero. A way to solve the inaccuracies of the LDA in non-homogeneous systems is to consider a new functional that takes into account not only the value of the density $\rho(\mathbf{r})$ at each point, but also of the magnitude of the gradient of the density $|\nabla\rho|$.

The generalized gradient approximation (GGA), which was used in this thesis, includes a variety of ways to modify the behavior of the exchange-correlation functional at large gradients. It can be expressed in a general form as:

$$E_{xc}^{GGA}[\rho] = \int d\mathbf{r} \, \rho(\mathbf{r}) \, \epsilon_{xc}^{hom}(\rho, |\nabla\rho|). \quad (4.19)$$

A large range of GGA functionals can be found in literature which differ in how the gradient of the density is introduced. The accuracy of GGA methods represent a significant improvement over LDA and gives satisfactory results for a wide range of chemical properties [140]. The PW91 functional [124] is one of the most widely used in the field and the one chosen for most of the calculations in this thesis.

Further improvements in calculated results are achieved by the use of hybrid functionals. They introduce non-local functionals, in which the contribution to the energy of a volume element depends on both its electron density and the electron density of its surroundings. This is done by including a portion of the exact exchange of Hartree-Fock theory with exchange and correlation from density functional theory. Inclusion of exact Hartree-Fock exchange is often found to improve the calculated results of chemical systems, but the amount of exact exchange to include depends on the system and the properties under study. An example of these hybrid functionals is the commonly used B3LYP [141]. Even though it is generally accepted that hybrid functionals give more accurate results than GGA functionals for finite systems, as those studied in this thesis, this is achieved at a higher computational cost [140]. Therefore, in the particular case of this thesis, all the calculations were performed using PW91, while B3LYP was often employed in a subset of the systems studied to corroborate the results.

The available approximations to the exchange-correlation functionals do not stop here. Increasingly complex variables constructed upon the electron density or the Kohn-Sham orbitals can be introduced. It can be concluded that the difference between various DFT methods lies in the choice of the exchange-correlation functional, which largely depends on the type of system one wants to study and the properties of interest.

4.5 Wave function expansion: basis sets

There is an unavoidable approximation in all *ab initio* methods due to the fact that the unknown wave functions must be represented in terms of a basis set of known functions. In particular, when one is to solve the Kohn-Sham problem, this expansion is applied to the wave functions/orbitals $\varphi_i(\mathbf{r})$ that appear in Eq. 4.10. There are three main methods for wave functions expansion: plane waves and grid, localized atomic orbitals (linear combination of atomic orbitals, LCAO) and atomic sphere methods (augmented functions) [129]. The choice of expansion method largely depends on the problem to be tackled.

If the basis set chosen for the expansion is complete, then the wave functions are completely represented and the procedure is not an approximation. However, a complete basis set means that an infinite number of functions are needed, which is not possible to achieve in a real calculation. The requirement of using a finite basis set implies that only some of the components of the wave function can be

represented and the expansion procedure becomes an approximation. Therefore, the accuracy of the method depends on the number of functions used in the basis set, i.e., a larger basis set allows for higher accuracy. On the other hand, the downside of a large basis set is that it increases the computational cost of the calculations. The decision of which basis set to use for a certain problem should balance accuracy against computational cost.

As explained in Chapter 3 – *Synthetic growth concept*, this thesis deals with atoms, molecules and clusters of atoms. This type of systems are best represented in LCAO basis sets. A large number of optimized LCAO basis sets have been developed and are readily available on websites and/or implemented in computer software. The main difference between them is the type and number of functions they use to describe the different type of orbitals in the atoms. A thorough description of the different types of LCAO basis sets and their performance can be found in a large number of textbooks and scientific publications (e.g., [131, 138, 142]). Here, only a description of the basis set used in this thesis is given.

All the calculations performed in this thesis employed the 6-31G basis [143] set including polarization functions (6-31G**) [144]. This is a contracted basis set of Gaussian type orbitals³ (GTO) which can be employed to model systems that contain atoms from hydrogen to krypton. The core orbitals are represented by six contracted GTOs, while the inner and outer part of the valence orbitals are represented by three and one contracted GTOs, respectively. The polarization is included by functions of higher angular momentum to improve the description when the electron distribution is different in different directions. To verify the obtained results, some calculations were replicated including diffuse functions (6-311++G**), which are known to improve the description of anions and large systems by giving a more accurate description of the wavefunction far from the nucleus [145].

³Gaussian type orbitals functional form is given by:

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\zeta r^2},$$

where $Y_{l,m}$ are spherical harmonic functions.

Overview of experimental techniques

This thesis is mainly concerned with the theoretical study of the carbon-based compounds: CS_x , CF_x , and CS_xF_y . It specifically predicts structural features that evolve upon incorporation of sulfur and fluorine in a carbon matrix, as well as acquires insights into the film deposition process by studying precursor species and structural growth. This theoretical work was carried out in parallel with extensive experimental work, i.e., synthesis and characterization of CS_x , CF_x , and CS_xF_y thin films. Susann Schmidt has been the main force behind the experiments regarding CF_x and the results are described in **Paper IV**, **Paper V**, and in Appendix A. For the case of CS_x and CS_xF_y , Chung-Chuan Lai and Hans Högberg have been in charge of most of the experiments. The corresponding results for CS_xF_y can be found in **Paper VII**. This chapter presents an overview of the experimental techniques used for deposition and characterization of these thin films.

5.1 Thin film deposition

Thin films are mainly deposited by vapor phase deposition techniques. Depending on the type of processes involved in the film deposition, these techniques can be classified as physical vapor deposition (PVD), which is ideally governed by physical processes, chemical vapor deposition (CVD) in which mainly chemical processes are involved, or processes that includes aspects of both PVD and CVD. The development of such a large range of deposition techniques has gained momentum due to increasingly varied requirements for thin film properties (e.g., composition, purity, structure, and mechanical and electrical properties) as well as demands on production characteristics (e.g., scale, time, efficiency, and substrate shapes).

Our CS_x , CF_x , and CS_xF_y thin films were deposited by a particular variant of physical vapor deposition: reactive magnetron sputtering. This process is de-

Figure 5.1. Schematic of a sputtering chamber.

scribed in this section based on reference [12].

5.1.1 The sputter deposition process

Fig. 5.1 shows a schematic of a sputtering set-up indicating the main parts involved in the deposition process. The sputter deposition process is conducted in an electrically grounded vacuum chamber. Prior to deposition, a *target* which contains the material that will form the film is introduced into the chamber. The target is attached to a conducting plate (*cathode*) connected to a negative voltage. Opposite to the target, the *substrate* on which the film is deposited is placed on a conductive holder (*anode*). The substrate holder may be at floating potential, grounded or connected to a negative potential. The third important component is the *sputter gas* which is an inert gas (commonly argon) that is introduced in the evacuated deposition chamber at low pressures¹.

When a sufficiently high voltage is applied between two conductive electrodes situated in a low pressure gas environment, a glow discharge or plasma² is ignited. The glow discharge is sustained by a cascade process of collisions represented by Eq. 5.1. An electron and a neutral gas species collide producing a positive ion and one additional electron (or more).

Since the cathode is connected to a negative voltage, an electric field is formed inside the chamber which accelerates the positive ions towards the target. The *sputtering process* occurs when the ions impinge on the target and atoms are ejected from the material matrix by momentum transfer. The collision of ions

¹In magnetron sputtering, the deposition pressures are typically kept between 0.2 and 1.6 mPa.

²A plasma is a quasi-neutral weakly ionized gas which consists of electrons, ions and neutral atomic or molecular species.

with the target also results in ejection of electrons (i.e., secondary electrons), reflection of ionic and neutral sputtering gas species, and emission of radiation. The secondary electrons play an important role in this process since they are repelled from the target and contribute to maintaining the plasma.

The sputtered species from the target have to travel through the plasma, to ultimately reach the substrate where they are continuously attached to form the film. During film deposition, not only sputtered species from the target reach the substrate. Different species with different energies and trajectories also bombard the growing film and species can be sputtered away. As long as the species attaching to the substrate are more than the ones being sputtered away, the film will grow.

The process of film growth by sputtering a target described above can be influenced and controlled in order to obtain thin films with particularly desired properties and to find more efficient growth processes. This can be achieved by applying different types of voltages to the target, using a reactive gas, introducing magnetic fields, connecting the substrate holder to a negative bias, and heating the substrate, to name a few alternatives.

Reactive sputtering

When the goal is to deposit a compound thin film, one or more of the elements that will form the compound can be introduced in the form of a reactive gas mixed with the sputtering gas or completely substituting it. During the deposition process, the reactive gas may:

- react with the species exposed on the surface of the target, resulting in the formation of molecules or small clusters of atoms that can be sputtered from the target. It can also lead to target poisoning;
- react with species sputtered from the target and present in the plasma (gas phase reactions), thus creating polyatomic species that may be deposited onto the substrate and form the film; and/or
- react with the film-forming species already attached to the substrate.

