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Microscopic and spectroscopic studies of metal deposition on carbon-based materials

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MICROSCOPIC AND SPECTROSCOPIC STUDIES OF METAL DEPOSITION
ON CARBON-BASED MATERIALS

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ABSTRACT

Microscopic and Spectroscopic Studies of Metal Deposition on Carbon-based Materials

by

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This dissertation is focused on studying the atomic and electronic structure of carbon-based materials, namely highly-ordered pyrolytic graphite (HOPG), single-walled carbon nanotubes (SWNT), and C₆₀ fullerenes, with and without metal (Ti and Li) deposition. The work is motivated by ongoing efforts to understand and improve the hydrogen storage capability of carbon-based nanomaterials as well as their potential applications for developing novel electronic devices.

Ti and Li deposition on the surface of SWNT, C₆₀, and HOPG samples have been performed in ultra-high vacuum. The morphology and local geometric and electronic structure of the samples was investigated by scanning tunneling microscopy and spectroscopy (STM and STS). The chemical and electronic structure of the samples was studied by X-ray and UV photoelectron spectroscopy (PES). Changes in the carbon core- and valence-electronic levels upon metal deposition were observed and correlated with detailed morphological and electronic characteristics. The results give detailed
information about the interaction between metal adatoms and carbon-based materials. In addition, several important aspects related to the deposited metals, such as the formation of oxides, were studied. The results provide fundamental insight into metal-carbon interactions and help to develop approaches to improve the performance of carbon-based materials for hydrogen storage and novel electronic devices.
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CHAPTER I

INTRODUCTION

Carbon-based nanomaterials such as fullerenes and carbon nanotubes, are forefront players in the development of nanotechnology due to their unique properties and their ability to form compounds with a large variety of other elements. The extraordinary properties of carbon-based nanomaterials stem from nano-sized carbon network structures with a large surface area, which facilitates chemical modifications by doping with other elements. Consequently, by proper choice of the type of modification, the electronic properties of carbon-based nanomaterials can be deliberately tailored to meet practical applications. For instance, modification of carbon nanostructures by decoration with transition metals or doping with alkali-metals offers a wide range of tunability of electronic and structural characteristics, such as conductivity and catalytic capability. Thus, the influence of metals and the interactions at the metal-carbon interface are important, both from a fundamental point of view as well as for potential applications of metal-modified (e.g., metal-decorated or -doped) carbon nanomaterials. In addition, effects of defects, impurities, oxidation could play critical roles to characteristics of metal formation.

This thesis presents surface investigations of two different modifications of carbon-based materials with metal depositions, namely the deposition of Ti (transition metal) and
Li (alkali-metal) on graphite (HOPG), C$_{60}$ fullerenes and single-walled carbon nanotubes (SWNTs). The investigations are motivated by potential applications of metal-decorated carbon nanostructures in hydrogen storage as well as in the fabrication of electronic devices on the nanoscale. The formation of selected metal adatoms on carbon-based structures and the induced metal-carbon interactions were investigated by spectroscopic and microscopic techniques. Moreover, fundamental issues related to practical uses of these metal-decorated carbon nanostructures, such as oxidation behavior and clustering of metal adatoms, were identified and characterized.

A brief description on atomic arrangement and electronic structure of carbon-based materials is given in Chapter II. Furthermore, the state-of-the-art of current theoretical and experimental investigations of metal-doped carbon-based materials is reviewed.

Chapter III describes the basic principles of the experimental techniques used in this investigation, namely photoelectron spectroscopy and scanning tunneling microscopy and spectroscopy. The experimental setup, the sample preparation procedures, and the experimental plan for the study of metal-decorated carbon-based materials are presented.

In Chapter IV, the deposition of Ti and Li on a Au/Si substrate is reported. Photoelectron spectroscopy is used to derive the metal deposition rates of Ti and Li for the subsequent deposition experiments on carbon-based materials. In this chapter, the formation and morphology of the deposited metal layers are described using results from scanning tunneling microscopy. Furthermore, the oxidation behavior of these metals in ultra-high vacuum will be discussed.

Chapter V presents a study of the electronic structure of the different carbon-based materials, especially in view of the presence of defects and impurities, as well as the
different atomic arrangements of carbon atoms in the systems under study. For these studies an optimized sample preparation to separate individual nanotubes was developed, and examples from the various preparation steps will be shown in this chapter. Furthermore, it presents microscopy and local electronic spectroscopy results from individual nanotubes on the atomic scale.

In Chapter VI and VII, the depositions of Ti and Li on carbon-based materials are discussed, respectively. The metal-carbon interaction in specific atomic arrangements of carbon-based materials is discussed using results from photoelectron spectroscopy. In addition, oxidation behavior of deposited metals on carbon-based materials in ultra-high vacuum will be described. Morphology and formation of metals on carbon-based materials are presented with the results of scanning tunneling microscopy.

The concluding Chapter VIII summarizes the experimental results and presents an outlook for future experiments to investigate the atomic and electronic structure of metal-deposited carbon-based materials, among others with a focus on the hydrogen storage capability of such materials.
CHAPTER II

LITERATURE REVIEW

Carbon is one of the most important elements, which can be found not only as a constituent of millions of compounds, but also in various stable forms of carbon allotropes. Carbon is capable of bonding with other elements to form various carbon-related materials with an enormous range of chemical and physical properties. Even for materials containing exclusively carbon, a wide range of material properties is observed. Elemental carbon in its well-known, three-dimensional, chemical allotropes of graphite and diamond has been developed as structural and functional materials for a large number of highly specialized applications. In addition to the bulk carbon structures, much attention has recently focused on small carbon clusters, formed on the basis of a (single) two-dimensional graphene layer. The discovery of fullerenes, which are “zero-dimensional” carbon allotropes, in 1985 [1] has been a direct stimulus to the systematic study of carbon nanostructures. This was followed by the discovery of carbon nanotubes in 1991 [2], which have a “one-dimensional” carbon structure. Since then, carbon nanostructures have motivated a large number of studies of their unique physical and chemical properties, both from a fundamental point of view as well as with respect to potential applications as building blocks for various nanoscale devices.
In this chapter, the basic concepts of the geometric and electronic structure of carbon-based materials, namely HOPG (graphite), \( C_{60} \) fullerene molecules, and single-walled carbon nanotubes (SWNT) will be reviewed (Section 2-1). Current research on modifications of carbon-based materials by metal deposition and their potential applications will be presented in Section 2-2.

Section 2-1

Electronic and Geometric Structure of Carbon and Carbon-based Materials

Carbon is the most studied element in the periodic table. There are many reviews, even whole textbooks, journals, and handbooks, describing the properties of carbon-based materials [3-8]. In this section, the basic concepts of the electronic structure and the atomic arrangement of carbon atoms in carbon-based materials relevant to this thesis will be presented.

The large range of properties for carbon materials is mainly caused by the fact that carbon can form different bonding configurations by rearranging its outer electrons. Carbon is a group IV element with atomic number 6. Each carbon atom has 6 electrons, which occupy 1s, 2s, and 2p atomic orbitals, as shown in Fig. 2.1. The 1s orbital contains two strongly bound core electrons. Four more weakly bound electrons occupy the 2s, and 2p valence orbitals, and the ground state electron configuration of an isolated atom is thus \( 1s^2 \ 2s^2 \ 2p^2 \) (by convention, the \( 2p^2 \) electrons occupy the \( 2p_x \) and \( 2p_y \) orbitals). In a bonded configuration, one of the \( 2s \) electron is promoted to the previously empty \( 2p_z \) orbital to give rise to a \( 2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1 \) electron configuration in the outer shell. Because the energy difference between the \( 2p \) levels and the \( 2s \) level in carbon is small compared with
the energy of chemical bonds, the four valence orbitals can readily mix with each other to form different covalent bonds. This hybridization of the 2s and 2p atomic orbitals in carbon leads to different structural arrangements of carbon atoms. There are three possible $sp^n$ hybridizations of the valence electrons in carbon ($n=1, 2, 3$), depending on
the mixing of a single 2s electron with one, two, or three 2p electrons (Fig. 2.1). The $sp^l$ hybridization consists of linear $\sigma$-bonds, giving rise to a chain structure, which is not relevant for the carbon-based materials in this thesis. The $sp^2$ hybridization leads to three planar $\sigma$-bonds directed to the corners of an equilateral triangle (i.e., uniformly distributed in the plane), while the un-hybridized 2p orbital is perpendicular to this plane. The adjacent 2p orbitals can overlap to form a $\pi$-bond, which is parallel to the $\sigma$-bond along the line connecting the two adjacent atoms. In $sp^3$ hybridization, all four of the singly occupied orbitals are hybridized, forming four tetrahedrally oriented $\sigma$-bonds of equal length.

Such different atomic arrangements and corresponding hybridization bonds are responsible for very different structural and electronic properties of the corresponding carbon structures. In graphene, a single layer of carbon atoms is packed into a hexagonal ring structure (benzene ring). The graphene sheet is a one-atom thick, two-dimensional layer of $sp^2$-bonded carbons and is predicted to have unusual properties [9]. Graphite has a planar layered structure and can be viewed as a three-dimensional system consisting of stacked two-dimensional graphene layers (Fig. 2.2, left), which interact by weak Van der Waals forces. Within each layer, the carbon atoms are interconnected by strong covalent $sp^2$-bonding, forming the honeycomb graphene lattice. The overlap of the un-hybridized 2p orbitals at each C site produces a delocalized intraplanar $\pi$-system that is responsible for the semi-metal character. Since the individual graphene layers are weakly bonded to each other they can easily be peeled off which makes graphite a soft material. In addition, the low surface free energy of graphite makes its surface hydrophobic and chemically inert to molecular adsorbates. In contrast, diamond is composed of a three-dimensional
tetrahedral network of covalently-bonded carbon atoms (Fig. 2.2, right). In diamond, single covalent bonds are formed by the overlap of $sp^3$ hybrid orbitals on each carbon atom, which makes diamond very hard and, due to the absence of a delocalized $\pi$-system, an insulating material.

Graphite is available in the form of natural single-crystal graphite flakes or synthetic single-crystal, called "kish graphite". The most commonly used high-quality graphitic material for scientific studies is *Highly Oriented Pyrolytic Graphite* (HOPG), which is prepared by pyrolysis of hydrocarbons at temperatures above 2000°C. The resulting pyrolytic carbon is subsequently heated to higher temperatures to improve its crystalline order [11]. High-quality HOPG exhibits electronic, transport, thermal, and mechanical properties very similar to those of single-crystal graphite. This material is commonly used because of its good physical properties, high chemical purity, and relatively large sample sizes. HOPG has a structure of polycrystals, the size of which varies and depends
on the quality of the synthesis and can be observed as a mosaic structure on the surface. Because of its layered structure, HOPG can be easily cleaved to produce a flat surface, which is suitable as a substrate for many samples in surface analytical studies. For example, the high-quality HOPG surface is usually used as a “calibration” sample for scanning probe microscopes. In this case, producing an atomically resolved image of the hexagonal carbon lattice is a suitable benchmark for a high-resolution instrument. The flatness (roughness) of the surface also depends on the quality of the HOPG sample. The freshly cleaved surface consists of terraces with atomic steps (3.35 Å - the distance between graphene layers, Fig. 2.2, left) and multi-atomic steps. As a result, the actual surface of HOPG may have a certain number of defects, such as grain boundaries, dangling bonds, voids, and adsorbates of oxidized carbons or hydrocarbons bonded in an $sp^3$ hybrid-like environment.

The graphene layer (basal plane) of an ideal crystal structure of graphite (Fig. 2.2, left) consists of carbon atoms arranged in a honeycomb network containing two atoms per unit cell, labeled A and B. The graphene layers are stacked in such a way that the A atoms on consecutive layers are on top of one another, but the B atoms in one plane are over the unoccupied centers of the adjacent layers (Fig. 2.3). In this arrangement, each carbon atom has three in-plane nearest-neighbors with a distance $ac-c$ of 1.42 Å, but the in-plane lattice constant $a$, the distance between nearest equivalent carbon sites, is 2.46 Å. Thus, there are two possible atomically resolved STM images of the graphite structure, as illustrated in Fig. 2.3 for STM images of a HOPG sample [10]. The image normally obtained looks like a close-packed trigonal network in which only one site of the carbon hexagonal network, e.g., the B site in Fig. 2.3a, is observed with high
Fig. 2.3: Schematic illustration and corresponding STM images of two types of atomic arrangements of the HOPG surface; (a) tetragonal network of carbon atoms with an atom-atom distance of 2.46 Å; (b) hexagonal network of carbon atoms with an atom-atom distance of 1.42 Å. The image frame is 2x2 nm². The linescan cross-sections below the images correspond to the lines drawn in the images. Images were taken from [10].
tunneling current. In this close-packed array, each atom is surrounded by six nearest neighbors. The distance between any two of these atoms is 2.46 Å. Under ideal conditions, particularly if the STM probe tip is truly a single atom, the hexagonal ring structure (i.e., the true structure of graphite) can be obtained, as shown in Fig. 2.3b. The center-to-center atomic distance in this image is 1.42 Å.

For many decades it was believed that carbon networks only exist in the structure of graphite and diamond. The discovery of new carbon networks in fullerenes and subsequently in carbon nanotubes was thus a real breakthrough in carbon science. These carbon allotropes can conceptually be described by the structure of a graphene layer. If the structure of graphite can be derived by stacking graphene sheets, then the graphene layer can also be wrapped up into “0-dimensional” fullerenes or seamlessly rolled into “1-dimensional” nanotubes (Fig. 2.4). The strain induced by the curvature of both fullerenes and nanotubes is compensated by the elimination of dangling bonds at the edge atoms of the graphene sheet. Thus, structures of carbon atoms in fullerenes and nanotubes are stable.