The resulting thin film composition is a mixture of the target material and the chemical species available in the reactive gas.

The thin films for this thesis were synthesized using graphite targets and a reactive gas containing sulfur, fluorine, or both. In the case of CS_x , the reactive gas was carbon disulfide (CS_2). For CF_x , two different gases were used: tetrafluoromethane (CF_4 , **Papers IV**, and **V**) and octafluorocyclobutane (C_4F_8 , **Paper V**). Finally, for CS_xF_y , the reactive gas used is sulfur hexafluoride (SF_6 , **Paper VII**).

It is important to emphasize that when a reactive gas is present during film deposition, the process of chemical sputtering (chemical desorption) may occur at the target surface and the growing film surface. Winters *et al.* described chemical sputtering as “a process whereby ion bombardment causes or allows a chemical reaction to occur which produces a particle that is weakly bound to the surface

and hence easily desorbed into the gas phase” [146]. This process is characterized by being highly selective, with a low energy threshold for molecular desorption, and it is activated by the surface temperature. In the case of the carbon-based thin films CN_x [75, 147] and CF_x [56], the desorption of species that are less favorably bonded to the growing film surface is supposed to assist the structural evolution of the thin film. If chemical sputtering occurs predominately at the growing film surface, lower deposition rates and lower contents of the heteroatom (nitrogen or fluorine) in the film are usually observed. Chemical sputtering at the target may in turn lead to increased deposition rates.

Magnetron sputtering

In the sputtering process described so far, there is no constraints to the movement of the electrons. Therefore, there is a high probability for the electrons escaping the plasma, hitting the grounded chamber walls and exiting the system. As a result, there is a reduced number of electrons colliding with the sputtering gas atoms and ionizing them to sustain the plasma. This makes glow discharges relatively inefficient ion sources.

An option to increase the plasma density³ is to introduce a magnetic field close to the target perpendicular to the existing electric field. This combination of electric and magnetic fields confine the electrons to the region near the cathode, increasing their lifetime and hence the probability of ionization of the sputtering gas neutral species. The magnetic field is typically introduced by placing permanent magnets at the back of the target (replacing the cathode’s conductive plate in Fig. 5.1). This results in higher deposition rates and the possibility of working with lower applied voltages. Another advantage is the possibility to operate at lower pressure, which means that the sputtered species interact less with the plasma species in their way to the substrate, thus achieving an increased deposition rate.

DC magnetron sputtering

In DC magnetron sputtering, used in **Paper VII**, the cathode is connected to a direct current (DC) power supply. The description of the sputtering deposition process given so far is based on this type of voltage source. Although DC magnetron sputtering is simple compared to other magnetron sputtering methods, it shows disadvantages due to the fact that the plasma formed is not dense enough, i.e., low ion flux. This often results in under-dense and columnar film morphologies [148].

High power impulse magnetron sputtering

To increase the ion flux, one can increase the power density applied to the cathode. This would increase the plasma density and the number of ionized species. The problem is that this procedure could lead to the development of high temperatures and eventually to the target melting. To counteract this effect, a technique based

³Plasma density refers to the electron density and is expressed as the number of free electrons per unit volume.

on conventional DC magnetron sputtering was developed: high power impulse magnetron sputtering (HiPIMS) [149, 150].

The idea behind HiPIMS is to apply short pulses ($5 - 200 \mu\text{s}$) of high voltage ($500 - 1000 \text{ V}$) while preserving the average power over time similar to the one applied in DC magnetron sputtering, and letting the system cool down between pulses (pulse frequencies from tens of Hz to kHz). This results in higher plasma densities and higher ionization, which in turn, permits the guidance of a large number of species by applying suitable bias voltage settings [151, 152]. This can lead to dense, featureless film morphologies, increased hardness and different crystalline structures [148, 153, 154].

5.1.2 Plasma characterization: Mass spectrometry

The growth and properties of compound thin films are highly dependent on the plasma species that arrive at the substrate during deposition, since these species are either the building blocks of the film or etching agents. Therefore, it is helpful to know the type, the flux and the energy values of the plasma species that reach the substrate. In the particular case of HiPIMS, it is also useful to know when the different species arrive at the substrate taking the beginning of the pulse as reference.

All this information can be obtained by mass spectrometry. The basic principle of operation of a mass spectrometer is the separation of ionic species according to their mass to charge ratio and their detection in proportion to their abundance [155]. The result is usually given as a plot of ion abundance as a function of the ions mass to charge ratio.

A mass spectrometer has four basic parts [155, 156]:

- *orifice*: where the species to be measured enter the spectrometer. Some spectrometers include an internal ionizer which allows measurement of neutral species by ionizing them during their way in;
- *energy analyser*: filters the ions according to their kinetic energy;
- *mass analyser*: filters the ions according to their mass to charge ratio;
- *detector*: counts the ions that impact it and convert them into electrical pulses that can be interpreted by a computer.

To measure the plasma species that reach the substrate at certain deposition conditions (e.g., target voltage and deposition pressure), the mass spectrometer should be placed in the chamber taking into account the geometry of the deposition process, i.e., the spectrometer's inlet facing the target at the same distance as the substrates are placed during deposition.

The results of the mass spectrometry are an important aid to understand the process of deposition as well as the film formation. For example, in **Paper V**, the results from mass spectrometry were combined with the SGC calculations of precursor species to study the behavior of the species in the plasma, as well as the role of the species in the formation of the film structure.

5.2 Thin film characterization

The characterization of thin films may involve determining their composition, structure, mechanical properties, or any other type of properties. A large number of techniques are available to address these issues and for some of them there are a range of techniques to choose from. The characterization techniques that one selects to study a thin film depends on the material and the underlying interest. In this section, only those characterization techniques that were used in the included papers are outlined.

5.2.1 Structural characterization

One of the property-defining characteristics of carbon-based materials is their structure, both at the micro- and the nano-level⁴. A suitable technique to study thin films' structural features is electron microscopy. Analogous to optical microscopes, where the sample is illuminated by visible light, electron microscopes illuminate the samples by electron beams.

Transmission electron microscopy and selected area electron diffraction

In transmission electron microscopy (TEM) [157], an electron beam is transmitted through a very thin sample. When this happens, the most important possible outcomes related to electron-matter interaction are:

- the electron is transmitted through the sample without interacting with any atom, and so it is undeflected;
- the electron is elastically scattered so it is deflected but loses no energy; or
- the electron loses a significant amount of energy and is probably scattered. As a result, electrons (i.e., secondary electrons) and X-rays may be emitted from the sample.

These are the different signals that TEM separates using electromagnetic lenses in order to obtain an image of the sample. Based on these signals, the microscope can be operated in different modes to extract different types of information. Details on microscope set-ups and operation modes can be found in reference [158].

To obtain information on the structure of the sample, all diffracted beams are excluded from the measurement and only the central beam that goes through is taken into account. This operation mode is called bright-field (BF) imaging. Accelerating voltages for the electron beam of up to 1 MV lead to a resolution that can reach the order of picometers. The left panel of Fig. 5.2 shows a micrograph obtained for a fullerene-like carbon nitride (FL-CN_x) thin film operating the microscope in the BF mode. In the image, curved parallel planes are easily observed throughout the inspected area.

⁴Thin film morphology and microstructure are highly related to their mechanical properties, see Chapter 2 – *Carbon-based compounds*.

Figure 5.2. High resolution TEM image (left), and SAED pattern and its intensity distribution (right) for a FL-CN_x thin film sample [159]. [Reprinted from Ultramicroscopy, Vol 110, Z. Czigány *et al.*, Interpretation of electron diffraction patterns from amorphous and fullerene-like carbon allotropes, Pages No. 815-819, Copyright (2010), with permission from Elsevier.]

Unlike the FL-CN_x sample in Fig. 5.2, most of the carbon-based thin films studied in this thesis consist of a mainly amorphous matrix including nanostructured or short range-ordered clusters. In these cases, BF imaging is not enough to find and visualize the types of ordered structures present in the film.

Using the signal produced by the elastically scattered electrons in a selected area of the sample, one can obtain electron diffraction patterns that allow the extraction of crystallographic information. This technique is called selected area electron diffraction (SAED) [158]. As opposed to X-ray diffraction, the short wavelength of electrons allow very small volumes of the sample to be studied and permits the identification of small regions with a particular order.

The lower right panel of Fig. 5.2 shows the SAED pattern obtained for the FL-CN_x thin film represented in the micrograph to the left. The plot on top of the pattern shows the corresponding intensity distribution. The peaks that appear in SAED patterns for carbon-based thin films are not easy to interpret. They are a mixture of peaks corresponding to amorphous carbon with peaks from ordered carbon allotropes as graphite and fullerenes. Moreover, broad and diffuse peaks, typical for disordered materials, makes the assignment of peaks more complicated. Nevertheless, reference [159] is a good starting point for the interpretation of SAED patterns of carbon-based thin films.

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to observe the cross section of the deposited films. With this technique the film thickness and thus deposition rates can be obtained together with qualitative information about the film morphology (e.g., columnar, featureless, dense).

In SEM [157], an electron beam is scanned across the surface of the sample. A detector monitors the intensity of a chosen secondary signal: secondary electrons, back-scattered electrons or X-rays.

The secondary electrons are generated when the electrons from the incident beam impinge on the sample and interact inelastically with it, transferring energy to other atomic electrons and the lattice. This results in electrons leaving the sample. Since the secondary electrons have low energy, they escape from a region very close to the surface and they provide an accurate representation of the features of the surface [12]. The electrons used for the irradiation are of lower energy than in TEM, so the maximum resolution that SEM can reach is in the nanometer scale.

5.2.2 Thin film composition and chemical bonding

To complement the structural characterization as obtained by microscopy, the composition of the films as well as their bonding characteristics need to be addressed. Three complementary techniques were used: X-ray photoelectron spectroscopy (XPS), elastic recoil detection analysis (ERDA), and Raman spectroscopy.

X-ray photoelectron spectroscopy

XPS [160] is a spectroscopic technique used to determine the elemental composition of solid surfaces and the chemical environment of each element. The main characteristic of XPS measurements is that they are surface sensitive, meaning that only the first 10 nanometers of the surface of the sample are probed. XPS can detect any element from lithium to uranium that is present in the material in concentrations down to 0.1 atomic %.

The technique is based on the detection of photoelectrons⁵ emitted by the sample under X-ray irradiation. When a photon interacts with an electron, the former transfers all its energy to the latter and the electron is ejected from the solid with a certain kinetic energy. XPS measures this kinetic energy, which is a function of the binding energy of the electron to the atom/ion and is specific for each element and its chemical environment.

Although the kinetic energy (KE) is the measured quantity in XPS, it is the derived binding energy (BE) that is used to construct the spectrum. These two quantities are related by the following equation:

$$KE = E_{\text{photon}} - \phi_{\text{XPS}} - BE, \quad (5.2)$$

⁵A photoelectron is produced when an electron initially bound to an atom or an ion is ejected by a photon.

where ϕ_{XPS} is the workfunction of the instrument⁶ and E_{photon} is the energy of the incident photon.

When the data obtained is arranged as an energy spectrum of all electron emissions falling within some predefined energy range, the energies corresponding to the detected photoelectrons appear as peaks. The position of these peaks are related to the chemical species the electron came from and the intensity is related to the atomic concentration of that particular element. Binding energy tables can be found for all elements detectable by XPS in different chemical environments.

Elastic recoil detection analysis

ERDA [161] is an ion beam analysis technique used to obtain elemental composition depth profiles of thin films. In this technique, the sample is bombarded with ions of known energy. When the ions collide with the atoms in the sample, the energy and momentum transfer allow the latter to be ejected. This interaction is considered elastic. Using the laws of conservation of energy and momentum, one can obtain the following equation for the energy transfer from the incident particle with energy E_1 and mass m_1 to the atom in the sample with mass m_2 , which is ejected with energy E_2 at an angle θ from the incident direction:

$$E_2 = \frac{4m_1m_2}{(m_1 + m_2)^2} E_1 \cos^2 \theta. \quad (5.3)$$

Fig. 5.3 shows a schematic representation of the most important details of an ERDA measurement. The ERDA detector is situated in a position where it can detect the species that are scattered with angles $\theta < 90^\circ$, and their energies and velocities are measured. There are dedicated softwares that analyze the set of measured energies to differentiate between different species with the same energy as well as to obtain the corresponding depth profiles.

Figure 5.3. Schematic representation of an ERDA set-up.

⁶The workfunction of the instrument is included since it is the minimum energy necessary to remove an electron from the conductive sample in physical contact with the instrument.

Raman spectroscopy

Raman spectroscopy is a technique used to observe vibrational, rotational, and other low-frequency modes in a molecular system [162]. It relies on the inelastic scattering of photons (usually with energies in the visible range) by interaction with molecular vibrations, lattice phonons, or other excitations in the sample.

When electromagnetic radiation impinges on a molecule, it interacts with the polarizable electron density, the bonds of the molecule in the phase, and the environment in which the molecule exists. As a result, the photon is scattered. This is known as the Raman effect. When a photon interacts with a molecule, the final state will be different from the original one. If the final state is of higher energy, then the scattered photon will have lower energy than the incident one and hence it will be shifted to lower frequencies by the relation $E = \hbar\omega$ (Stokes shift in frequency). If the interaction is such that the final state is a lower energy state, the scattered photon has higher energy than the incident one and is shifted to higher frequencies (anti-Stokes shift). The difference in the frequencies of the photon is called the Raman frequency (or shift) and is usually expressed by the wavenumber (cm^{-1}).

During Raman spectroscopy measurements, the scattered photons are detected along with the measurement of their energies. The results are shown as a spectrum with intensity peaks as a function of the Raman frequency.

Since vibrational information is specific to the chemical bonds and symmetry of molecules, Raman spectroscopy provides a fingerprint by which the molecule can be identified. As with single molecules, a given solid material has characteristic phonon modes that can help in its identification.

In the case of disordered carbon-based materials, the Raman spectrum shows broad bands caused by the structural disorder. Typically, one broad band is observed at about 1500 cm^{-1} with widths that can go up to 600 cm^{-1} . This band has been shown to have two contributions: the G or graphite band at 1600 cm^{-1} and the D or disorder band at about 1350 cm^{-1} . Analyzing the intensity relation between this two bands, the peak positions and their width, one can obtain information about the relative content of sp^2 - and sp^3 -hybridized atomic species in the material [163].

5.2.3 Mechanical characterization

As explained in Chapter 2 – *Carbon-based compounds*, the mechanical properties are a very important characteristic of carbon-based thin films and are represented by the hardness (H) and the elastic modulus (E) values. Hardness is defined as a measure of how resistant a solid material is to permanent deformation under a compressive force. Elastic modulus is a measure of the resistance of a solid material to elastic (non-permanent) deformation when a force is applied. To determine these properties for a thin film, nanoindentation is an appropriate technique.

Figure 5.4. Illustration of a) the nanoindentation process and b) the load-displacement data.

Nanoindentation

To perform a nanoindentation experiment, the sample is pressed by a nanometer-sized sharp diamond tip (*loading*) and then released (*unloading*). The process is illustrated in Fig. 5.4 a), where P designates the load and h is the displacement relative to the initial undeformed surface. Fig. 5.4 b) represents the data that can be acquired during one cycle of loading and unloading.

From the measurement of the indentation load and displacement, the values of hardness and elastic modulus can be obtained by using the model of Oliver and Parr [164]. This model assumes that the load deformation is both elastic and plastic, but the unload deformation is only elastic. The important quantities that need to be determined are the maximum load $P_{\max}$, the maximum displacement $h_{\max}$, the elastic unloading stiffness $S = dP/dh$ and the final depth h_f (the permanent depth of penetration after the indenter is fully unloaded).

After this, the hardness can be estimated by the following equation:

$$H = \frac{P_{\max}}{A}, \quad (5.4)$$

where A is the contact area between the indenter and the sample and must be estimated for the specific tip used [164].

The estimation of the elastic modulus comes from the following equation:

$$S = \beta \frac{2}{\pi} E_{\text{eff}} \sqrt{A}, \quad (5.5)$$

where β is a parameter that accounts for any physical processes that may affect the equation and E_{eff} is the effective elastic modulus. E_{eff} takes into account the elastic displacements that occur both in the thin film, with Young modulus E and Poisson's ratio ν , as well as in the indenter with the elastic constants E_i and ν_i following the relationship:

$$\frac{1}{E_{\text{eff}}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}. \quad (5.6)$$

The Oliver and Parr model also assumes that the response observed in the load-displacement curves corresponds to the film only and is independent of the substrate. Therefore, special considerations should be made when the samples under consideration are thin films to avoid or to account for the influence of the substrate. For this, the 10% rule is commonly applied, which is an empirical rule that establishes that the substrate influence can be avoided if the maximum penetration depth h_{max} is smaller than the 10% of the film thickness. Nevertheless, the applicability of this rule depends on the film thickness⁷ and the type of materials in both the film and the substrate [165].

When the studied thin films are soft and highly elastic, the elastic deformation during the indentation process involves increased local stresses that extend into the substrate. Therefore, the load-displacement curves show a mixed response of the film and the substrate. This has been the case with the deposited CF_x films in **Papers IV** and **V**.

To rigorously account for the mixed response of the film and the substrate, the model proposed by Korsunsky *et al.* [166] is an alternative to the Oliver and Parr one [164]. Korsunsky *et al.* assume that the hardness value of the coating/substrate composite H_c is related to the hardness of the substrate H_s and the hardness of the coating H_f by the following relation:

$$H_c = H_s + \frac{H_f - H_s}{1 + k\beta^2}, \quad (5.7)$$

where β is the normalized indentation depth calculated as the maximum displacement h_{max} divided by the film thickness, and k is a constant that takes into account effects such as film cracking and plastic deformation, which can be determined by fitting the obtained values of H_c and β .