The majority of studies in fullerene chemistry have involved C_{60}, which is the most common fullerene. The C_{60} molecule consists of sixty equivalent carbon atoms in a closed cage structure with a diameter of \sim 7 Å. The hexagonal \textit{sp}^2 carbon network is closed by introducing 12 pentagons into the structure of C_{60}, in addition to 20 hexagons. Consequently, there are two distinct types of C-C bonds in C_{60}. The bonds in a hexagon ring (bond length 1.38 Å) are shorter than the bonds at hexagon-pentagon junctions (bond length 1.45 Å) [13].
The first experimental observation of carbon nanotubes revealed a structure consisting of several coaxial tubes. These carbon nanotubes are termed “multi-walled carbon nanotubes” (MWNTs) [2]. Carbon nanotubes consisting of a single graphitic layer are called “single-walled carbon nanotubes” (SWNTs) [15, 16]. As-growth carbon nanotubes are usually capped by hemispherical structures of fullerenes. SWNTs can be classified into “armchair”, “zigzag”, or “chiral” types (Fig. 2.5), depending on the way the graphene sheet is rolled up, which determines the geometric structures (radius and chirality) of the nanotubes (Fig. 2.6). As a consequence of the different geometric structures, the electronic structure of the $sp^2$-hybridized carbon network in carbon nanotubes can exhibit characteristics of a semiconductor or a metal, depending on their diameter and chiral vector [17-19]. In other words, similar molecules consisting of only one element (carbon) may have very different electronic behaviors. These predicted remarkable electronic properties of carbon nanotubes have been confirmed experimentally using scanning tunneling microscopy and spectroscopy [20, 21].
Fig. 2.5: Three types of SWNTs: "zigzag", "armchair", and "chiral" [12].

Fig. 2.6: Seamlessly "rolling up" a graphene sheet to form an "armchair" nanotube [12].
Detailed considerations of the relationship between geometric structures and electronic properties of nanotubes can be found in References 20-22. A schematic presentation on the construction of the nanotube from a graphene sheet is shown in Fig. 2.7. Any carbon nanotube can be uniquely described by a pair of integer numbers \((m,n)\), called "chiral index", which in turn is representative for the "chiral vector" and the "chiral angle" of the tube. The chiral vector \(C_h\) defines the "direction" in which the graphite sheet is rolled up into a tube, so that the points O and A in Fig. 2.7a will end up on top of each other. The circumference of the tube can then be expressed by a vector \(C_h = na_1 + ma_2\), where \(a_1\) and \(a_2\) are unit vectors of the hexagonal lattice of the graphene sheet. The nanotube diameter is given by:

\[
d = \frac{|C_h|}{\pi} = 3a_{C-C} \frac{\sqrt{m^2 + mn + n^2}}{\pi},
\]

where \(a_{C-C}\) is the C-C bond length (1.42 Å).

The chiral angle \(\theta\) defines the angle between chiral vector \(C_h\) and the "zigzag" direction \((\theta = 0)\), as indicated in Fig. 6a and can be defined by:

\[
\theta = \tan^{-1}\left(\frac{\sqrt{3}n}{2m + n}\right), \text{ where } 0 \leq \theta \leq 30^\circ
\]

It can be seen from Fig. 2.7a that the choice of vector \(C_h\) (in length and angle) in the hexagonal plane of the graphene sheet specifies a particular way to "roll up" the graphene sheet and hence describes a unique nanotube. The two most common nanotubes are formed when \(m = n \ (\theta = 30^\circ)\) and \(n = 0 \ (\theta = 0^\circ)\), corresponding to an "armchair tube" and a "zigzag tube", respectively. The "chiral" nanotubes have chiral angles of \(0 < \theta < 30^\circ\).
Fig. 2.7: (a) Mathematic presentation on the construction of the nanotube from hexagonal lattice of a graphite sheet; (b) Possible nanotubes constructed from a graphene sheet, together with their electronic properties [22].
As mentioned above, the geometric structure of the tubes determines their electronic properties. According to theoretical calculations [17-19], armchair tubes \((m = n)\) have bands crossing the Fermi level and are therefore metallic. The zigzag and chiral tubes can be either metallic or semiconducting, depending on the relationship of the pair index \((m, n)\). If \(m - n = 3l\), where \(l\) is an integer, the tubes are expected to be metallic. If \(m - n \neq 3l\), the tubes are predicted to be semiconducting. Fig. 2.7b presents a map of possible constructions of nanotubes from a graphene sheet with denoted indices and corresponding electronic characteristics.

Experimentally synthesized SWNTs usually have a diameter of \(\sim 1-2\) nm. The smallest carbon nanotubes with a diameter of \(0.4\) nm, corresponding to possible chiral indices of \((3, 3), (4, 3),\) or \((5, 1)\), have just recently been reported [23]. It also has been found that the smallest tubes are capped with a hemisphere made of a C\(_{20}\) molecule, the smallest stable fullerene [24].

It is clear that to correlate the electronic properties of a tube in such a small dimension with its geometric structure, atomically resolved images are required. Scanning tunneling microscopy and spectroscopy, which can both resolve the geometric structure on an atomic scale and characterize the local electronic structure, are a great choice for investigating this fascinating class of carbon-based materials. An excellent review on the application of STM to investigate the atomic and electronic structure of carbon nanotubes is given in Ref [25]. In Chapter V of this thesis, experimental spectroscopic characterizations of the electronic structure of carbon-based materials with different atomic arrangements of carbon atoms will be discussed. In particular, results of
sample preparations for individual nanotubes and STM investigations on carbon nanotubes will be presented.

Section 2-2

Modification of Carbon-based Materials by Metal Deposition:

Fundamental Studies and Potential Applications

The unique atomic configurations and electronic structures of carbon atoms in the above described allotropes have attracted strong research interest in both fundamental and applied studies [3-8, 26-31]. It is now well established that fullerenes and carbon nanotubes are ideal models for studying the physics of zero- and one-dimensional systems, respectively. They also have significant potential as building blocks for various practical nanoscale devices, which is particularly true for carbon nanotubes. The attractiveness of carbon-based materials results from two basic properties: (a) nano-sized carbon structures have a large surface area and (b) the surface carbon atoms can bind in various ways with other elements. The large surface area of these materials offers a large active area for chemical interaction. The second feature allows an enhancement of the properties of carbon-based materials by chemical modifications with other elements or chemical groups. Consequently, by choosing a proper type of modification, the electronic properties of carbon-based materials can be tuned to specific applications. The chemical modification is usually referred to in the literature as “doping”. Different approaches to chemical modifications of carbon-based materials and potential applications can be found in References [14, 32]. In this section, a review of research related to the characteristics and applications of carbon-based materials after Ti and/or Li deposition will be
presented. In the literature, the modification of the carbon surface by deposition of a material is often called "coating" or "decoration".

Zhang et al. reported a coating of SWNTs with Ti, among other transition metals, using e-beam evaporation [33]. Investigating their samples with Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), they find that Ti adatoms exhibit the highest condensation/sticking coefficient, which facilitates a continuous and homogeneous layer of Ti for various film thicknesses ranging from 5 to 15 nm. For a 0.5 nm thick coating, it was observed that the nanotube is not completely covered by Ti adatoms, but there is no evidence of clustering of Ti adatoms on the sidewall of the nanotube. The strong Ti-SWNT interaction, possibly in the form of partial covalent bonding between the metal and carbon atoms, was attributed to the high affinity of Ti for carbide formation and the rehybridization effect induced by the curvature of the tube. It was suggested that carbon nanotubes can be used as novel one-dimensional substrates for obtaining stable metal wires with diameters of the order of nanometers [34].

The deposition of Ti on a thin film of pure C_{60} was investigated by photoelectron spectroscopy using x-rays and synchrotron radiation [35]. It was reported that a closed Ti monolayer was formed, but subsequent Ti depositions produced clusters. The tendency to form a single layer for Ti on C_{60} at low coverage (1.5 Å) was attributed to the hybridization of metal d and fullerene p orbitals. When depositing 5 Å Ti onto C_{60}, nonmetallic bonds between Ti and C_{60} were found with minimal change of the structure of the C_{60} cage. Wang and Wang [36] reported X-ray Diffraction (XRD), Photoelectron spectroscopy (PES), and Auger Electron Spectroscopy (AES) investigations of the interface interactions between Ti and a C_{60} film. They found that the structure of C_{60} at
the Ti/C₆₀ interface is modified by the Ti atoms when Ti is deposited onto the surface of a C₆₀ film. During low-temperature (150°C-200°C) annealing, Ti atoms were found to strongly intermix with carbon atoms, resulting in a solid state amorphization reaction at the Ti/C₆₀ interface and the formation of amorphous Ti carbide. Doping of C₆₀ by Ti in a co-evaporation experiment was reported by Norin et al. [37] and Qian et al. [38]. The authors conclude that Ti and C₆₀ can form stable fulleride compounds TiₓC₆₀ (x=2.1 and 3.5) by bonding of Ti atoms to the six-ring site of the C₆₀ molecules. Theoretical calculation [39], supported by resonant inelastic x-ray scattering measurements [40] indicate a hybridization between the HOMO level of C₆₀ and the Ti orbitals.

The interaction between adsorbed Ti and HOPG was examined by Ma and Rosenberg using soft x-ray photoelectron spectroscopy [41]. It was found that, despite an unfilled d band and a strong affinity for C, Ti does not form chemical bonds with a pristine HOPG surface, but only interacts through weak Van der Waals forces. The diffusion and cluster formation of Ti on an HOPG surface was revealed by time-dependent measurements of the C 1s peak intensity. It was demonstrated that the reaction between adsorbed Ti atoms and a pristine HOPG surface occurs only when oxygen is present and that the amount of TiC produced is independent of the quantity of Ti deposited, but is proportional to the amount of oxygen. The TiC formation at room temperature was attributed to a reaction assisted by oxide and/or hydroxide species on the surface of HOPG; in this interpretation, the oxide and/or hydroxide species only play a catalytic role [42].

The lithium-graphite intercalation compound has been extensively studied [43, 44] and is widely used as the negative electrode in commercial rechargeable lithium ion batteries [45]. In graphitic carbon, lithium ions intercalate between graphene layers in
states that result in a maximum coordination of one lithium atom with six carbon atoms. The electronic structure of LiC₆ has been examined by x-ray photoemission [46]. Core- and valence-level shifts were found, indicating a charge transfer from Li to carbon atoms. At low Li concentration and high temperatures, strongly anisotropic diffusion of Li in HOPG has been observed [47].

Li-nanotube complexes have been synthesized by intercalating lithium atoms both into the interstitial channels between carbon nanotubes and into the interiors of the nanotubes themselves [48, 49]. High lithium capacities up to Li₁.₆C₆ and Li₂.₇C₆ have been achieved in SWNTs [48] and concentrations up to LiC₂ are predicted [50]. The electronic structure of Li-doped SWNTs has been investigated using high-resolution synchrotron radiation photoemission [51]. Induced by Li deposition, a chemical shift of about 0.25 eV was observed at a Li/C concentration of about 6%. Li intercalation induces charge transfer from Li to C atoms and is responsible for an upwards shift of Fermi level [52]. A change of the shake-up features of the photoemission peaks as a function of the Li concentration has also been observed [53], which is derived from a broadening of the spectra with increasing Li-intercalation.

Hydrogen storage is one of the key issues in the development of a hydrogen technology. Carbon-based nanostructures, in particular fullerenes and carbon nanotubes, are considered as potential candidates for hydrogen storage materials [30, 54-56]. Due to their large surface area, these materials are expected to effectively store molecular hydrogen exceeding 9 weight percent (wt %) [57]. However, experiments have so far failed to show absorption of H₂ molecules on pure carbon nanotube structures exceeding 1 wt % [58-60]. Recent experimental investigations using an atomic hydrogen source
have shown a promising hydrogen storage capacity of 5.1 wt.% for SWNT [61, 62]. The important implications of these investigations are that hydrogen dissociation may play a critical role in enhancing the chemisorption capability of hydrogen on SWNTs. Theoretical considerations have demonstrated that much higher hydrogen uptake of carbon-based materials can be achieved by doping or introducing metal atoms or charged sites, such as Li or transition metals. Furthermore, the hydrogen dissociation step could potentially also be performed by transition-metal atoms decorating the surface of carbon-based nanomaterials. Yildirim and Ciraci, for example, considered a specific Ti-decorated carbon nanotube surface and predicted that the binding of H\textsubscript{2} considerably improves to 7 wt% of hydrogen [63]. A similar theoretical behavior is found when Ti is placed on graphene and fullerene structures [64, 65]. In these theoretical studies, metal adatoms serve as a dissociative catalyst and also play an active role in the storage process; thus, increasing the storage capacity of the substrate. Sun et al. predict that hydrogen molecules bind to Li atoms on a nanotube surface and that the storage capacity can reach to 13 wt% [66]. They also predict that Li atoms are bound strongly to the surface of C\textsubscript{60}; thus, an isolated Li\textsubscript{12}C\textsubscript{60} cluster theoretically can store up to 60 hydrogen atoms in molecular form [67] and lithium-decorated C\textsubscript{60} may bond sufficient hydrogen to reach 9 wt% of stored hydrogen. According to this study, the advantage of alkali atoms over transition metal atoms is that they prefer to be isolated instead of forming clusters. As a result, all metal sites remain active and can adsorb the maximum amount of H\textsubscript{2}.