⁷In the case of films with small thicknesses, the data obtained using the 10% rule might give no relevant information.

Summary and conclusions

Today's technological advancement asks for new and improved materials in order to develop devices with enhanced functionality and increasing complexity. In these devices, each material has its own purpose and serves a specific function. This requires that the material's structure and properties can be efficiently manipulated to achieve the desired characteristics. In this context, carbon-based compounds appear to be a particularly suitable family of materials.

Of key interest to this thesis are the carbon-based thin films which range from amorphous to nanostructured. They are composed of carbon and sometimes hydrogen or other elements from the p-block of the Periodic Table. The structure and properties of these films can be guided by selecting appropriate deposition methods and synthesis parameters.

Among the various carbon-based thin films, my doctoral studies were focused on modeling the sulfocarbide (CS_x) and carbon fluoride (CF_x) compounds. The initial questions to answer were whether they could exist as fullerene-like materials and if this type of structure could be developed during physical vapor deposition. To address these issues, I used the approach given by the synthetic growth concept with electronic structure calculations based on density functional theory.

My results have shown that both CS_x and CF_x can be obtained as fullerene-like compounds, but with significant differences between them. I found that the case of CS_x is similar to that of its predecessors, carbon nitride (CN_x) and phosphorus-carbide (CP_x). All of these heteroatoms (i.e., sulfur, nitrogen, and phosphorus) can form three bonds with three different carbon atoms in a graphene-like network, which induces the formation of ring defects (e.g., pentagons) and local curvature, all desirable characteristics to obtain a well-developed fullerene-like structure. I also found that the ideal sulfur concentration to obtain FL- CS_x is in the range of 10 to 15 at.% and the resulting mechanical properties should be between those of FL- CN_x and FL- CP_x .

CF_x on the other hand, was anticipated to pose a different case from the other three, since fluorine can form only one single bond and is the element with the highest electronegativity. My modeling results showed that CF_x can form a variety

of structures (e.g., fullerene-like, diamond-like, and polymer-like) depending on the fluorine concentration and deposition conditions. The formation of FL-CF_x can occur for fluorine concentrations below 10 at.% but by means of different kinds of defects than the ones showed by FL-CS_x, FL-CN_x, and FL-CP_x. The structural diversity that I predicted for CF_x was confirmed experimentally by my colleagues and the most important observation for my thesis is the formation of short-range ordered thin films for fluorine concentrations under 5 at.%. Moreover, we could combine my studies on precursor species and CF_x structural features with the results on plasma and thin film characterization to better understand the deposition process and the properties exhibited by the CF_x thin films.

Combining the experience I obtained with CS_x and CF_x, I moved on to study the ternary system CS_xF_y. I found that the structural characteristics that can be achieved for this new compound can be explained in terms of the structural characteristics of the binaries CS_x and CF_x and fullerene-like structures can be obtained for a combined concentration of sulfur and fluorine below 10 at.%. Contemporary deposition and characterization of CS_xF_y thin films have shown that this compound can form short-range ordered structures for the compositions stated above.

In conclusion, the main achievement of my doctoral studies has been the prediction of three new materials: FL-CS_x, FL-CF_x, and FL-CS_xF_y, together with general criteria on how to achieve them. Additionally, by using and improving the synthetic growth concept, I have shown that molecular modeling based on density functional theory is an appropriate and inexpensive approach to study nanostructured carbon-based thin films. Finally, this thesis demonstrates how much modeling and experiments can gain from each other and that a strong collaboration leads to useful results and understanding.

Short-range order in CF_x thin films

Summary of experimental details and results

The description of experimental details and results regarding CF_x thin films presented herein are based on ongoing work by Susann Schmidt together with myself and others.

Experimental details

CF_x thin films were deposited by reactive high power impulse magnetron sputtering (rHiPIMS) in an industrial coating system CC800/9 (CemeCon AG, Germany) at Linköping University. A base pressure of less than 1 mPa was achieved prior to deposition. During deposition the Si(001) and NaCl substrates faced a rectangular, pure graphite target (440 cm²) at a distance of 60 mm. A constant deposition pressure of 400 mPa was maintained during reactive sputtering of the graphite target in an Ar/ CF_4 (argon/tetrafluoromethane) atmosphere, using a CF_4 partial pressure of 11 mPa. HiPIMS was performed in a power-regulated mode with a pulse frequency of 300 Hz and a pulse width of 200 μs . An average power of 1300 W was supplied to the cathode. A pulsed bias voltage of -100 V, synchronized to the cathode pulse, was applied to the substrate table. Depositions were performed at constant substrate temperatures of 110°C and 430°C, respectively.

The composition of the CF_x thin films was extracted from X-ray photo electron spectroscopy (XPS) measurements performed with an Axis UltraDLD instrument from Kratos Analytical, Manchester, UK using monochromatic Al($K\alpha$) radiation ($h\nu = 1486.6$ eV). The base pressure in the analysis chamber during acquisition was below 1×10^{-7} Pa. XPS core level spectra of the C1s, F1s, and O1s regions were recorded on as-received samples. Automatic charge compensation was applied throughout the acquisition. In order to extract the sample composition, a Shirley-type background was subtracted from the core level spectra and elemental cross sections provided by Kratos Analytical were applied.

The microstructure of CF_x thin films was investigated by transmission electron

microscopy using a Tecnai G2 TF 20 UT TEM (FEI, The Netherlands). For TEM sample preparation, the CF_x films deposited on NaCl substrates were floated off in water, rinsed twice in de-ionized water and subsequently in isopropanol. The samples were collected on filter paper, dried and grinded into a fine powder, which was transferred onto a TEM powder grid (300 mesh Cu, Holey Carbon Film).

Results

The fluorine content in the CF_x thin films shows a clear dependency on the deposition temperature; the film deposited at a substrate temperature of 110°C contained 13 at.% of fluorine, while CF_x deposited at a temperature of 430°C contained 4 at.%. The lower fluorine content in the sample deposited at 430°C is attributed to an increased chemical sputtering of fluorine-rich precursor fragments at the substrate's surface. Chemical sputtering is triggered by an increased ad-atom mobility due to an increased substrate temperature.

Fig. A.1 a) and b) present TEM images obtained from the sample deposited at 110°C and 430°C , respectively. The CF_x in Fig. A.1 a) appears amorphous without short-range order, while a short-ranged ordered microstructure is visible in Fig. A.1 b) for the CF_x sample deposited at 430°C . The structural evolution of CF_x is mainly attributed to a lower fluorine content in the film. Another factor that contributed to the finger-print like microstructure is the deposition temperature, where the deposition process is characterized by the constant adsorption and desorption of precursor fragments as well as their rearrangement.

Figure A.1. TEM micrographs for CF_x thin films deposited at a) 110°C and b) 430°C .

These experimental findings corroborate my results from SGC¹ modeling that predict the formation of CF_x compounds with short-range order for fluorine concentrations below 10 at.% and published in **Papers III** and **VI**.

¹See Chapter 3 – *Synthetic growth concept*.

Bibliography

- [1] "Design". Oxford Dictionaries. Oxford University Press. <http://www.oxforddictionaries.com/definition/english/design>. Accessed: 2015-07-22.
- [2] N. W. Ashcroft and N. D. Mermin. *Solid state physics*. Brooks/Cole, Cengage Learning, Belmont, CA, 1976.
- [3] Richard Zallen. *The physics of amorphous solids*. John Wiley & Sons, Inc., USA, 1983.
- [4] A. Hirsch. The era of carbon allotropes. *Nature materials*, 9(11):868–71, 2010.
- [5] G. M. Whitesides, J. K. Kriebel, and B. T. Mayers. Self-assembly and nanostructured materials. In *Nanoscale assembly chemical techniques*, chapter 9, pages 217–239. Springer, USA, 2005.
- [6] EU. Commission recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU). *Official Journal of the European Union*, L275(June 2010):38–40, 2011.
- [7] H. Gleiter. Nanostructured materials: basic concepts and microstructure. *Acta materialia*, 48:1–29, 2000.
- [8] G. Cao. *Nanostructures & Nanomaterials - Synthesis, Properties & Applications*. Imperial College Press, London, 2004.
- [9] M. Haruta. Size- and support-dependency in the catalysis of gold. *Catalysis Today*, 36(1):153–166, 1997.
- [10] Nanomaterials and their applications. UnderstandingNano.com. Hawk's Perch Technical Writing, LLC. <http://www.understandingnano.com/nanomaterials.html>. Accessed: 2015-07-23.