This enormous discrepancy between theoretical predictions and experimental findings is extremely puzzling. Thus, it is of utmost importance to understand the origin of this discrepancy. Unless the underlying microscopic interaction mechanisms are even
rudimentarily understood, further progress in the field of hydrogen storage on carbon-based nanomaterials will heavily rely on "accidental" breakthroughs.

It is therefore the purpose of this thesis to study fundamental aspects of metal-doped carbon-based materials, such as the electronic and chemical properties of interface formation between the metals and the carbon nanomaterials. Furthermore, aspects associated with the practical use of metal-doped carbon-based materials also need to be investigated to find a solution for an optimal surface modification. For example, it is necessary to characterize the oxidation behavior of deposited metals and the role of defects and impurities present in carbon-based materials. The research presented in this thesis uses a unique combination of spectroscopic and microscopic techniques to study these problems, and the results will be presented in the following chapters.
CHAPTER III

EXPERIMENTAL DETAILS

In this chapter, the experimental techniques are reviewed and the instrumental setup is described in Section 3-1. Methods for data analysis are explained in Section 3-2. Details of sample preparation and an overview of the performed experiments is presented in Section 3-3.

Section 3-1

Techniques and Instrumentations

Experiments presented in this thesis utilize surface sensitive techniques, such as photoelectron spectroscopy and scanning probe microscopy, to characterize electronic, atomic, and chemical structures of samples. In this section, a brief discussion of photoelectron spectroscopy and scanning tunneling microscopy and spectroscopy will be given. The basic concepts of photoelectron spectroscopy can be found in the books of Hüfner [68] and Briggs and Seah [69]. Detail information on scanning probe microscopy is discussed in the books by Birdi [70] and Meyer et al. [71].

3-1.1. Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is a widely used technique for obtaining elemental and chemical information of various material surfaces. In photoelectron spectroscopy
experiments, either X-rays or ultraviolet photons, with energy of $h\nu$, are directed at the surface of a sample, causing photo-ionization and emission of electrons (photoelectrons) from atoms in the near-surface region (a few nanometers) of the sample. Emitted electrons are collected and their kinetic energy $E_k$ distribution can be measured using an appropriate electron energy analyzer to produce a photoelectron spectrum.

Photoemission is a photon-in-electron-out process and can be considered by looking at the overall process as follows:

$$A + h\nu \rightarrow A^+ + e^- \quad (1)$$

Energy conservation then requires that:

$$E_A + h\nu = E_{A^+} + E_e \quad (2)$$

The energy of the emitted electron is solely its kinetic energy $E_k$ that can be deduced by rearranging Eq. 2:

$$E_k = h\nu - (E_{A^+} - E_A) \quad (3)$$

The bracketed term in Eq. 3 represents for energy difference between the ionized and neutral system and, in a one-electron picture, is generally called the binding energy $E_b$ of the electron, i.e., the energy required to remove the electron from its initial level to the vacuum level. Eq. 3 is then rewritten in the following commonly quoted form:

$$E_k = h\nu - E_b \quad (4)$$

The binding energies $E_b$ of energy levels in solids are conventionally measured with respect to the Fermi-level $E_F$ of the solid, rather than the vacuum level. Eq. 4 then becomes:

$$E_k = h\nu - E_b - \Phi, \quad (5)$$
where $\Phi$ is the work function of the solid, i.e., the energy difference from Fermi level $E_F$ to the vacuum level, and is defined as the minimum energy required to remove the electron from the solid to vacuum. Experimentally, the emitted electrons are recorded and analyzed by a spectrometer (e.g., an electron analyzer) and the sample Fermi level is equal to the Fermi level of spectrometer (by electrically connecting the sample and the spectrometer). The kinetic energy of the electron is determined with respect to the vacuum level at the spectrometer, and thus the work function of the spectrometer is used in Eq.5. In practice, the work function of the spectrometer is considered a constant and is thus included in the spectrometer calibration.

The photoelectron spectrum is presented as a distribution of emission intensity versus electron binding energy $E_g$, roughly reflecting the electron density of occupied states of atoms on the sample surface. Depending on the excitation photon energy used, PES in a laboratory setting is also called X-ray Photoelectron Spectroscopy (XPS) or Ultraviolet Photoelectron Spectroscopy (UPS). The process in XPS and UPS is described schematically in Fig. 3.1. Since PES (and as described shortly, X-ray Auger Electron Spectroscopy- XAES) relates to electrons in occupied orbital, the unoccupied electronic levels are omitted from Fig. 3.1. In XPS, the X-ray photon is absorbed by an atom in the near-surface region of the sample, leading to ionization of the atom and emission of a photoelectron from either a valence or inner core electron shell. The overall transition probability of photoemission process is proportional to the photoionization cross-section, which varies for different elements and atomic-levels [72]. The energy level of the ejected photoelectron is described by the quantum numbers of atomic orbitals, $nlj$. For XPS, the most commonly employed X-ray sources are those of Mg $K_\alpha$ ($h\nu = 1253.6$ eV)
and Al Kα (hν =1486.6 eV). Although both core-level and valence-level XPS spectra can be recorded, XPS with a non-monochromatized source is most commonly used for core-level investigations since the natural emission line includes satellite features that obscure the valence band information. By contrast, in UPS the lower energy photon interacts only with electrons in valence levels of atoms. UPS experiments are usually carried out with rare-gas discharge lamp, for example He lamp, which produces He I (hν =21.2 eV) and He II (hν =40.8 eV) ultraviolet radiations. Low energy photons (in UPS) have larger cross-section for valence levels than high energy photons (in XPS). Furthermore, the line width of He I or He II is narrower than that of Mg Kα or Al Kα. Thus, UPS provides better energy resolution for valence band investigation. Nevertheless, XPS with a monochromatized source (i.e., without satellite features) can give very valuable additional insights into the valence band since it averages over the entire Brillouin zone and therefore less susceptible to final state dispersion effects.

The final state of the photoemission process is an excited state with a core hole (core-level PES) or a valence hole (valence band PES) in the excited atom. The core hole, left behind after a photoemission process, is filled by electron from higher levels during relaxation of the excited atom. The energy difference associated with the transition is released through either radiative decay by emitting of photon or non-radiative decay by emitting of electron in the same or higher levels. The latter process is an Auger electron emission process, and the emitted electron is called an Auger electron, giving rise to X-ray-excited Auger Electron Spectroscopy (XAES). For shallow core levels (Eg < 2 keV), core-hole relaxation via the Auger process is dominant [68]. The X-ray-excited Auger process is also schematically described in Fig. 3.1, which shows that the final state of the
emitting atom is doubly ionized and the kinetic energy of the Auger electron is defined only by the involved atomic energy levels. The Auger decay can be classified as core—core—core, core—core—valence, and core—valence—valence, named according to the involved energy levels. In all X-ray photoelectron spectra, features appear as a result of both photoemission and Auger emission processes. As seen in Fig. 3.1, XAES also probes valence levels of the molecule or solid, which gives additional information besides core-level investigation in XPS, particular regarding hole-hole correlation effects.

![Schematic diagram of electronic transition in the XPS, XAES, and UPS process.](image)

**Fig. 3.1**: Schematic diagram of electronic transition in the XPS, XAES, and UPS process.

Several important aspects of the PES and XAES techniques can be derived from characteristics of the emitted electrons.

- **Surface Sensitivity**: Emitted electrons from photoemission and Auger emission processes will contribute to spectral features of PES and XAES only if
they can reach the sample surface without undergoing an inelastic scattering process. The low kinetic energy (0 - 1500 eV) corresponds to a small inelastic mean free path $\lambda$ (IMFP) [68, 73, 74] of the emitted electrons in the range of few nanometers. This makes PES and XAES surface-sensitive techniques. As a consequence, in order to prevent undesired interactions of emitted electrons with surface contamination and avoid energy losses due to collisions with gas molecules in the analyzer, ultra high vacuum is required to carry out PES and XAES experiments.

- **Elemental Sensitivity**: For each element, there will be a characteristic binding energy associated with each atomic orbital. Thus, each element will give rise to a characteristic set of peaks at particular energies in the photoelectron and Auger electron spectrum, which can be used to identify the presence of the element in samples. Furthermore, the intensity of the peaks is related to the concentration of the element within the probing region. Thus, these techniques are capable of yielding a quantitatively elemental and compositional analysis.

- **Chemical Information**: The exact binding energy of an electron depends not only on the energy level from which the electron is emitted, but also the overall potential of the atom and its local chemical and physical environment. Changes of these factors give rise to small shifts of peak positions in the XPS spectrum, the so-called chemical shift. Therefore, high resolution XPS studies can provide chemical state information of the elements on the surface. Such shifts are readily observable and interpretable in XPS spectra (unlike in Auger spectra) because the technique can be interpreted as a one-electron process (thus
simplifying the interpretation) and is of high intrinsic resolution (as core levels are 
discrete and only broadened by lifetime broadening and the limited energy 
resolution of the experimental apparatus). The emission of a photoelectron or an 
Auger electron leaves behind an ionized atom with one core hole (XPS) or a 
double-valence hole (XAES), which also changes the overall potential of the 
system. The interaction of the photoelectron with the potential of the core hole 
(XPS) and the interaction of two holes in valence states (XAES) lead to final state 
effects that may affect spectral features. In both cases, the effect of a screening of 
the holes by the other (N-1) electrons of the system also needs to be taken into 
account. Therefore, not only initial state effects, but also final state effects should 
be included in the analysis of the photoemission and Auger emission processes.

As Fig. 3.2 illustrates for a common setup of a photoelectron experiment, X-rays or 
UV lights are directed onto the sample and the resulting photoelectrons are then focused 
onto the entrance slit of a concentric hemispherical analyzer. Here a negative and positive 
potential are applied to the outer and inner cylinders, respectively. Adjusting the 
potentials controls the energy range of electrons that are allowed to pass through the 
analyzer (pass energy) and onto the detector, usually a channel electron multiplier 
(channeltron). The pass energy, together with entrance and exit slit width of the analyzer, 
is one of the parameters to control the overall spectral resolution. In practice, the ability 
to resolve between atoms exhibiting slightly different chemical shifts is limited by the 
peak widths, which are governed by a combination of factors: (1) the intrinsic width of 
the initial level and the lifetime of the final state; (2) the line width of the incident 
radiation; (3) the resolving power of the electron-energy analyzer. In most cases, the
second factor is the major contribution to the overall line width, which for traditional x-ray sources can be greatly improved by using X-ray monochromators [68, 69].

![Fig. 3.2: Schematic diagram of PES experiment setup.](image)

**III-1.2. Scanning Probe Microscopy**

Scanning Probe Microscopy is a general term for a family of microscopy techniques, developed after the invention of the Scanning Tunneling Microscope [70, 71]. The main principle of scanning probe microscopy is based on the interaction between a physical nanoscale probe and the sample surface. The probe mechanically scans, line by line, the sample surface, and the probe-surface interaction is recorded as a function of probe position. The probe-surface interaction not only depends on the local atomic arrangement of the surface, but also reflects the local electronic structure of the atoms on the surface. Thus, an image (microscopy) or the local electronic structure (spectroscopy) of the surface can be obtained. The motion of the probe is performed by piezoelectric actuators, which convert a controlling voltage into mechanical motion with precision and accuracy.
at the atomic level. Various forms of probe-surface interaction can be monitored, such as the tunneling current in the Scanning Tunneling Microscope (STM) or force in the Atomic Force Microscope (AFM), which leads to different techniques (or modes) of scanning probe microscope. Many scanning probe microscopes are capable of operating and monitoring several interactions simultaneously. The resolution varies from technique to technique, but some techniques can easily observe individual atoms (atomic resolution). While a conductive sample is required for imaging with STM, other techniques, such as AFM, are capable of imaging surfaces of non-conductive materials on the sub-nanometer scale.

The governing principle of scanning tunneling microscopy is the quantum tunneling of electrons through a thin potential barrier separating two electrodes. Fig. 3.3 shows a schematic diagram for operation of an STM.

The instrument consists of a very (nanoscale) sharp tip connected to scanner, i.e., an XYZ positioning device controlled by piezoelectric elements. The tip is scanned line by line (varying the $X$ and $Y$ coordinates) above the sample surface following the topography of the sample. By applying a voltage $U$ between the tip and a conductive sample, a small current, the "tunneling current" $I$, can flow between these electrodes when their distance $Z$ is approaching a few atomic diameters. The amplitude of the current depends on the
distance between the tip and the sample, and also the applied voltage $U$. This tunneling current is amplified and measured. An electronic feedback loop based on the tunneling current is used to control the distance between the tip and the sample. If the tunneling current exceeds its preset value, the distance between tip and sample is increased, if it falls below this value, the feedback decreases the distance. Thus reading the relative $Z$ position of the tip, one obtains real-space imaging of the sample surface. Using sharp tips and a very precise control of the tip position, atomic resolution can be achieved. As shown in Fig. 3.4, the instrument can work in two operational modes: constant height or constant current mode. In the constant height mode, the preset distance between tip and sample surface is fixed and the variation of the tunneling current on sample surface is recorded. In the constant current mode, the preset value of the tunneling current is kept constant, while the distance between the tip and sample is varied giving the topography of the sample surface.