- [11] Nanomaterials and their applications. AZO Materials. AzO.com. <http://www.azom.com/article.aspx?ArticleID=1066>. Accessed: 2015-07-23.
- [12] M. Ohring. *Materials Science of Thin Films*. Academic Press, Burlington, MA, USA, second edition, 2001.
- [13] J.-E. Sundgren. Structure and properties of TiN coatings. *Thin Solid Films*, 128(1-2):21–44, 1985.
- [14] S. P. Chuan, J. A. Ghani, S. H. Tomadi, and C. H. C. Hassan. Analysis of Ti-base Hard Coating Performance in Machining Process: A Review. *Journal of Applied Sciences*, 12(18):1882–1890, 2012.
- [15] M. G. Kanatzidis. Semiconductor physics: quick-set thin films. *Nature*, 428(6980):269–71, 2004.
- [16] B. Parida, S. Iniyar, and R. Goic. A review of solar photovoltaic technologies. *Renewable and Sustainable Energy Reviews*, 15(3):1625–1636, 2011.
- [17] S. Franssila. Thin film materials and processes. In *Introduction to microfabrication*, chapter 5, pages 47–64. John Wiley & Sons Ltd, Chichester, West Sussex, 1st edition, 2004.
- [18] E. B Tadmor, R. Phillips, and M. Ortiz. Hierarchical modeling in the mechanics of materials. *International Journal of Solids and Structures*, 37(1-2):379–389, 2000.
- [19] E. B. Tadmor and R. E. Miller. *Modeling materials - Continuum, atomistic and multiscale techniques*. Cambridge: Cambridge Univ. Press, 2011.
- [20] A. R. Leach. *Molecular modelling: principles and applications*. Pearson Education Limited, Harlow, Essex, 2nd edition, 2001.
- [21] K. Bewilogua and D. Hofmann. History of diamond-like carbon films - From first experiments to worldwide applications. *Surface and Coatings Technology*, 242:214–225, 2014.
- [22] J. Robertson. Comparison of diamond-like carbon to diamond for applications. *Physica Status Solidi (A) Applications and Materials Science*, 205(9):2233–2244, 2008.
- [23] A. H. Lettington. Applications of diamond-like carbon thin films. *Carbon*, 36(5-6):555–560, 1998.
- [24] J. C. Angus and C. C. Hayman. Low-pressure, metastable growth of diamond and "diamondlike" phases. *Science*, 241(4868):913–921, 1988.
- [25] H. Lipson and A. R. Stokes. A New Structure of Carbon. *Nature*, 149(3777):328–328, 1942.

- [26] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
- [27] A. K. Geim and K. S. Novoselov. The rise of graphene. *Nature materials*, 6(3):183–91, 2007.
- [28] A. L. Ivanovskii. Graphene-based and graphene-like materials. *Russian Chemical Reviews*, 81(7):571–605, 2012.
- [29] T. Kuila, S. Bose, A. K. Mishra, P. Khanra, N. H. Kim, and J. H. Lee. Chemical functionalization of graphene and its applications. *Progress in Materials Science*, 57(7):1061–1105, 2012.
- [30] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, and S. Seal. Graphene based materials: Past, present and future. *Progress in Materials Science*, 56(8):1178–1271, 2011.
- [31] D. W. Boukhvalov and M. I. Katsnelson. Chemical functionalization of graphene. *Journal of Physics: Condensed Matter*, 21(34):344205, 2009.
- [32] S. Iijima. Helical microtubules of graphitic carbon. *Nature*, 354(6348):56–58, 1991.
- [33] S. Reich, C. Thomsen, and J. Maultzsch. *Carbon nanotubes: basic concepts and physical properties*. Wiley-VCH, Berlin, 2004.
- [34] Y. Gogotsi, editor. *Carbon nanomaterials*. CRC Press, Taylor & Francis Group, Boca Ratón, FL, 1st edition, 2006.
- [35] J. L. Delgado, M. A. Herranz, and N. Martín. The nano-forms of carbon. *Journal of Materials Chemistry*, 18(13):1417, 2008.
- [36] F. Langa De La Puente and J.-F. Nierengarten, editors. *Fullerenes: principles and applications*. RSC Nanoscience & Nanotechnology. Royal Society of Chemistry, Cambridge, 2nd edition, 2011.
- [37] J. Robertson. Diamond-like amorphous carbon. *Materials Science and Engineering: R: Reports*, 37(4-6):129–281, 2002.
- [38] S. R. P. Silva, editor. *Properties of amorphous carbon*. Institution of Engineering and Technology (IET), London, 2002.
- [39] S. Muhl and J. M. Méndez. A review of the preparation of carbon nitride films. *Diamond and Related Materials*, 8(10):1809–1830, 1999.
- [40] L. Hultman, J. Neidhardt, N. Hellgren, H. Sjöström, and J.-E. Sundgren. Fullerene-like carbon nitride: a resilient coating material. *MRS Bulletin*, 28(03):194–202, 2003.

- [41] B. Marchon, X.-C. Guo, B. K. Pathem, F. Rose, Q. Dai, N. Feliss, E. Schreck, J. Reiner, O. Mosendz, K. Takano, H. Do, J. Burns, and Y. Saito. Head-disk interface materials issues in heat-assisted magnetic recording. *IEEE Transactions on Magnetics*, 50(3):137–143, 2014.
- [42] N. Tamura, M. Aono, T. Harata, H. Kishimura, N. Kitazawa, and Y. Watanabe. DC electrical conductivity study of amorphous carbon nitride films prepared by reactive RF magnetron sputtering. *Japanese Journal of Applied Physics*, 53(2S):02BC03, 2014.
- [43] F. Claeysens, G. M. Fuge, N. L. Allan, P. W. May, S. R. J. Pearce, and M. N. R. Ashfold. Phosphorus carbide thin films: experiment and theory. *Applied Physics A*, 79(4-6):1237–1241, 2004.
- [44] G. K. Gueorguiev, A. Furlan, H. Högberg, S. Stafström, and L. Hultman. First-principles calculations on the structural evolution of solid fullerene-like CP_x . *Chemical Physics Letters*, 426(4-6):374–379, 2006.
- [45] A. Furlan, G. K. Gueorguiev, Zs. Czigány, H. Högberg, S. Braun, S. Stafström, and L. Hultman. Synthesis of phosphorus-carbide thin films by magnetron sputtering. *physica status solidi (RRL) - Rapid Research Letters*, 2(4):191–193, 2008.
- [46] J. N. Hart, P. W. May, N. L. Allan, K. R. Hallam, F. Claeysens, G. M. Fuge, M. Ruda, and P. J. Heard. Towards new binary compounds: Synthesis of amorphous phosphorus carbide by pulsed laser deposition. *Journal of Solid State Chemistry*, 198:466–474, 2013.
- [47] A. Furlan, G. K. Gueorguiev, Zs. Czigány, V. Darakchieva, S. Braun, M. R. Correia, H. Högberg, and L. Hultman. Structure and properties of phosphorus-carbide thin solid films. *Thin Solid Films*, 548:247–254, 2013.
- [48] M. Künle, T. Kaltenbach, P. Löper, A. Hartel, S. Janz, O. Eibl, and K.-G. Nickel. Si-rich a-SiC:H thin films: Structural and optical transformations during thermal annealing. *Thin Solid Films*, 519(1):151–157, 2010.
- [49] X.-A. Fu, J. L. Dunning, M. Mehregany, and C. A. Zorman. Low stress polycrystalline SiC thin films suitable for MEMS applications. *Journal of The Electrochemical Society*, 158(6):H675–H680, 2011.
- [50] S. Wan, L. Wang, and Q. Xue. Investigation of microstructure and photo-magnetic properties of sulfur-doped DLC nanocomposite films by electrochemical method. *Applied Physics A*, 102(3):753–760, 2010.
- [51] A. Saeheng, N. Tonanon, W. Bhanthumnavin, and B. Paosawatanyong. Sulphur doped DLC films deposited by DC magnetron sputtering. *The Canadian Journal of Chemical Engineering*, 90(4):909–914, 2012.
- [52] B. T. Pierce, J. L. Burke, L. B. Brunke, T. J. Bullard, D. C. Vier, and T. J. Haugan. Search for superconductivity in doped amorphous carbon thin films.

- IEEE Transactions on Applied Superconductivity*, 23(3):7000205–7000205, 2013.
- [53] I. Felner, O. Wolf, and O. Millo. Superconductivity in sulfur-doped amorphous carbon films. *Journal of Superconductivity and Novel Magnetism*, 26(3):511–514, 2013.
- [54] H. Touhara and F. Okino. Property control of carbon materials by fluorination. *Carbon*, 38(2):241–267, 2000.
- [55] A. Bendavid, P. J. Martin, L. Randeniya, M. S. Amin, and R. Rohanizadeh. The properties of fluorine-containing diamond-like carbon films prepared by pulsed DC plasma-activated chemical vapour deposition. *Diamond and Related Materials*, 19(12):1466–1471, 2010.
- [56] S. Schmidt, G. Greczynski, C. Goyenola, G. K. Gueorguiev, Zs. Czigány, J. Jensen, I. G. Ivanov, and L. Hultman. CF_x thin solid films deposited by high power impulse magnetron sputtering: Synthesis and characterization. *Surface and Coatings Technology*, 206(4):646–653, 2011.
- [57] S. Schmidt. *Carbon nitride and carbon fluoride thin films prepared by HiP-IMS*. PhD thesis, Linköping University, 2013.
- [58] L. Zhang, F. Wang, L. Qiang, K. Gao, B. Zhang, and J. Zhang. Recent advances in the mechanical and tribological properties of fluorine-containing DLC films. *RSC Adv.*, 5(13):9635–9649, 2014.
- [59] R. G. Turri, R. M. Santos, E. C. Rangel, N. C. Da Cruz, J. R. R. Bortoleto, J. H. Dias Da Silva, C. A. Antonio, and S. F. Durrant. Optical, mechanical and surface properties of amorphous carbonaceous thin films obtained by plasma enhanced chemical vapor deposition and plasma immersion ion implantation and deposition. *Applied Surface Science*, 280:474–481, 2013.
- [60] D. Banerjee and K. K. Chattopadhyay. Enhanced field emission properties of PECVD synthesized chlorine doped diamond like carbon thin films. *Surface and Coatings Technology*, 253:1–7, 2014.
- [61] T. Abraham. Diamond, Diamond-like and CBN Films & Coating Products. Technical report, bbc Research, 2010.
- [62] C. A. Charitidis. Nanomechanical and nanotribological properties of carbon-based thin films: A review. *International Journal of Refractory Metals and Hard Materials*, 28(1):51–70, 2010.
- [63] K. A. H. Al Mahmud, M. A. Kalam, H. H. Masjuki, H. M. Mobarak, and N. W. M. Zulkifli. An updated overview of diamond-like carbon coating in tribology. *Critical Reviews in Solid State and Materials Sciences*, 40(2):90–118, 2014.
- [64] A. Grill. Diamond-like carbon: state of the art. *Diamond and Related Materials*, 8(July 1998):428–434, 1999.

- [65] Gillete Mach 3 Razor. Gillete. The Procter & Gamble Company. <http://www.gillette.com/en/in/products/razors/mach3-razor.aspx>. Accessed: 2015-07-10, 2015.
- [66] C. Casiraghi, J. Robertson, and A. C. Ferrari. Diamond-like carbon for data and beer storage. *Materials Today*, 10(1-2):44–53, 2007.
- [67] R. K. Roy and K.-R. Lee. Biomedical applications of diamond-like carbon coatings: a review. *Journal of biomedical materials research. Part B, Applied biomaterials*, 83(1):72–84, 2007.
- [68] C. A. Love, R. B. Cook, T. J. Harvey, P. A. Dearnley, and R. J. K. Wood. Diamond like carbon coatings for potential application in biological implants—a review. *Tribology International*, 63:141–150, 2013.
- [69] Racing performance. DLC Company. <http://www.dlc-coating.ca/oneseven/index.php/projects/automotive-parts>. Accessed: 2015-08-11.
- [70] H. Sjöström, S. Stafström, M. Boman, and J.-E. Sundgren. Superhard and elastic carbon nitride thin films having fullerene-like microstructure. *Physical Review Letters*, 75(7):1336–1339, 1995.
- [71] I. Alexandrou, H.-J. Scheibe, C. Kiely, A. Papworth, G. Amaratunga, and B. Schultrich. Carbon films with an sp^2 network structure. *Physical Review B*, 60(15):10903–10907, 1999.
- [72] P. Wang, X. Wang, B. Zhang, and W. Liu. Structural, mechanical and tribological behavior of fullerene-like carbon film. *Thin Solid Films*, 518(21):5938–5943, 2010.
- [73] M. D. Tucker, Zs. Czigány, E. Broitman, L.-Å. Näslund, L. Hultman, and J. Rosen. Filtered pulsed cathodic arc deposition of fullerene-like carbon and carbon nitride films. *Journal of Applied Physics*, 115(14):144312, 2014.
- [74] Zs. Czigány, I. F. Brunell, J. Neidhardt, L. Hultman, and K. Suenaga. Growth of fullerene-like carbon nitride thin solid films consisting of cross-linked nano-onions. *Applied Physics Letters*, 79(16):2639–2641, 2001.
- [75] J. Neidhardt. *Fullerene-like carbon nitride thin solid films*. PhD thesis, Linköping University, 2004.
- [76] D. G. Liu, J. P. Tu, C. D. Gu, C. F. Hong, R. Chen, and W. S. Yang. Synthesis, structure and mechanical properties of fullerene-like carbon nitride films deposited by DC magnetron sputtering. *Surface and Coatings Technology*, 205(7):2474–2482, 2010.
- [77] A. Y. Liu and M. L. Cohen. Prediction of new low compressibility solids. *Science (New York, N.Y.)*, 245(4920):841–842, 1989.

- [78] A. Liu and M. Cohen. Structural properties and electronic structure of low-compressibility materials: β - Si_3N_4 and hypothetical β - C_3N_4 . *Physical Review B*, 41(15):10727–10734, 1990.
- [79] H. Sjöström, L. Hultman, J.-E. Sundgren, S. V. Hainsworth, T. F. Page, and G. Theunissen. Structural and mechanical properties of carbon nitride CN_x ($0.2 \leq x \leq 0.35$) films. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 14(1):56–62, 1996.
- [80] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart. AM1: a new general purpose quantum mechanical molecular model. *Journal of the American Chemical Society*, 107(13):3902–3909, 1985.
- [81] Sven Stafström. Reactivity of curved and planar carbon–nitride structures. *Applied Physics Letters*, 77(24):3941–3943, 2000.
- [82] G. K. Gueorguiev, J. Neidhardt, S. Stafström, and L. Hultman. First-principles calculations on the curvature evolution and cross-linkage in carbon nitride. *Chemical Physics Letters*, 410(4-6):228–234, 2005.
- [83] S. Schmidt, Zs. Czigány, G. Greczynski, J. Jensen, and L. Hultman. Ion mass spectrometry investigations of the discharge during reactive high power pulsed and direct current magnetron sputtering of carbon in Ar and Ar/ N_2 . *Journal of Applied Physics*, 112(1):013305, 2012.
- [84] R. Gago, G. Abrasonis, A. Mücklich, W. Möller, Zs. Czigány, and G. Radnóczy. Fullerene-like arrangements in carbon nitride thin films grown by direct ion beam sputtering. *Applied Physics Letters*, 87(7):071901, 2005.
- [85] A. Furlan. *Fullerene-like CN_x and CP_x thin films; synthesis, modeling and applications*. PhD thesis, Linköping University, 2009.
- [86] A. Furlan, G. K. Gueorguiev, H. Högborg, S. Stafström, and L. Hultman. Fullerene-like CP_x : A first-principles study of the relative stability of precursors and defect energetics during synthetic growth. *Thin Solid Films*, 515(3):1028–1032, 2006.
- [87] X. Ji, K. T. Lee, and L. F. Nazar. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nature materials*, 8(6):500–6, 2009.
- [88] C. Lai, X. P. Gao, B. Zhang, T. Y. Yan, and Z. Zhou. Synthesis and electrochemical performance of sulfur/highly porous carbon composites. *The Journal of Physical Chemistry C*, 113(11):4712–4716, 2009.
- [89] W. Kiciński, M. Szala, and M. Bystrzejewski. Sulfur-doped porous carbons: Synthesis and applications. *Carbon*, 68:1–32, 2014.
- [90] N. Moolradoo and S. Watanabe. Deposition and tribological properties of sulfur-doped DLC films deposited by PBII method. *Advances in Materials Science and Engineering*, 2010:1–7, 2010.