Fig. 3.3: Schematic diagram of an STM [75]
Fig. 3.4: Schematic diagram of the topography imaging mode in an STM; (a) Constant current mode; (b) Constant height mode. [76]

The high spatial resolution achieved with an STM stems from the physical behavior of the tunneling current. The tunneling current flows across the narrow gap that separates the tip from the sample, a current that is forbidden in classical physics but that can be explained by quantum mechanics when the electrons "tunnel" across the gap. The tunneling current, $I$, decays exponentially with an increase of the gap $d$:

$$I = KU \exp(-kd), \quad (6)$$

where $k$ and $K$ are constants and $U$ is the applied voltage.
An important property of the exponential dependence of the tunneling current on the tip-sample distance is that a very small change in the tip-sample distance can induce a large change in the tunneling current, as shown in Fig. 3.5. Thus, the tip-sample distance can be controlled very exactly. The tunneling current is contributed mostly by electronic transfer from/to the very last atoms of the tip apex to/from the sample surface. Thus the sample surface is scanned effectively by a single atom, which inherently provides atomic resolution.

In addition to the ability to image the surface topography, an STM can be used to perform local spectroscopy (Scanning Tunneling Spectroscopy or STS), and therefore provide local electronic structure information of the sample surface. In this mode, the tip is fixed at a constant distance above the point of interest on the sample surface. By varying the voltage between the tip and the sample, one can measure $I(V)$ spectra as well as the differential conductance $dI/dV(V)$. In a very simple but realistic model, the

\[ I = K^* U^* e^{-k^*d} \]
tunneling current is approximately proportional to the integral of all the electronic states between the Fermi level and the tunneling bias. Therefore, the differential conductance reflects directly the local electronic density of states (LDOS) at the probed point of the sample surface. If the sample is a semiconductor, one can identify and characterize the energy gap around the Fermi level ($E_F$). An example of $I(V)$ and corresponding $dI/dV(V)$ curves on a semiconductor SWNT is presented in Fig. 3.6.

3-1.3. Instrumentation

The experiments in this thesis were performed in an ultra-high vacuum surface science system that consists of two connected instruments: a surface analytical electron spectroscopy system ("Andere ESCA", based on a VG MkII ESCALab) and an Omicron scanning probe microscopy system (VT AFM XA 50/500). The unique instrumental
setup allows in-situ spectroscopic and microscopic investigations, for which the samples can be transferred between the two instruments under vacuum. A schematic diagram of the system is sketched in Fig. 3.7.

Samples are introduced into the system through a glove box filled with dry nitrogen gas. In the glove box, samples are mounted on sample holders and transferred to the load-lock vacuum chamber. The distribution chamber is used to deliver samples to the different instrumentation chambers for specific investigation. Gate valves are installed in between the chambers to maintain vacuum isolation of each instrument while allowing the flexibility to transfer samples throughout the system without breaking vacuum.

Various sample treatments for spectroscopic or microscopic investigations can be performed under vacuum in the preparation chamber. The sample stage is equipped with a heating element to heat the sample, and the temperature is measured by an attached thermo-couple. Deposition of metals on the sample surface is performed with either an e-beam evaporator (Ti in this thesis) or an alkali metal (Li in this thesis) dispenser element that is resistively heated. The deposition rate of the e-beam evaporator is controlled by the internal evaporator flux rate, and the flux of the dispenser element is controlled by the heating current. The base pressure of the preparation chamber is at $\sim 5 \times 10^{-10}$ mbar.
The analysis chamber of the Andere ESCA system is equipped with an XR50 SPECS twin-anode X-ray source, which produces Al K$_\alpha$ and Mg K$_\alpha$ characteristic radiation for XPS and XAES investigations. A Helium gas discharge lamp serves as the UV light source for UPS experiments. The electron detection is performed with a SPECS PHOIBOS 150MCD concentric hemispherical electron analyzer, equipped with multichannel detector (9 channeltrons). The electron analyzer is carefully calibrated by scaling the Ag 3d$_{5/2}$, Au 4f$_{7/2}$, and Cu 2p$_{3/2}$ core-level lines of metal reference samples to the reference values given in Ref. 77. The base pressure of the analysis chamber is better than 2.0x10$^{-10}$ mbar.

The Omicron SPM system is one of VT-XA series, which can operate in STM/STS and AFM modes with variable temperatures in the range of 50K to 500K. It is also...
capable of *Kelvin Probe Force Microscopy* (KPFM). A high quality vibration decoupling system is employed that allows the collection of high-resolution SPM images with atomic resolution. Sharp tips were cut from a 0.25 mm Pt-Ir wire and used for STM and STS measurements. The base pressure of the SPM vacuum chamber is $2 \times 10^{-11}$ mbar.

Section 3-2

Spectroscopic Data Analysis Methods

This section describes techniques used to analyze experimental spectra from XPS, XAES, and UPS measurements in order to extract information about the electronic structure of the sample surface, the formation of metal cover layers, and the interaction of metal adatoms with the respective substrate. The data analysis methods were applied to all spectra in a consistent manner, so that all data have the same systematic error.

For a typical XPS investigation, a survey spectrum with lower energy resolution (large pass energy and step size) is measured first. The typical energy range of the survey spectra from 1200 or 1400 to 0 eV BE for Mg $K_\alpha$ or Al $K_\alpha$ respectively, is sufficient to identify all detectable elements on the sample surface. Detailed high resolution scans of regions of interest for selected elements are measured in order to identify their chemical state and to perform quantitative analyses. The high resolution scans are obtained using a low-pass energy and small step size. Peak-fitting procedure and difference-spectra techniques are employed for quantitative data analysis of the high-resolution spectra.

3-2.1. Elemental Analysis:

The presence of elements on the sample surface can be determined qualitatively by identifying spectral features (peaks) in the survey spectrum. Both XPS core-level peaks
and corresponding XAES Auger lines are used to identify chemical elements after comparing to reference binding energies [77]. The peaks are assigned to identify element with quantum numbers of the involved atomic orbitals. For p, d and f levels, the core-level peaks split by spin–orbit coupling into doublets with characteristic differences in energies and peak intensity ratios [68, 69]. An example of such elemental analysis is presented in Fig. 3.8, where survey spectra with identified elements are shown for SWNT sample before and after Ti deposition. The intensity of the spectra was normalized to the intensity of C 1s lines and offset vertically. The presence of Ti adatoms on the SWNT sample is seen by the appearance of new spectral features (XPS and Auger lines) characteristic for Ti. Table 3.1 lists the identified elements on the sample surface by comparing the experimental BE with reference values. By comparing survey spectra of samples before and after Ti deposition, it also can be observed that the carbon signals decrease due to attenuation of electrons in the deposited Ti layer, while the oxygen signals increase due to oxygen adsorption from the residual gas.

Fig. 3.8: XPS survey spectra of SWNT samples before and after Ti deposition.
Table 3.1: Elemental analysis from XPS survey spectra of SWNT samples before and after Ti deposition.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Experimental BE (eV)</th>
<th>Reference BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>284.8</td>
<td>284.5</td>
</tr>
<tr>
<td>C KVV</td>
<td>990</td>
<td>990</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.5</td>
<td>531</td>
</tr>
<tr>
<td>O KLL</td>
<td>742</td>
<td>745</td>
</tr>
<tr>
<td>Fe 2p</td>
<td>708</td>
<td>707</td>
</tr>
<tr>
<td>Ti 2p_{3/2}</td>
<td>455.1</td>
<td>454</td>
</tr>
<tr>
<td>Ti 2p_{1/2}</td>
<td>461.1</td>
<td>460</td>
</tr>
<tr>
<td>Ti L_{3M23M45}</td>
<td>834.7</td>
<td>835</td>
</tr>
<tr>
<td>Ti L_{M23M23}</td>
<td>867</td>
<td>865</td>
</tr>
<tr>
<td>Ti 2s</td>
<td>562</td>
<td>561</td>
</tr>
<tr>
<td>Ti 3s</td>
<td>59.7</td>
<td>59</td>
</tr>
<tr>
<td>Ti 3p</td>
<td>34.6</td>
<td>33</td>
</tr>
</tbody>
</table>

3-2.2. Compositional Analysis:

The relative intensities of the core-level photoelectron lines are roughly proportional to the populations of the electron orbitals. Thus, concentration quantification can be performed using the intensity of suitable (sufficient intensity, no spectral overlap with other elements) characteristic lines as a measure for the number of atoms of a certain element in the analysis region.

Once the elements are identified, the strongest core-level peaks corresponding to each element can be extracted from the XPS survey spectra and their integrated areas can be used to estimate the relative concentration of a species on the surface of a sample. All spectral features in the survey spectrum are generally measured with the same set of parameters for the X-ray source (photon flux) and the electron analyzer (pass energy and slits), and thus the relative intensity of the characteristic core-level peaks can be used to derive the relative concentrations of the elements. Assuming a homogenous sample, the number of photoelectrons per second in a specific spectral peak ($I$) is proportional to the
number of atoms of the element per cm$^3$ of the sample ($n$) and can be determined by [68, 69, 77]:

$$I = n.S$$  \hspace{1cm} (7)

where $S$ is defined as the atomic sensitivity factor, which is a function of instrument-dependent quantities and is proportional to the photoionization cross-section $\sigma$ for the atomic orbital of interest and the inelastic mean free path $\lambda$ of the photoelectron in the sample [77].

If we assume that all experimental conditions are unchanged then from Eq. 7 the atomic fraction $C_x$ of elements in the sample can be estimated by:

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x/S_x}{\sum I_i/S_i}$$  \hspace{1cm} (8)

In this thesis, the above-described analysis was used to estimate the elemental concentration of species in pristine and metal-deposited samples of HOPG, C$_{60}$, and SWNTs.

3-2.3. Deposition Thickness Analysis:

Photoemission signals from the substrate decrease in intensity due to the overlayer formation on the sample surface after metal deposition. Assuming a uniform growth of the deposited overlayer on the sample surface, its average (effective) thickness can be estimated from the attenuation of the substrate signal, following [68, 69]:

$$I = I_0 \exp\left(-\frac{d}{\lambda}\right),$$  \hspace{1cm} (9)

where $I_0$ and $I$ is the intensity of the substrate signal before and after deposition, respectively, $\lambda$ is the inelastic mean-free path (IMFP) at the kinetic energy of the photoelectron in the deposited overlayer material, and $d$ is the thickness of the deposited
overlayer. The \( \lambda \) value is calculated by the QUASES-IMFP-TPP2M software according to the Tanuma, Powell, and Penn formula [73].

3-2.4. Work Function Determination:

In addition to information about the electronic structure of the valence band, the work function of a sample surface can also be derived from UPS experiments [68, 69]:

\[
\Phi = h \nu - (E_F - E_{\text{min}}) \quad (10)
\]

where \( E_{\text{min}} \) is the secondary electron cutoff, i.e., the kinetic energy of the slowest electron emitted from the sample surface.

![UPS Hel Cut-off](image)

Fig. 3.9: Determination of the work function of a SWNT sample before and after Ti deposition using the secondary electron cut-off of the respective UPS spectra.

Fig. 3.9 shows an example of a work function determination for SWNT samples before and after Ti deposition. The secondary electron cut-off was measured with He I radiation and a bias voltage of 15V was applied to sample. The measured valence band
spectra were normalized and plotted in kinetic energy above the Fermi energy $E_F$, which was determined by measuring a Fermi edge of a sputter-cleaned Au sample. The cutoff energies were determined by linear extrapolation of the leading edge of the secondary electron maximum and the baseline. Fig. 3.9 shows that the work function of the SWNT sample decreases by $\Delta \Phi \sim 0.65$ eV due to the deposition of Ti on the sample surface.

3-2.5. Detail Analysis: Chemical Information

While elemental and compositional information can be derived from the presence of XPS and XAES peaks in survey spectra, a more sophisticated analysis of the core-level photoelectron lines is required to obtain information about chemical interactions and chemical bonding involving the core-ionized atom. The analysis is focused on the determination of the peak shape and core-level binding energy [78-81]. One of the main advantages of XPS is the possibility of obtaining chemical information from emission processes that involve only one electron level, while for XAES three energy levels have to be considered.

The overall shape of the photoelectron peaks is governed by experimental and physical effects. Experimental broadening occurs typically as the result of the limited energy resolution of the spectrometer and the energetic width of the X-ray source. A Gaussian width is usually used to represent instrumental broadening of the photoelectron peaks. The width of the instrumental broadening is reasonably assumed to be constant under the same experimental conditions, i.e., for constant pass energy and slit size. An intrinsic (natural) line width, characterized by the lifetime of the core hole, also contributes to the broadening of the photoelectron peaks via the Heisenberg uncertainty principle [68, 69]. In addition, final state effects due to screening of the created core or
valence holes by the other N-1 electrons can influence the peak shape [68, 69]. Broadening due to core-hole lifetime effects is represented by a Lorentzian function. The resulting peak width is quantified by a convolution of Gaussian and Lorentzian peaks and usually defined as the full width at half maximum (FWHM) contributions to a Voigt lineshape.

The binding energy of a core-level component depends on the bonding configuration and local environment of the emitting atom. The nominal energy of the core-level state is determined by the atomic orbital, but the binding energy is modified in forming a molecule or solid. In addition, the exact binding energy associated with a particular arrangement of atoms within a solid depends on many other factors. The amount that the binding energy changes when an atom goes from one chemical state or environment to another is referred to as the chemical shift.

3-2.6. Detail Analysis: Spectral Feature Separation and Quantification

In XPS spectra of multi-element samples, overlap of spectral features from several elements may occur. Furthermore, photoemission from the same element but in different environments may contribute to a given XPS peak. In order to interpret XPS data, it is thus often necessary to decompose the spectra into their individual components, e.g., by curve-fitting using nonlinear least-square algorithms [69, 82-89]. Curve-fitting allows the determination of a minimal number of separate states that may exist for each element in the surface region, the binding energy associated with each state, and their relative abundance.