- [91] S. Wan, L. Wang, and Q. Xue. Electrochemical deposition of sulfur doped DLC nanocomposite film at atmospheric pressure. *Electrochemistry Communications*, 12(1):61–65, 2010.
- [92] K. Honglertkongsakul, P. W. May, and B. Paosawatyanong. Effect of temperature on sulfur-doped diamond-like carbon films deposited by pulsed laser ablation. *Diamond and Related Materials*, 20(8):1218–1221, 2011.
- [93] I. Felner and Y. Kopelevich. Magnetization measurement of a possible high-temperature superconducting state in amorphous carbon doped with sulfur. *Physical Review B*, 79(23):233409, 2009.
- [94] I. Felner, O. Wolf, and O. Millo. High-temperature superconductivity in sulfur-doped amorphous carbon systems. *Journal of Superconductivity and Novel Magnetism*, 25(1):7–10, 2011.
- [95] I. Felner and E. Prilutskiy. Unusual magnetic properties and superconductivity in sulfur-doped amorphous carbon powder. *Journal of Superconductivity and Novel Magnetism*, 25(8):2547–2555, 2012.
- [96] I. Sakaguchi, M. N.-Gamo, Y. Kikuchi, E. Yasu, H. Haneda, T. Suzuki, and T. Ando. Sulfur: A donor dopant for n-type diamond semiconductors. *Physical Review B*, 60(4):R2139–R2141, 1999.
- [97] D. Saada, J. Adler, and R. Kalish. Sulfur: A potential donor in diamond. *Applied Physics Letters*, 77(6):878–879, 2000.
- [98] R. da Silva, J. Torres, and Y. Kopelevich. Indication of superconductivity at 35 K in graphite-sulfur composites. *Physical Review Letters*, 87(14):147001, 2001.
- [99] P. A. Denis, R. Faccio, and A. W. Mombru. Is it possible to dope single-walled carbon nanotubes and graphene with sulfur? *Chemphyschem : a European journal of chemical physics and physical chemistry*, 10(4):715–722, 2009.
- [100] G. Kucukayan, R. Ovali, S. Ilday, B. Baykal, H. Yurdakul, S. Turan, O. Gulseren, and E. Bengu. An experimental and theoretical examination of the effect of sulfur on the pyrolytically grown carbon nanotubes from sucrose-based solid state precursors. *Carbon*, 49(2):508–517, 2011.
- [101] J. M. Romo-Herrera, D. A. Cullen, E. Cruz-Silva, D. Ramírez, B.G. Sumpter, V. Meunier, H. Terrones, D.J. Smith, and M. Terrones. The role of sulfur in the synthesis of novel carbon morphologies: from covalent Y-junctions to sea-urchin-like structures. *Advanced Functional Materials*, 19(8):1193–1199, 2009.
- [102] C. Goyenola, G. K. Gueorguiev, S. Stafström, and L. Hultman. Fullerene-like CS_x : A first-principles study of synthetic growth. *Chemical Physics Letters*, 506(1-3):86–91, 2011.

- [103] C. Goyenola, S. Stafström, L. Hultman, and G. K. Gueorguiev. Structural patterns arising during synthetic growth of fullerene-like sulfocarbide. *The Journal of Physical Chemistry C*, 116(39):21124–21131, 2012.
- [104] K. Endo, K. Shinoda, and T. Tatsumi. Plasma deposition of low-dielectric-constant fluorinated amorphous carbon. *Journal of Applied Physics*, 86(5):2739–2745, 1999.
- [105] S. Agraharam, D. W. Hess, P. A. Kohl, and S. A. Bidstrup Allen. Comparison of plasma chemistries and structure-property relationships of fluorocarbon films deposited from octafluorocyclobutane and pentafluoroethane monomers. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 19(2):439–446, 2001.
- [106] H.-S. Jung and H.-H. Park. Structural and electrical properties of co-sputtered fluorinated amorphous carbon film. *Thin Solid Films*, 420-421:248–252, 2002.
- [107] M. Ishihara, M. Suzuki, T. Watanabe, T. Nakamura, A. Tanaka, and Y. Koga. Synthesis and characterization of fluorinated amorphous carbon films by reactive magnetron sputtering. *Diamond and Related Materials*, 14(3-7):989–993, 2005.
- [108] S. Bai, T. Onodera, R. Nagumo, R. Miura, A. Suzuki, H. Tsuboi, N. Hatakeyama, H. Takaba, M. Kubo, and A. Miyamoto. Friction reduction mechanism of hydrogen- and fluorine-terminated diamond-like carbon films investigated by molecular dynamics and quantum chemical calculation. *The Journal of Physical Chemistry C*, 116(23):12559–12565, 2012.
- [109] G. Tang, X. Ma, M. Sun, and X. Li. Mechanical characterization of ultrathin fluorocarbon films deposited by R.F. magnetron sputtering. *Carbon*, 43(2):345–350, 2005.
- [110] Y. Yun, E. Broitman, and A. J. Gellman. Oxidation of fluorinated amorphous carbon (α -CF_x) films. *Langmuir: the ACS journal of surfaces and colloids*, 26(2):908–914, 2010.
- [111] E. J. Winder and K. K. Gleason. Growth and characterization of fluorocarbon thin films grown from trifluoromethane (CHF₃) using pulsed-plasma enhanced CVD. *Journal of Applied Polymer Science*, 78(4):842–849, 2000.
- [112] A. Milella, F. Palumbo, P. Favia, G. Cicala, and R. D’Agostino. Continuous and modulated deposition of fluorocarbon films from $\text{c-C}_4\text{F}_8$ plasmas. *Plasma Processes and Polymers*, 1(2):164–170, 2004.
- [113] E. Sardella, F. Intranuovo, P. Rossini, M. Nardulli, R. Gristina, R. D’Agostino, and P. Favia. Plasma enhanced chemical vapour deposition of nanostructured fluorocarbon surfaces. *Plasma Processes and Polymers*, 6(S1):S57–S60, 2009.

- [114] G. K. Gueorguiev, C. Goyenola, S. Schmidt, and L. Hultman. CF_x : A first-principles study of structural patterns arising during synthetic growth. *Chemical Physics Letters*, 516(1-3):62–67, 2011.
- [115] S. Schmidt, C. Goyenola, G. K. Gueorguiev, J. Jensen, G. Greczynski, I. G. Ivanov, Zs. Czigány, and L. Hultman. Reactive high power impulse magnetron sputtering of CF_x thin films in mixed Ar/CF_4 and $\text{Ar}/\text{C}_4\text{F}_8$ discharges. *Thin Solid Films*, 542:21–30, 2013.
- [116] C. Goyenola, S. Stafström, S. Schmidt, L. Hultman, and G. K. Gueorguiev. Carbon fluoride, CF_x : structural diversity as predicted by first principles. *The Journal of Physical Chemistry C*, 2014.
- [117] G. K. Gueorguiev and J. M. Pacheco. Silicon and metal nanotemplates: Size and species dependence of structural and electronic properties. *The Journal of Chemical Physics*, 119(19):10313–10317, 2003.
- [118] G. K. Gueorguiev, J. M. Pacheco, S. Stafström, and L. Hultman. Silicon–metal clusters: Nano-templates for cluster assembled materials. *Thin Solid Films*, 515(3):1192–1196, 2006.
- [119] J. Pacheco, G. K. Gueorguiev, and J. Martins. First-principles study of the possibility of condensed phases of endohedral silicon cage clusters. *Physical Review B*, 66(3):033401, 2002.
- [120] G. K. Gueorguiev, S. Stafström, and L. Hultman. Nano-wire formation by self-assembly of silicon–metal cage-like molecules. *Chemical Physics Letters*, 458(1-3):170–174, 2008.
- [121] A. Kakanakova-Georgieva, G. K. Gueorguiev, R. Yakimova, and E. Janzén. Effect of impurity incorporation on crystallization in AlN sublimation epitaxy. *Journal of Applied Physics*, 96(9):5293–5297, 2004.
- [122] R. Yakimova, A. Kakanakova-Georgieva, G. R. Yazdi, G. K. Gueorguiev, and M. Syväjärvi. Sublimation growth of AlN crystals: Growth mode and structure evolution. *Journal of Crystal Growth*, 281(1):81–86, 2005.
- [123] A. Kakanakova-Georgieva, G. K. Gueorguiev, S. Stafström, L. Hultman, and E. Janzén. AlGaInN metal-organic-chemical-vapor-deposition gas-phase chemistry in hydrogen and nitrogen diluents: First-principles calculations. *Chemical Physics Letters*, 431(4-6):346–351, 2006.
- [124] J. P. Perdew, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Physical Review B*, 46(11):6671–6687, 1992.
- [125] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al. Gaussian 09, Gaussian Inc. Wallingford CT, 2009.

- [126] S. Oae. *Organic sulfur chemistry: structure and mechanism*. CRC Press, 1st edition, 1991.
- [127] J. Neidhardt, L. Hultman, B. Abendroth, R. Gago, and W. Möller. Diagnostics of a N_2/Ar direct current magnetron discharge for reactive sputter deposition of fullerene-like carbon nitride thin films. *Journal of Applied Physics*, 94(11):7059, 2003.
- [128] G. K. Gueorguiev, J. Neidhardt, S. Stafström, and L. Hultman. First-principles calculations on the role of CN precursors for the formation of fullerene-like carbon nitride. *Chemical Physics Letters*, 401(1-3):288–295, 2005.
- [129] R. M. Martin. *Electronic structure: basic theory and practical methods*. Cambridge: Cambridge Univ. Press, 2004.
- [130] R. G. Parr and W. Yang. *Density functional theory of atoms and molecules*. Oxford: Clarendon Press; New York: Oxford Univ. Press, 1989.
- [131] F. Jensen. *Introduction to computational chemistry*. Chichester: Wiley, cop., 2nd edition, 2007.
- [132] M. Born and R. Oppenheimer. Zur quantentheorie der molekeln. *Annalen der Physik*, 20(84):457–484, 1927.
- [133] L. H. Thomas. The calculation of atomic fields. *Mathematical Proceedings of the Cambridge Philosophical Society*, 23(05):542, 1927.
- [134] E. Fermi. Un Metodo Statistico per la Determinazione di alcune Prioprietà dell’Atomo. *Rend. Accad. Naz. Lincei*, 6:602–607, 1927.
- [135] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864–B871, 1964.
- [136] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133–A1138, 1965.
- [137] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka. Prescription for the design and selection of density functional approximations: More constraint satisfaction with fewer fits. *Journal of Chemical Physics*, 123(6), 2005.
- [138] A. Szabo and N. S. Ostlund. Configuration Interaction. In *Modern Qunatum Chemistry - Introduction to advanced electronic structure theory*, chapter 4, pages 231–270. Dover Publications, Inc., New York, 2006.
- [139] J. P. Perdew and K. Schmidt. Jacob’s ladder of density functional approximations for the exchange-correlation energy. *AIP Conference Proceedings*, 577(Density Functional Theory and Its Application to Materials):1–20, 2001.