In a fitting procedure, the experimental data points \( \{y(x_i)\} \) are approximated by a sum of functions ("profiles") \( \{f_j(x_i)\} \), represented for each component of the peak. Each
profile is characterized by a set of parameters, including height, area, width and shape, which are adjustable during fitting. The fitting process is usually performed by an iterative non-linear least-square algorithm and variation of function parameters to minimize the “chi-square” function, which characterizes the goodness of the fit:

\[ \chi^2 = \sum \frac{[y(x_i) - f(x_i)]^2}{\sigma_i^2}, \]  

where \( \sigma_i \) is standard deviation of \( i \)-th data point.

Several “idealized” profiles are usually used for fitting XPS peaks, such as Voigt profiles for semiconductors and Doniach-Sunjic functions for metals. In all cases, the line width (or broadening) of the photoemission lines is decomposed into natural (intrinsic) and instrumental contributions. For the Voigt profile, the intrinsic line shape of the photoemission lines is described by a Lorentzian distribution, while the instrumental broadening is represented by a Gaussian distribution.

Section 3-3

Sample Preparations and Measurements

3-3.1. Preparation of Individual Nanotubes on Surfaces:

Since single-walled carbon nanotubes tend to form bundles (ropes of several hundreds tubes), it is necessary to find a way to separate the bundles to be able to study an individual tube with STM/STS. In this thesis, two different approaches were carried out for this purpose, namely electrochemical separation [90] and a combination of dispersion and ultrasonication [91]. We found that the latter method provides an easier and more controlled way to separate the SWNT bundles. One challenge in applying this technique is to find an optimal dispersion solution for SWNTs due to their inertness and
hydrophobic characteristics [91-96]. We have tried to disperse SWNT in water, acetone, propanol, \(N,N\)-dimethylformamide (DMF), and \(N,N\)-dimethylacetamide (DMA). After ultrasonication, DMF and DMA give the best-dispersed solution of SWNTs that are stable for weeks, while SWNTs are poorly dispersed in water and SWNTs dispersed in acetone and propanol solutions become aggregated again in bundles and precipitate to the bottom of the test tube within one day. Note that the ultrasonication step may also introduce defects to the tubes and even shorten the tubes [91]. Thus, the pulse intensity, frequency, and sonication time need to be chosen appropriately.

For an SPM experiment, especially if one attempts to obtain atomic resolution, a very flat and uniform sample is required. Even a good dispersion of SWNT, when cast onto a flat gold surface, is not sufficiently flat for atomic-resolution imaging, but rather leads to a non-homogenous sample with different bundle sizes, tube diameters, and also catalyst nanoparticles. We thus found that a separation step by centrifugation is necessary. In this process, the individual tubes and small bundles rise to the top layer of the solution due to their smaller density, while the SWNTs in larger bundles sink to the bottom of the test tube. Thus, a sample prepared from the top layer of solution exhibits more homogenous individual tubes and leads to a better-suited film when cast onto a flat gold surface.

3.3.2. Details of Sample Preparation

For the experiments in this thesis, highly ordered pyrolytic carbon (HOPG, SPI-1 grade, 10x10x1.75 mm\(^3\)) samples were purchased from Structure Probe, Inc./SPI Supplies. Sample was cleaved in the glove box under dry Nitrogen gas environment before introduction into the preparation and analysis chambers. Separate HOPG samples were prepared for Ti- and Li-deposition experiments.
Single-walled carbon nanotube SWNT starting material, produced by the HiPCO process [97, 98], was purchased from CNI Inc (now Unidym Inc.), batch # P0288. The pristine sample was categorized to be of the “Super Pure” type and in the form of dry powder of nanotubes bundled in ropes, with the amorphous content less than 5 wt%. The tube diameter is in the range of 0.8-1.2 nm, with lengths ranging from 100 to 1000 nm. A thermogravimetric (TGA) analysis, provided by the manufacturer, shows that the sample contained less than 5 wt% impurities in the form of residual Fe catalyst nanoparticles. The moisture content was also less than 5 wt%.

In our SPM and XPS experiments, the following procedures were employed to prepare samples of C\textsubscript{60} and SWNT: The substrates for SWNT and C\textsubscript{60} samples used in all SPM and XPS experiments were cut in 10 x 10 mm\textsuperscript{2} pieces from 4" diameter, 525 µm-thick Silicon wafers coated with 100 nm of Au. The Au/Si wafers were provided by Platypus Technologies (Product # AU-10000-SL1, Lot # FC-1458). Approximately 0.1 mg of SWNTs powder was dispersed in 1 ml of DMF solution in a test tube. For the SPM experiments, the solution was first ultrasonicated by a UP100H pulsed sonicator (Hielscher USA) using a 1 mm MS1 sonotrode with 5-10 0.5-second-pulse cycles at 40% intensity. The dispersion was further sonicated for 30 minutes in a Branson 1510 bath sonicator operating at 40 kHz. The dispersed solution was then centrifuged at 3500 rpm for 30 minutes in a Fisher Scientific - Centrifuge Model 228. The top layer of the solution was carefully decanted for SPM sample preparation as described above. We found that a better sample of individual nanotubes can be obtained after repeated sequences of ultrasonication, centrifugation, and separation. STM samples were prepared by dropping the dispersed and decanted solution of SWNTs onto 1 x 1 cm\textsuperscript{2} Au/Si substrates, mounted
on the Omicron STM sample holder with metallic clips to ensure a good electrical contact. The sample was first dried under a stream of nitrogen and then placed into vacuum in the loadlock segment of the glove box (P ~ 10^{-2}-10^{-3} mbar) for 60 minutes. The solvent was evaporated and removed, leaving nanotubes cohesively attached to the surface of the Au substrate.

For electron spectroscopy experiments, samples were prepared by dropping the dispersed solution (i.e., without the additional separation step) onto 1 x 1 cm^2 Au/Si substrates. After drying in vacuum of the loadlock segment of the glove box for 60 min, a dense and uniform film of SWNTs was formed on the surface of the Au substrate. The sample was mounted on the ESCA stub sample holder and secured by a metallic clip to make a good electric contact between sample and the holder. In order to reduce the residual surfactant, samples for spectroscopic experiments were heated in ultra-high vacuum in the preparation chamber at 200°C for 30 minutes. Separate SWNT samples were prepared for Ti- and Li-deposition experiments.

Sample of C_{60} was purchased from TCI America, product # B1641, with a purity of 99.5% fullerene content. The pristine C_{60} powder was also dispersed in DMF for thin film preparation, similar to SWNT sample preparation. Separate sample series of C_{60} were prepared for Ti- and Li-deposition experiments.

Ti depositions were performed using an Omicron EFM3 UHV evaporator equipped with an integrated flux monitor, which was calibrated to yield reproducible real-time control of the deposition rate via ion current measurement [99]. The thickness of the films is derived from the deposition time and flux rate based on the linear relationship between the ion current and the amount of the evaporated material at a constant emission.
current. The evaporation cell of the EFM3 is contained in a water-cooled copper cylinder (cooling shroud). During evaporation, only a restricted region of the evaporant (i.e., the tip of the evaporant wire) is heated by electron bombardment, making it possible to keep the background pressure below $10^{-10}$ mbar. 2.0 mm-diameter wire of Ti (Alfa Aesar, Product # 14004, Lot # B08P11, 99.99% purity) was used as evaporant for the Ti deposition experiments. The flux monitor was calibrated by depositing Ti onto a Au/Si substrate at a constant current of 100 nA. The film thickness was controlled via the Ti evaporation time and measured by using the exponential attenuation of the Au 4f XPS intensity. The result of this calibration and the characteristics of the Ti deposition on the Au substrate will be presented in Chapter IV. Depositions of Ti on carbon-based materials were also performed at a constant current of 100 nA and Ti evaporation times of 2 minutes.

Li deposition was performed using a Li dispenser element (SAES Getters USA Inc., Product # 5G0070). The Li dispenser was heated by a current source and cracked open upon heating, which produces evaporation of Li starting at a nominal heating current of ~7.3 A (manufacturer parameter). The deposition rate depends on the heating current and was determined experimentally by deposition of Li on a Au/Si substrate. The result of Li deposition on the Au substrate will also be presented in Chapter IV. For Li deposition on carbon-based materials, a heating current of 9 A and a deposition time of 2 minutes were employed.

Both Li- and Ti-sources were mounted on the preparation chamber with feedthroughs, which allow easily varying the distance from sample to deposition sources. For all deposition experiments, this distance was fixed at ~10 cm. In this experimental setup, the
Ti-source output was directed toward the sample from bottom and normal to the sample surface, while the output of the Li-source was set from bottom at a 45° angle to the sample surface. The samples were kept at room temperature for all deposition experiments. The base pressure of the preparation chamber, maintained at ~10^{-10} mbar, rose to typically ~5 × 10^{-9} mbar for Ti and ~1 × 10^{-9} mbar for Li during deposition.

3-3.3. Details of Performed Measurements:

XPS and XAES measurements were performed on all sample series with the same X-ray source power (15 kV and 20 mA) and at normal emission. For each time-dependent measurement series, the relative sample position was kept unchanged, so that the evolution of spectral features, if any, are observed at the same location on the sample surface. The survey spectra were recorded as the sum of 3 scans using 50 eV pass energy with 0.5 eV energy step. Detailed spectra of O 1s and Ti 2p were recorded for 20 scans with 20 eV pass energy and 0.02 eV energy step. Detailed spectra of C 1s were recorded for 20 scans with 10 eV pass energy and 0.02 eV energy step. Detailed XAES spectral features were measured for 10 scans with 20 eV pass energy and 0.05 eV energy step. As mentioned previously, the binding energies were referred to the Fermi energy, which was calibrated by measuring core-level photoelectron lines of Au, Ag, and Cu reference samples. Elemental and compositional analysis as well as an estimation of the thickness of the overlayers was performed following the procedures described in Section 3-3. Detailed spectra were also normalized to either integrated area or to maximum height. With integrated area normalization, the change of peak components can be observed. The shape change, e.g., peak shift and broadening, is best observed for the spectra normalized to maximum height. In many cases, difference spectra, taken from spectra of successive
time-dependent measurements, were used to qualitatively identify the spectral features of peak components and their evolution.

Fitting procedures using the "Fityk" software [100] were employed for the detailed spectra of C 1s and O 1s in order to quantify the peak components and their evolution in the time-dependent measurement series. The number of peak components was determined either from the apparent presence of spectral features under the peak or from difference spectra. In some cases, a reasonable model of chemical composition of the sample surface was compared with references from literature and used to assign spectral features in the fitting model. Voigt profiles were used to represent the peak components of C 1s and O 1s spectra. A linear background was simultaneously fitted. It was assumed that the Gaussian contribution to the Voigt functions, characteristic for instrumental broadening, is identical for all spectra taken at a given pass energy. Therefore, the Gaussian width was coupled for all peak components, leaving the peak position, the relative height, peak area, the Lorentz width (characteristic for the core-hole lifetime) and the background as freely varied parameters.

To derive the work function, the UPS secondary electron cutoff was measured for 5 scans with 2 eV pass energy and 0.01 eV energy step with He I UV radiation. The valence band was measured by both He I and He II radiation; With He I, a pass energy of 2 eV was used and 10 scans with 0.01 eV energy step were recorded. For He II, the valence band was measured by 20 scans with 15 eV pass energy and 0.02 eV energy step. The energy axis of the UPS measurements was calibrated by measuring the Fermi edge of a sputter-cleaned Au reference sample. For all UPS experiments, a bias voltage of 15 V was applied to the sample.
CHAPTER IV

Ti AND Li DEPOSITION ON AU:
A STUDY OF OVERLAYER FORMATION AND OXIDATION

Deposition experiments of Ti and Li on bare Au-coated Si substrates were performed to determine the deposition parameters for Ti and Li deposition and to calibrate the effusion rates of the two sources. Furthermore, the deposited Ti and Li films were employed to investigate the oxidation behavior in ultra-high vacuum. All of these studies are necessary prerequisites for an accurate investigation of the interaction of Ti, Li, carbon nanomaterials, hydrogen, and residual gases in the ultra-high vacuum system.

There are several parameters of the experimental setup that can potentially affect the deposition conditions: the relative position and orientation of the sample with respect to the metal sources, and the sample substrate temperature. If all of these parameters are kept constant for all deposition experiments, the effective deposited film thickness is proportional to the metal effusion flux (i.e., the deposition rate) and the deposition time. Section 4-1 describes the experimental procedure for Ti deposition on a Au-coated Si substrate and the deposition rate calibration for the EFM3 e-beam evaporator. A deposition time for very thin (~ few monolayers) deposition of Ti was determined, which will be employed for deposition experiments on carbon-based nanomaterials. Similarly, a
determination of the effective thickness of Li on a Au-coated Si substrate is presented in Section 4-2.

In Section 4-3, results of oxidation studies of the Ti and Li overlayers are presented, as characterized by XPS, UPS, and STM. Later in this thesis, the results of these studies will be used as a reference for similar deposition experiments on carbon nanomaterials.

Section 4-1

Ti Deposition on a Au-coated Si Substrate

4-1.1. Ti deposition rate determination

The deposition rate for Ti was determined by consecutive depositions of Ti on Au-coated Si substrates and a detailed analysis of the attenuation of the XPS Au 4f signals. The ion current of the e-beam evaporator was fixed by setting the integrated flux monitor at 100 nA and the deposition time was varied, resulting in the formation of Ti layers with different thicknesses. Fig. 4.1 sketches the Ti layers subsequently deposited on a Au-coated Si substrate (after varying deposition times as listed in the figure). First, Ti was deposited on Au-coated Si substrate for 10 min (layer A) and the Ti-deposited sample was characterized by XPS. Subsequently, a 20-minute and a 30-minute layer were deposited on top of the first Ti layer and analyzed with XPS. The deposited sample was stored in ultra-high vacuum for 24 hours, then the deposition sequence was repeated with the formation of layer A', B', and C' as shown in Fig. 4.1. The total Ti deposition time thus amounted to 120 minutes.
Fig. 4.1: Schematic Ti layer formation on a Au-coated Si wafer substrate at constant Ti flux and after different deposition times (as listed).

Fig. 4.2 shows the XPS survey spectra after each Ti deposition step in the above-described series. The spectra were offset along the intensity axis. XPS and XAES spectral features characteristic for Au, Ti, O and C were identified by comparing the experimentally observed binding energies to reference values as described in Chapter III. As expected, all Ti signals increase and all Au signals decrease with increasing Ti deposition time. Note that the small residual carbon signal on the Au-coated Si substrate is also reduced as a function of deposition time, while the oxygen signal does not show a clear trend.

The attenuation of the Au 4f XPS detail spectra shown in Fig. 4.3 was used to estimate the effective thicknesses of the Ti overlayer on the Au-coated Si substrate. The Au 4f signal disappears after 120 minutes of deposition, suggesting that the surface of the Au-coated Si substrate is fully covered by a closed Ti film and that the Ti film is significantly thicker than the inelastic mean free path of the Au 4f photoelectrons.
Fig. 4.2: XPS survey spectra taken after the various Ti/Au deposition steps described in Fig. 4.1.

Fig. 4.3: Time-dependent attenuation of Au 4f XPS spectra after the various Ti deposition steps.
The Au 4f XPS peaks were fitted simultaneously using Doniach-Sunjic profiles and linear backgrounds. The integrated areas under the peaks were taken as the peak intensities and listed in Table 4.1. The behavior of the Au 4f peak intensity as a function of Ti deposition time is plotted in Fig. 4.4a, which shows an exponential decay of the Au 4f signal due to attenuation in the Ti overlayer. As mentioned above, the Ti flux rate was kept constant for all depositions; hence the Ti layer thickness is proportional to the deposition time, as shown in Fig. 4.4b.

Table 4.1: Au 4f XPS peak intensities and calculated Ti film thickness, derived from the stepwise Ti deposition on a Au-coated Si substrate.

<table>
<thead>
<tr>
<th>Deposition Time (min)</th>
<th>Peak Intensity (Integrated counts)</th>
<th>Calculated Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.37E+07</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.58E+07</td>
<td>6.5</td>
</tr>
<tr>
<td>30</td>
<td>8.61E+06</td>
<td>33.0</td>
</tr>
<tr>
<td>60</td>
<td>1268763</td>
<td>79.2</td>
</tr>
<tr>
<td>70</td>
<td>674153.6</td>
<td>94.4</td>
</tr>
<tr>
<td>90</td>
<td>231447.7</td>
<td>120</td>
</tr>
<tr>
<td>120</td>
<td>23398</td>
<td>176</td>
</tr>
</tbody>
</table>

For the values shown in Tab. 4.1 and Fig. 4.4b, the effective thickness of the Ti overlayer was calculated using Eq. 9 (Chapter III). Note that the here-discussed thickness is an "effective" one, i.e., the thickness that is obtained under the assumption of a homogeneous layer growth (as opposed to, e.g., island formation). An inelastic mean free path (IMFP) of \( \lambda = 24.13 \) Å was used for Au 4f photoelectrons (kinetic energy of 1170 eV) in a Ti environment [73]. A linear fit for the experimental data points in Fig. 4.4b yields a slope of \( -1.52 \), which results in a deposition rate of 1.52 Å/min for Ti on the Au-coated Si substrate for our deposition conditions.
4-1.2. Optimization of Ti deposition on Au-coated Si substrates

Based on the deposition rate calibration for Ti deposition on Au-coated Si substrates described above, a deposition time of 2 minutes at an ion current of 100 nA would produce a film with effective thickness of ~3 Å, i.e., in the range of a few monolayers. Therefore, these parameters were chosen for all Ti deposition experiments on carbon-based materials. To investigate the behavior of Ti deposition on Au as a reference for the deposition on carbon-based substrates and to obtain a more accurate thickness calibration for such short deposition times, the following experiment was conducted. First, the pristine Au-coated Si substrate was heated in vacuum of ~5 x 10⁻⁹ mbar at 200°C for 30 minutes to remove water and oxygen contaminants absorbed on the sample surface. As shown in Fig. 4.5, the O 1s signal decreases significantly by this additional step, and there is a small increase of the Au 4f signal after heat treatment, indicating a substantial reduction of the oxygen contained in the top (contamination) layer on the sample surface.
Fig. 4.5: Change of (a) O 1s and (b) Au 4f spectra of Au-coated Si substrate before and after heat treatment.

The carbon contamination at the surface of the Au layer was also reduced after additional heat treatment, as shown by a decrease in intensity of the C 1s XPS signal in Fig. 4.6. The high BE tail of C 1s, characteristic for oxidized carbon, was reduced. The main C 1s peak became narrower and the maximum shifted ~0.5 eV to lower BE after the heat treatment.

XPS detail spectra of the Au 4f photoemission lines as measured for a bare (uncovered) Au-coated Si substrate and after the standard (2 minutes, 100 nA) Ti deposition is shown in Fig. 4.7. It can be observed that the Au 4f intensity for the Ti/Au sample is significantly decreased compared to that of the bare Au-coated Si substrate. The effective thickness of the Ti layer, estimated from the observed attenuation of the Au 4f XPS line is $4 \pm 0.5$ Å. This value is slightly higher than that estimated from the
calibration series described above, most likely due to the modified sticking coefficients after the oxygen-removing annealing step.

Fig. 4.6: Change of the C 1s XPS spectrum of a Au-coated Si substrate before and after heat treatment.

Fig. 4.7: XPS detail spectra of the Au 4f photoemission line of a bare (uncovered) Au-coated Si substrate and after Ti deposition (2 min, 100 nA current rate).
4.1.3. Microscopic investigation of the morphology of Ti films on Au-coated Si substrates

STM was used to examine the morphology of the Au sample before and after Ti deposition to investigate the homogeneity of the deposited Ti layer. The formation of Ti layers on Au surfaces was investigated with different deposition times, namely 1 minute, 2 minutes, and 10 minutes at a fixed flux current of 100 nA.

The bare Au-coated Si substrate consists of ~100-200 nm Au particles with an RMS surface roughness ~ 2 nm, as shown in Fig. 4.8. The particle size and surface roughness were analyzed by SPIP image processing software [101]. Comparing the STM image of the bare Au-coated Si substrate on a magnified scale (Fig. 4.9a) with that of the Ti/Au sample (Fig. 4.9b), it becomes clear that the Ti deposition significantly changes the sample morphology. Ti nanoparticles of ~ 5 Å diameter are formed that uniformly cover all Au particles.

The deposition of Ti on Au-coated Si substrate is further explored by examining STM images obtained from samples with increasing deposition time, as shown in Fig. 4.10. Ti nanoparticles with a mean diameter of ~5 Å are formed and distributed uniformly on the substrate already after 1 minute of Ti deposition. As the deposition time is increased, the size of the individual Ti nanoparticles remains constant and tendency of clustering of Ti nanoparticles is observed. After 10 minutes of Ti deposition, the Ti clusters become larger, form a layer, and increasingly cover the Au surface. As previously mentioned, the thickness estimation using XPS is based on the assumption of a homogenous layer formation. The here-presented STM observation of nanoparticle formation of Ti on Au shows that this thickness estimation is just an approximation, giving an “effective”
(average) thickness, rather than the thickness of true homogeneous layer of Ti. Nevertheless, it should be pointed out that the Ti nanoparticles are distributed homogeneously across the surface and that no significant "bare" regions are observed.

Fig. 4.8: (left) STM image of a Au/Si substrate before Ti deposition, showing Au particles of ~100-200 nm size; (right) line scan extracted from the STM image showing the low roughness of the Au-coated Si substrate (~2 nm) and the size of the Au particles.

Fig. 4.9: STM image of Au-coated Si substrate before (a) and after (b) standard Ti deposition (2 min, 100 nA flux rate). Ti adatoms form ~5 Å-diameter nanoparticles on the 100-200 nm-Au particles. Scale bar is 50 nm.
Section 4-2

Li Deposition on a Au-coated Si Substrate

4-2.1. Li deposition rate determination

To perform quantitative Li deposition studies on carbon-based materials, the chemical and morphological effects of Li deposition on an Au-coated Si substrate was studied. For the deposition, a heating current of 9 A was applied to the Li getter element for 2 minutes after careful outgassing. The sample was positioned in front of the Li source at a distance of about 10 cm. XPS measurements were performed on the Au sample before and after Li deposition.

The XPS Au 4f spectra before and after Li deposition are presented in Fig. 4.11. The effective thickness of the Li layer, as estimated from the attenuation of the XPS Au 4f signal, is approximately 28 Å, which corresponds to a deposition rate of ~ 14 Å/min. As in the case for Ti, this analysis assumes a uniform Li layer. An inelastic mean-free path (IMFP) of \( \lambda = 38.82 \) Å was used to describe the attenuation of the Au 4f photoelectrons at a kinetic energy of 1170 eV in the Li layer [73].
Fig. 4.12 show the XPS spectra obtained for the Li 1s region before and after Li deposition. The BE of the Li 1s core-level is close to that of the Au 5p$_{3/2}$ photoemission line at around 57 eV [102-105], such that the peaks overlap. Furthermore, the photoionization cross-section is 0.06 for Li 1s and 0.88 for Au 5p$_{3/2}$ (i.e., about 15 times lower) [72]. Thus, it is impossible to unambiguously quantify the Li 1s XPS peak.

To derive some qualitative information, the spectra in the overlap region before and after Li deposition were normalized to the same intensity at 50 eV and the difference spectrum was used to derive the spectral feature of Li 1s, as shown in Fig. 4.12, bottom. The Li 1s contribution is clearly seen around ~56 eV and confirms the presence of Li on the surface of the Au-coated Si substrate.

Fig. 4.11: XPS Au 4f spectra of the Au-coated Si wafer before and after Li deposition.
Fig. 4.12: Top - XPS Li 1s/Au 5p$_{3/2}$ before and after Li deposition; the spectra were normalized to the same intensity at a binding energy of 50 eV. Bottom – difference spectrum obtained after subtracting the spectrum before Li deposition from the spectrum measured after Li deposition. The difference indicates the spectral weight contributed to Li 1s photoelectrons.

4-2.2. Microscopic investigation of the morphology of Li films on Au-coated Si substrates

STM experiments were carried out on a Li-covered Au/Si substrate to investigate the morphology of the sample surface. In comparison to the Ti deposition experiments using the e-beam evaporator, it is more difficult to obtain a uniform deposition of Li using our Li source for two reasons. First, unlike the (small spot) e-beam evaporator, the Li evaporates from the Li getter element along a 1cm-long line, and thus an inhomogeneous distribution can be expected. Second, the Li source was set at a 45° angle to the sample surface, as described in Chapter III, which produces an unequal flux distribution of incoming metal on the sample surface. As a result, after Li deposition on Au-coated Si
substrate, we observe a difference in coverage and thickness of the Li film, as can easily be seen from the coloration of the film. At the center of sample a bluish coloration of the film suggests the presence of a thick Li layer, while at the sample edge the color of the Au-coated Si substrate dominates. Fig. 4.13 shows the respective STM images of the Li-deposited Au-coated Si substrate, taken at the center of the sample. It shows that the Au-coated Si substrate is covered by a continuous layer of Li. The observed particles have sizes of about 200 nm, which suggests that the Li layer uniformly coated the Au particles observed for the substrate (see Fig. 7) [106]. The thickness of the Li film, estimated from the line scan in STM image (Fig. 4.13, right) is approximately 5-10 nm. In the off-center region, only discrete Li clusters are observed (Fig. 4.14). The size of the Li clusters becomes smaller when moving from the sample center towards the edge. Likewise, the number of Li clusters decreases towards the edge. However, high resolution STM images (Fig. 4.15) in this area reveal that the surface of the Au film (Au particles) is covered by nano-clusters of ~5-10 nm diameter, presumably formed by Li atoms.

![STM image and line scan](image.png)

Fig. 4.13: STM image (left) and line scan (right) of a thick Li layer deposited on a Au-coated Si substrate; images were taken at the center of the sample. The scale bar is 200 nm.
Fig. 4.14: STM image of a Li layer, deposited on a Au-coated Si substrate, (a) in an area intermediate between the center and the edge; (b) near the edge of the sample. The scale bar is 200 nm.

Fig. 4.15: High-resolution STM images of a Li layer on a Au particle near the edge of the sample. The scale bars are 50 nm (a) and 10 nm (b).