- [140] S. F. Sousa, P. A. Fernandes, and M. J. Ramos. General performance of density functionals. *The journal of physical chemistry A*, 111(42):10439–52, 2007.
- [141] A. D. Becke. Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*, 98(7):5648–5652, 1993.
- [142] J. A. Plumley and J. J. Dannenberg. A comparison of the behavior of functional/basis set combinations for hydrogen-bonding in the water dimer with emphasis on basis set superposition error. *Journal of computational chemistry*, 32(8):1519–27, 2011.
- [143] W. J. Hehre. Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *The Journal of Chemical Physics*, 56(5):2257, 1972.
- [144] M. J. Frisch, J. A. Pople, and J. S. Binkley. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *The Journal of Chemical Physics*, 80(7):3265, 1984.
- [145] M. M. Francl. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *The Journal of Chemical Physics*, 77(7):3654, 1982.
- [146] H. F. Winters and J. W. Coburn. Surface science aspects of etching reactions. *Surface Science Reports*, 14(4-6):162–269, 1992.
- [147] P. Hammer and F. Alvarez. Influence of chemical sputtering on the composition and bonding structure of carbon nitride films. *Thin Solid Films*, 398-399:116–123, 2001.
- [148] J. Alami, K. Sarakinos, F. Uslu, and M. Wuttig. On the relationship between the peak target current and the morphology of chromium nitride thin films deposited by reactive high power pulsed magnetron sputtering. *Journal of Physics D: Applied Physics*, 42(1):015304, 2008.
- [149] V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson, and I. Petrov. A novel pulsed magnetron sputter technique utilizing very high target power densities. *Surface and Coatings Technology*, 122(2-3):290–293, 1999.
- [150] D. Lundin. *The HiPIMS process*. PhD thesis, Linköping University, 2010.
- [151] J. Bohlmark, M. Lattemann, J. T. Gudmundsson, A. P. Ehiasarian, Y. Aranda Gonzalvo, N. Brenning, and U. Helmersson. The ion energy distributions and ion flux composition from a high power impulse magnetron sputtering discharge. *Thin Solid Films*, 515(4):1522–1526, 2006.
- [152] G. Greczynski, J. Lu, M. P. Johansson, J. Jensen, I. Petrov, J. E. Greene, and L. Hultman. Role of Ti^{n+} and Al^{n+} ion irradiation ($n=1,2$) during $\text{Ti}_{1-x}\text{Al}_x\text{N}$ alloy film growth in a hybrid HIPIMS/magnetron mode. *Surface and Coatings Technology*, 206(19-20):4202–4211, 2012.

- [153] A. P. Ehiasarian and W. D. Münz. High power pulsed magnetron sputtered CrN_x films. *Surface and coatings*, 164:267–272, 2003.
- [154] A. P. Ehiasarian, P. Eh Hovsepien, L. Hultman, and U. Helmersson. Comparison of microstructure and mechanical properties of chromium nitride-based coatings deposited by high power impulse magnetron sputtering and by the combined steered cathodic arc/unbalanced magnetron technique. *Thin Solid Films*, 457(2):270–277, 2004.
- [155] E. de Hoffmann and V. Stroobant. *Mass spectrometry: Principles and applications*. John Wiley & Sons Ltd, 2008.
- [156] For thin films, plasma and surface engineering. Hiden Analytical. http://www.hidenanalytical.com/en/?option=com_content&view=article&id=521&catid=192&Itemid=149. Accessed: 2015-07-10, 2015.
- [157] D. Chescoe and P. J. Goodhew. *The operation of transmission and scanning electron microscopes*. Oxford University Press, New York, 1990.
- [158] D. B. Williams and C. B. Carter. *Transmission electron microscopy - A textbook for materials science*. Plenum Press, New York, 1996.
- [159] Zs. Czigány and L. Hultman. Interpretation of electron diffraction patterns from amorphous and fullerene-like carbon allotropes. *Ultramicroscopy*, 110(7):815–819, 2010.
- [160] P. van der Heide. *X-ray photoelectron spectroscopy : An introduction to principles and practices*. John Wiley & Sons,, Hoboken, NJ, 2011.
- [161] F. Schiettekatte and M. Chicoine. Elastic recoil detection analysis. In *Characterization of Materials*, pages 1994–2006. John Wiley & Sons, Inc., Hoboken, NJ, 2012.
- [162] S.-L. Zhang. *Raman spectroscopy and its application in nanostructures*. John Wiley & Sons, Hoboken, NJ, 2nd edition, 2012.
- [163] A. C. Ferrari. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Communications*, 143(1-2):47–57, 2007.
- [164] W. C. Oliver and G. M. Pharr. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *Journal of Materials Research*, 19(01):3–20, 2004.
- [165] J.L. Hay, M. E. O’Hern, and W. C. Oliver. The importance of contact radius for substrate-independent property measurement of thin films. *MRS Proceedings*, 522:27, 2011.
- [166] A. M. Korsunsky, M. R. McGurk, S. J. Bull, and T. F. Page. On the hardness of coated systems. *Surface and Coatings Technology*, 99(1-2):171–183, 1998.

List of included Publications

- [I] **Fullerene-like CS_x : A first-principles study of synthetic growth**
C. Goyenola, G. K. Gueorguiev, S. Stafström, L. Hultman
Chemical Physics Letters, **506**, 86-91 (2011)
- [II] **Structural patterns arising during synthetic growth of fullerene-like sulfocarbide**
C. Goyenola, S. Stafström, L. Hultman and G. K. Gueorguiev
The Journal of Physical Chemistry C, **116**, 21124-21131 (2012)
- [III] **CF_x : A first-principles study of structural patterns arising during synthetic growth**
G. K. Gueorguiev, C. Goyenola, S. Schmidt, L. Hultman
Chemical Physics Letters, **516**, 62-67 (2011)
- [IV] **CF_x thin solid films deposited by high power impulse magnetron sputtering: Synthesis and characterization**
S. Schmidt, G. Greczynski, C. Goyenola, G. K. Gueorguiev, Zs. Czigány, J. Jensen, I. G. Ivanov, L. Hultman
Surface & Coatings Technology, **206**, 646-653 (2011)
- [V] **Reactive high power impulse magnetron sputtering of CF_x thin films in mixed Ar/CF_4 and $\text{Ar}/\text{C}_4\text{F}_8$ discharges**
S. Schmidt, C. Goyenola, G. K. Gueorguiev, J. Jensen, G. Greczynski, I. G. Ivanov, Zs. Czigány, L. Hultman
Thin Solid Films, **542**, 21-30 (2013)
- [VI] **Carbon fluoride, CF_x : structural diversity as predicted by first principles**
C. Goyenola, S. Stafström, S. Schmidt, L. Hultman, G. K. Gueorguiev
The Journal of Physical Chemistry C, **118**, 6514-6521 (2014)
- [VII] **Theoretical prediction and synthesis of CS_xF_y thin films**
C. Goyenola, C.-C. Lai, L.-Å. Näslund, J. Lu, H. Högberg, L. Hultman, J. Rosen, G. K. Gueorguiev
In manuscript

My contribution to the papers

With the input of my supervisor Gueorgui K. Gueorguiev and other coauthors I planned, executed, and performed all the calculations and analyzed the results of all the theoretical work presented in all the papers. I wrote the first draft of Papers I, II, VI, and VII, I have conducted the re-writing process and submitted them. For Paper III, I participated of the writing process after the first draft and made all the figures. For Papers IV and V, I wrote the first draft of the theoretical part including the corresponding figures, and I participated in the discussions and in the re-writing process.

Related, not included Publications

[1] **Designing carbon-based thin films from graphene-like nanostructures**

C. Goyenola, G. K. Gueorguiev

Chapter 39, Graphene Science Handbook: Nanostructure and Atomic Arrangement, Edited by Z. A. Niknam, CRC Press, 2015 - In press

Publications

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-121021>