Section 4-3

Oxidation of Ti and Li Films on a Au-coated Si Substrate

Both metallic Ti and Li are very reactive with regards to oxidation. The oxidation may occur even under ultra-high vacuum by interactions between the metal atoms and
molecules from the residual gas. In fact, Ti is used as a very effective pump (Ti-sublimation pump) in ultra-high vacuum environments to getter residual gas molecules, most commonly water. Such (oxidation) processes would also have an influence on studies with adsorbed metal adatoms on nanomaterials, as in the present case. Thus, XPS measurements were performed to monitor the characteristics of adsorbate oxidation. Furthermore, the interaction of Ti and Li with adventitious carbon on the sample surface was also investigated. The results help to identify oxidation issues and give first indications for metal-carbon interactions for metal adatoms on carbon-based materials (which will be discussed in subsequent chapters).

4-3.1. Oxidation behavior of Ti on Au-coated Si substrates

The oxidation behavior of Ti on Au-coated Si substrates was investigated by XPS measurements on both thickness-incremented and standard Ti layers. The former gives insight into the thickness-dependent (deposition time-dependent) oxidation behavior of the Ti layer. For the latter, measurements were performed on a sample after different resident times after deposition, providing time-dependent information on the oxidation characteristics of the thin (standard) Ti layer.

Evolution of the XPS Ti 2p and XAES Ti LMM spectra as a function of deposition time is shown in Fig. 4.16. The presence of Ti on the surface of Au-coated Si substrate is characterized by appearance of Ti 2p spin-orbit doublet at BE = 453.9 eV and 459.2 eV [77], and the corresponding Ti LMM Auger line at KE = 420.8 eV. The Ti signals increase with increasing deposition time, as expected. The formation of the Ti layer during the early stage of Ti deposition (i.e., "10min-Ti/Au") is affected by residual oxygen species on the surface of Au (note that this Au/Si sample did not undergo the
additional annealing step described in Section 4-1.2.). Thus, the Ti signals have contributions of both Ti metallic and oxides [89, 107-112]. For further Ti deposition steps, a shift of ~0.8 eV of Ti 2p to lower BE is observed for spectra taken after additional Ti depositions. The main Ti LMM peak appears as a new feature, shifted ~1.2 eV to lower KE. Both of these features are attributed to metallic Ti.

The Ti layer does not only oxidize at the interface with the Au-coated Si substrate, but also at the outermost layer, where oxygen species from the residual gas are adsorbed. This can best be seen in the spectral changes of Ti 2p and Ti LMM between the 60min-Ti/Au and the 70min-Ti/Au layers. After the Ti deposition and XPS analysis of the former, the sample was stored under ultra-high vacuum for 24 hours before the next Ti deposition occurred. Consequently, we observe a relative decrease of the main Ti 2p peak, a peak broadening, and a small shift to higher BE. Likewise, we find a decrease of the main Ti LMM peak and a relative increase of the low-KE component.

![Graph](image)

Fig. 4.16: Evolution of (a) Ti 2p Ti LMM and (b) Ti LMM signals as a function of Ti deposition time. For further details see text.
The oxidation of the Ti layer at both the substrate interface and at the outermost layer is further confirmed by examining the evolution of the O 1s spectra (Fig. 4.17a) at consecutive stages of Ti deposition. Oxygen and water vapor adsorbed on the surface of the bare Au/Si substrate is responsible for a broad O 1s peak at ~ 530.8 eV. After 10 minutes of Ti deposition, the main O 1s peak shifts ~ 0.6 eV to lower binding energy, indicative for the presence of a Ti-O-C-Au compound [107-112]. As the thickness of the Ti layer increases, signals from the oxides formed at the substrate/Ti interface decrease due to attenuation in the Ti overlayer. The O 1s main peak shifts to higher BE, most likely due to the reaction of Ti with residual gas, which forms intermediate Ti oxides or hydroxides at the outermost Ti layer. There is a sharp increase of the O 1s signal from the 70min-Ti/Au layer. As described above, this layer was stored in UHV for 24 hours before Ti deposition, and hence adsorption of oxygen species from the residual gas is to be expected. Since the additional Ti layer is thin (10 minutes of deposition), the observed increase of the O 1s signal is due to contribution of both Ti oxides at the surface of this layer as well as buried directly underneath it. Note that the O 1s line for these oxides is observed at the same binding energy as for the previous (and following layers).

As mentioned above, carbon contamination is always found on previously air-exposed sample surfaces in various forms of hydro-, oxide- or amorphous carbon. It is interesting to examine how Ti interacts with adventitious carbon on the surface of the Au-coated Si substrate. Fig. 4.17b shows the C 1s spectra as a function of Ti deposition time. The adventitious carbon on the Au surface is characterized by a broad C 1s peak at ~283.6 eV. After 10 minutes of Ti deposition, the main C 1s peak shifts ~0.6 eV to higher BE and is reduced in intensity due to attenuation in the Ti layer. A new peak emerges at ~
281.2 eV. The positive BE shift of the main C 1s peak is ascribed to the formation of a Au-C-O-Ti compound at the Ti/Au interface. The low BE feature at 281.2 eV is attributed to the formation of Ti-C bonds [113]. As the deposition time increases, the signal from adventitious carbon on the Au surface decreases and disappears due to attenuation in the Ti overlayer. The spectra are dominated by the signal from Ti-C bonds due to the reaction of Ti with hydro- or oxide carbon from the residual gas at the outermost layer. This contribution is most evident for the 70min-Ti/Au layer, where an accumulation of carbon-containing adsorbates from the residual gas on the sample surface after 24 hours of storage in UHV leads to a sharp increase of the C signal.

Fig. 4.17: Evolution of (a) O 1s and (b) C 1s signals as a function of Ti deposition time.

The characteristics of the standard Ti deposition on a Au substrate were investigated by time-dependent XPS measurements. A detailed understanding of the Ti oxidation characteristics under these deposition parameters is very important, because the identical
deposition parameters will be employed for the study of carbon-based samples described in later chapters.

Two different time-dependent characterization series of the standard Ti deposition were carried out. Single scans for spectral windows of Ti 2p, O 1s, C 1s and Au 4f were measured consecutively after each other. Each scan took place in ~1.0 min. 10 series of single scans were measured that made up the “fast series” of measurements. This series were measured immediately after Ti deposition to monitor the “fast” changes in the chemical state of the sample surface. Due to sample transfer, 5 minutes elapsed between the end of deposition and the start of the XPS measurements.

After the “fast series” in the first hour after deposition, the second series of detailed measurements was performed on the same as-deposited sample after 1 hour, 4 hours, and after 5 days of storage in ultra-high vacuum of either the analysis chamber or the preparation chamber. The sample was then intentionally exposed to air for 30 minutes to investigate the change of the sample surface under ambient condition. In this series, Ti 2p, O 1s, C 1s, and Au 4f XPS detailed spectra were measured. Details of the sample treatment and the performed measurements are shown in Tab. 4.2.

Fig. 4.18 shows XPS survey spectra of the Au/Si substrate before and after standard Ti deposition, measured after different “exposures” to UHV. The spectra were normalized to the Au 4f lines and offset along the intensity axis. The most prominent features that can be observed from the survey spectra is the emergence of the Ti features after Ti-deposition, the attenuation of the Au signals after Ti deposition, and, most notably, the increase of the O signals with increasing storage time. Furthermore, the O signals clearly increase after the air exposure step.
Table 4.2: List of time-dependent measurements of (Li/Ti) thin film deposition on Au/Si substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS</th>
<th>UPS</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat-treated Au</td>
<td>X</td>
<td>X</td>
<td>Heat-treated Au/Si substrate</td>
</tr>
<tr>
<td>Ti/Au-01-10</td>
<td>X</td>
<td></td>
<td>Standard Ti deposition on Au/Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Single scans measured right after deposition</td>
</tr>
<tr>
<td>Ti/Au-1h</td>
<td>X</td>
<td>X</td>
<td>As-deposited sample of Ti deposition on Au/Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Detailed scans measured 1 hour after deposition</td>
</tr>
<tr>
<td>Ti/Au-11</td>
<td>X</td>
<td></td>
<td>As-deposited sample of Ti deposition on Au/Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Detailed scans measured 4 hours after deposition</td>
</tr>
<tr>
<td>Ti/Au-5d</td>
<td>X</td>
<td></td>
<td>As-deposited sample of Ti deposition on Au/Si</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Detailed scans measured 5 days in vacuum</td>
</tr>
<tr>
<td>Ti/Au-EA</td>
<td>X</td>
<td>X</td>
<td>Sample Ti/Au-5d exposed to air for 30 minutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Detailed scans measured after exposing sample to air</td>
</tr>
<tr>
<td>Li/Ti/Au</td>
<td>X</td>
<td>X</td>
<td>2min-9A Li deposition on Ti/Au-EA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Detailed scans measured after additional Li deposition on exposed-to-air Ti/Au</td>
</tr>
</tbody>
</table>

Fig. 4.18: XPS survey spectra of a Au/Si sample before and after standard Ti deposition. For the latter, the sample was stored in UHV for 1 hour (1h) and 5 days (5d) and also exposed to air for 30 minutes (EA).
The “fast-series” spectra of Ti 2p and O 1s, measured in 10 scans (with a separation of ~5 minutes between scans) in the first hour after Ti deposition are shown in Fig. 4.19. In addition, a scan from the second series, taken after 4 hours in UHV, is also shown for reference (red spectra). The vertical lines at the main peaks of Ti 2p and O 1s indicate the peak maximum in the first spectrum for each region. Right after deposition (5 min), the Ti 2p spin-orbit doublet, consisting of Ti 2p_{1/2} and 2p_{3/2} peaks, is observed at ~455 eV and ~461 eV, respectively, corresponding to metallic Ti [89, 107, 110]. As the time after deposition increases, the Ti 2p peaks shift to higher BE and the O 1s peak shifts to lower BE, indicative of the oxidation of the Ti adatoms. After 4 hours, the Ti 2p peaks are shifted by +0.2 eV and the O 1s peak is shifted by -0.2 eV. Since the oxygen species on the Au surface were previously minimized by the heat treatment, the oxidation is expected to be dominated by the reaction of Ti adatoms with residual gas molecules at the outermost layer.

Fig. 4.19: (a) Ti 2p and (b) O 1s “fast-scan” spectra of a Au sample after standard Ti deposition.
In order to further evaluate the oxidation of the Ti layer, the Ti 2p and O 1s lines were measured in detailed after the Ti layer had been exposed to UHV for 1 hour and for 5 days. The corresponding Ti 2p XPS detail spectra are shown in Fig. 4.20. The spectra were normalized at BE = 452 eV, i.e., at lower BE than the main Ti 2p feature, and plotted on the same intensity scale. In addition, the difference spectrum (Ti/Au-5d minus Ti/Au-1h) is also shown to demonstrate the spectral changes induced by the Ti oxidation. The spectrum of the “fresh” Ti/Au sample (Fig. 4.20a, 1 hour after deposition) represents Ti that is mainly in metallic form. The Ti 2p spin-orbit doublet separation is found to be ~6.0 eV with the Ti 2p$_{3/2}$ main peak at ~454.7 eV. After 5 days in vacuum, the Ti 2p peaks reduce in peak height, broaden, and shift to higher BE by ~0.2 eV. Furthermore, the high BE shoulder of the Ti 2p peaks increases in intensity. The difference spectrum shows that the intensity at the main peaks is reduced and that a broad peak emerges in the valley between the Ti 2p doublets, suggesting contributions of several intermediate forms of Ti oxides [89, 107, 110]. Furthermore, the secondary electron background is increased, indicating inelastic scattering processes in the oxide layer on the surface. These results indicate a transformation of deposited Ti from metallic Ti to Ti oxides, presumably due to reaction of Ti with residual H$_2$O from the ultra-high vacuum. It should be noted that this oxidation is not surprising – in fact, Ti is known to be an excellent getter material for residual gas molecules. This process is used in Ti-sublimation pumps, which are generally considered to be the most efficient pumps in the ultra-high vacuum regime.

To identify the “end point” of Ti oxidation, the Ti/Au sample was exposed to air for 30 minutes (i.e., to both O$_2$ and H$_2$O as potential oxygen sources). The respective spectra of the vacuum stored (-5d) and air exposed (-EA) Ti/Au sample are compared in Fig.
4.20b. The measured Ti 2p spectrum consists of features from two Ti species. The Ti 2p features ascribed to Ti metal decrease substantially (features A and A' in Fig. 4.20b). At the same time, the high BE shoulder (at 458.8 eV) increases in intensity and becomes the major Ti 2p contribution (features B and B'). The spin-orbit doublet separation changes from 6.0 eV (for the Ti 2p of Ti metal) to approx. 5.7 eV. A comparison with literature data [89, 107, 110] reveals that this Ti 2p photoemission lines can be ascribed to TiO₂. The data shows that the deposited Ti becomes partially oxidized, presumably at the outermost layer.

Fig. 4.20: Ti 2p XPS lines of a Ti/Au sample measured 1 hour after deposition and after 5 days of UHV-storage (a); after 30 minutes of air exposure (b). The dashed lines indicate the peak maxima of the various spectra.
The evolution of the O 1s and C 1s XPS spectra measured at different stages of Ti/Au sample after deposition are shown in Fig. 4.22. The signals from the initial Au-coated Si substrate after heat treatment in vacuum at 200°C for 30 minutes are also included for reference. An increase of the oxygen signal (at ~530.7 eV) is observed after Ti deposition (Ti/Au-1h) and further after storage in vacuum for 5 days, probably due to accumulation and adsorption of residual gas on the sample surface. There is a shift (~0.3 eV) of the main O 1s peak to lower BE side, which is in accord with the oxidation of Ti and transformation of metallic Ti to higher intermediate oxidation states, as observed in Fig. 4.20a. The O 1s signal increases strongly after exposing the Ti-deposited sample to air, indicating a strong interaction with oxygen and the formation of the above-described TiO₂ layer on the sample surface.
The interaction of Ti with adventitious carbon on the surface of the Au sample was examined by monitoring the evolution of the C 1s peak, as shown in Fig. 4.21b. A behavior similar to that observed for the thicker Ti film (Fig. 16b) is found. The deposition of Ti broadens and shifts the main C1s peak about 0.5 eV to higher BE. This chemical shift is probably induced by the electric field of Ti atoms surrounding the carbon atoms [78-81]. In addition, a new feature emerges at lower BE (at around 282.1 eV). This feature is associated with C-Ti bond formation, similar to the one observed for thicker Ti deposition. The C-Ti bond formation is driven by charge transfer from Ti to C atoms, which induces a shift of the carbon core-level to lower BE side. For the standard (thin) Ti layer deposition, the C-Ti bonds appears to be instable towards further oxidation, as is evident from the C 1s spectrum after air exposure. In this case, the C-Ti feature disappears and an additional increase of the C 1s main peak is observed.

4-3.2. Oxidation behavior of Li on a Au-coated Si substrate

Similar to Ti, Li is also reactive with regards to oxidation. Thus, XPS measurements were also used to characterize behaviors of Li layer, specially its formation, oxidation and reaction with adventitious carbon on Au-coated Si substrate.

XPS survey spectra of Au sample before and after Li deposition are shown in Fig. 4.22. It can be observed that signals from Au-coated Si substrate (Au 4f and Au 4d) decrease due to formation of Li layer, while oxygen signals (O1s and O KLL) increase, indicating adsorption of oxygen species from vacuum due to gettering effect of Li.
Fig. 4.22: Survey spectra of the Au/Si sample before and after Li deposition.

The XPS O1s detail spectra of the Au-coated Si substrate before and after Li deposition are shown in Fig. 4.23. A sharp increase of the oxygen signal is observed after Li deposition, which is attributed to the reaction of Li with molecules from the residual gas. Comparing with the oxygen adsorption on Ti (see section 4.3.1), Li reacts with even more strongly. On the uncovered Au-coated Si substrate, there is only a broad O 1s peak centered at approximately 531.8 eV, which can be attributed to oxygen species adsorbed on the Au surface [77]. After Li deposition, the O 1s spectrum clearly shows the contributions of two chemical species. The first is at approximately 530.6 eV, which can be ascribed to Li oxides, probably in the form of Li₂O as a result of reaction of Li with
oxygen [103, 104]. The second is at approximately 533.3 eV. There is possibility of formation of other forms of Li oxides, such as peroxides, in which oxygen is less negative and their features shift to higher BE. Li also can react with H₂O molecules of the residual gas to produce LiOH on the surface. The peak at 533.3 eV, therefore, can be ascribed to peroxides, hydroxides and/or other sub-oxide forms [103, 104, 114].

Fig. 4.23: O1s XPS detail spectra of the Au-coated Si substrate before and after Li deposition.

The related C 1s XPS detail spectra are shown in Fig. 4.24. A clear change in peak shape and energetic position is observed upon Li deposition. The main peak decreases in intensity due to the formation of the Li overlayer and shifts almost 2 eV to higher BE. This large positive shift indicates a charge transfer of Li 2s electrons to unoccupied states of the C atoms [102-105, 114-116]. It is also noticed that the shoulder of the main C1s peak at higher BE side, which is attributed to oxidized carbon, is reduced or possibly even disappears after Li deposition. This suggests that Li can even react with oxygen bonded to the adventitious carbon of the Au-coated Si substrate.
4.3.3. Oxidation behavior of coadsorbed Li and Ti on a Au-coated Si substrate

The strong reactivity of Li suggests that it may be potentially used to prevent oxidation of Ti in the deposition experiments on carbon-based materials. To explore this possibility, we examine how Li would affect the oxidized Ti layer on a Au substrate (Ti/Au-EA in section 4.3.1). A subsequent deposition of Li on top of the air-exposed Ti layer was performed using the standard Li deposition conditions, and XPS measurements were performed to characterize the Li/Ti bi-layer on the Au surface.

The Au 4f XPS detail spectrum of the Li/Ti/Au sample is shown in Fig. 4.25, comparing with that of Ti/Au-EA (i.e., air-exposed and before Li deposition). As expected, the Au 4f signal of the substrate decreases further due to Li deposition. On the basis of the observed attenuation, the effective Li layer thickness can be estimated to
approximately 13 Å, using Eq. 11 of Chapter III with \( \lambda = 38.82 \) Å for photoelectrons at a kinetic energy of 1170 eV in a Li layer [73].

Fig. 4.25: Au 4f XPS signal before (Ti/Au-EA) and after (Li/Ti/Au) Li deposition on an air-exposed Ti/Au sample.

This effective Li thickness is about half of the thickness that was deposited on a bare Au-coated Si substrate using the same Li deposition conditions (see section 4.2). There are two possible explanations for this discrepancy. First, it would have been possible that the deposition rate for Li, provided by the current experimental setup, was not constant. Given the short Li deposition time (2 min), a temporal instability of the heating source could have resulted in a significant variation of the evaporated Li flux. Second, the formation of a Li layer on a relatively flat Au surface could be quite different from the layer formation on the surface of Ti nanoparticles. The rough surface, induced by Ti nanoparticles, may reduce the wettability of Li and may be responsible for a less homogeneous surface cover. Moreover, the thickness estimation by XPS, as discussed for Ti on Au, provides an effective, average film thickness based on the assumption of a
homogeneous layer formation. Clustering of Li, for example, would result in significantly reduced effective thickness.

The deposition of Li on top of the oxidized Ti/Au sample induces further changes in the Ti 2p XPS line shapes, as shown in Fig. 4.26. After Li deposition, the TiO₂-derived Ti 2p features (features B and B’) decrease in intensity, while the features associated with metallic Ti (features A and A’) increase. The Ti 2p spectrum measured at 1 hour after Ti deposition is also included for comparison.

The intensity variations suggest a reaction of the deposited Li with oxygen from the previously formed TiO₂ layer. This result is important as it would suggest that it is possible to use Li as a TiO₂ reducing agent, preventing oxidation of Ti or converting already formed TiO₂ back to metallic Ti. In the context of hydrogen storage in Ti-decorated carbon-based materials, this approach could circumvent the detrimental effects of Ti oxidation (note that it is much simpler to evaporate Li from a commercially available dispenser element than to deposit metallic Ti in a non-UHV environment). A co-evaporation experiment of Ti and Li could shed further light on this concept, and such experiments are currently in the planning phase.

The O 1s XPS signal increases after Li deposition, as seen in Fig. 4.27a, which indicate further oxygen absorption on the sample surface due to gettering of residual gas molecules by the deposited Li. We notice that the all peaks in the spectra of O 1s, C 1s, and Ti 2p shift to higher BE after Li deposition. The main peak of O 1s shifts about 0.3 eV, and feature B of Ti 2p (Fig. 25) shifts about 0.4 eV. An even larger shift of ~1.0 eV is observed for the C 1s spectrum (Fig. 4.27b).
These shifts and their varying magnitude indicate a complicated behavior in both, initial and final state of the photoemission process. Apparently, the Li atoms interact with the Au, Ti, C, and O atoms by changing the initial state charge distribution as well as (most likely) the final state screening in the affected Au, O, C, and Ti atoms. As speculated above, for carbon atoms, the injection of Li 2s electrons into unoccupied states of the carbon atom can lead to an increase of the BE of the C 1s core level.
The characteristics of the metals on the Au-coated Si substrate are further explored by examining the valence band spectra measured by UPS (He I and He II excitation). Fig. 4.28 shows the secondary electron cutoff for the pristine (annealed) Au/Si sample, one hour after Ti deposition, after air exposure, and after subsequent Li deposition. The work function of the Au/Si substrate, determined by linear approximation of the secondary electron cut-off decreases from 4.37 eV by 0.30 eV due to the Ti deposition. After air exposure, there is little change (~0.04 eV) in the work function of the sample surface, although the Ti atoms on the surface have been oxidized in the process (as confirmed by XPS measurements). The subsequent deposition of Li on top of the oxidized Ti layer further shifts the secondary electron cutoff, which results in an even lower work function (2.78 eV), close to that of metallic Li (2.9 eV) [117-119].

Fig. 4.27: Evolution of (a) O 1s and (b) C 1s spectra of exposed-to-air Ti/Au sample after additional Li deposition.
Fig. 4.28: UPS-derived secondary electron cutoffs for the bare Au-coated Si substrate after annealing, after Ti deposition, after air exposure, and after Li deposition. The linear extrapolations to determine the work function as well as the work function values are also shown.

Fig. 4.29: UPS valence band spectra recorded with He I (left) and He II (right) excitations of the Au, Ti/Au, air-exposed Ti/Au, and Li/Ti/Au sample. The dashed lines serve as guides to the eye.
Fig. 4.29 shows the corresponding UPS valence band spectra. It can be observed that the Au valence band features at 2.6 and 6.1 eV [120, 121] decrease in intensity after deposition of the Ti layer. At the same time, the Fermi edge (at BE = 0 eV) becomes more pronounced. This is due to a much higher density of states for Ti (Ti 3d) around the Fermi edge compared to Au (Au 6s) [109, 112]. After exposing the sample to air, the Fermi edge vanishes, which is in agreement with our XPS results showing that Ti oxides are formed. Since these are generally semiconducting or insulating, a band gap is formed and no density of states at the Fermi energy is observed [112]. A broad valence band feature is formed around 6-7 eV, most likely characteristic for the $\sigma$-band of Ti oxides. A shoulder at about 8.5 eV below $E_F$ is ascribed to O 2p states [109, 112]. After additional Li deposition, this shoulder becomes more evident. In the latter case, a small feature appears at approx. 0.75 eV below $E_F$. This feature probably relates to a $\sigma$-band originating from Li 2s electrons.

CHAPTER IV SUMMARY

Ti and Li deposition on Au-coated Si substrates has been performed to optimize the deposition parameters for further deposition experiments on carbon-based materials. By controlling the ion flux current of the e-beam evaporator at 100 nA, the Ti deposition rate on Au-coated Si substrate was estimated to about 2 Å/min. The Li getter element source was heated to evaporate Li onto sample. At a heating current of 9A, the Li deposition rate was estimated to be about 14 Å/min on pure Au-coated Si substrate, and about 7 Å/min on the Ti-covered surface. The Ti layer on Au-coated Si substrate consists of uniform nanoparticles with a size of about 5 nm, while Li forms larger clusters (up to ~ 200 nm
for a thick film). Both Ti and Li layers become oxidized due to reaction of Ti and Li with residual gas molecules. We find indications that Li can react with oxygen already bonded to the substrate (oxygen bond to adventitious carbon on bare Au-coated Si substrates and Ti oxides on the Ti/Au sample, respectively). The reduction of Ti oxides by Li could have important implications, since Li could be a potential candidate for a co-evaporation approach with Ti to prevent oxidation of Ti. Both Li and Ti interact with adventitious carbon on the surface of Au-coated Si substrates. Charge transfer from Ti to C atoms induces a Ti-C bond formation with amorphous carbon or carbon oxides or hydroxides. The charge transfer between Li and C atom appears even stronger, as derived from the shift of the C 1s core level binding energy. The Ti-C and Li-C interactions could depend on characteristics and configuration of carbon atoms. These results are, therefore, important for the studies of Ti- and Li-deposition on carbon-based materials, which will be discussed in Chapters VI and VII.
CHAPTER V

CHARACTERISTICS OF CARBON-BASED MATERIALS

Microscopic and spectroscopic techniques were used to characterize the atomic and electronic structure of carbon in different geometric configurations, namely highly-ordered pyrolytic graphite (HOPG), C₆₀, and single-walled carbon nanotubes (SWNTs). Results of these investigations give detailed insight into the electronic and chemical properties of these materials, which will form the basis for further investigation in the Ti and Li deposition experiments described in Chapters VI and VII.

First, the elemental concentrations of the main species in the samples were assessed. The presence of intrinsic impurities in the investigated samples, including metallic catalyst nanoparticles and oxygenated functional groups, is discussed in Section 5-1. As previously described in Chapter III, a heat treatment was employed to desorb possible residue of the solvent used to disperse carbon-based nanomaterials (C₆₀ and SWNTs) for the spectroscopic experiments. The characteristics of samples before and after heat treatment are presented and discussed in Section 5-2. Finally, Section 5-3 characterizes and discusses how the atomic and electronic structure of C atoms varies between HOPG, C₆₀, and SWNT samples.
Section 5-1

Elemental Analysis of Carbon-based Materials: Assessment of impurities

Fig. 5.1 shows normalized XPS survey spectra of HOPG, C_{60} and SWNT, which are offset vertically for easier viewing. An elemental analysis was carried out to identify the main constituents of the sample surface by comparing XPS and XAES peaks and their BE values to reference values [77]. As expected, all samples show characteristics of carbon with a prominent C 1s core-level peak at about 285 eV, and the C KVV Auger line at KE = 263 eV. Oxygen signals are detected from all samples with a broad O 1s peak at 528-538 eV and O KLL line at KE = 510 eV. A small Au 4f\textsubscript{7/2} peak at about 84 eV is observed in the SWNT and C_{60} spectra, which stems from the Au substrate. There are no other detectable impurities in the samples of C_{60} and HOPG, while small peaks at \sim 710 eV and 720 eV, characteristic for the spin-orbit doublet of Fe 2p\textsubscript{3/2} and Fe 2p\textsubscript{1/2}, respectively, and traces of a Cl 2p signal at \sim 200 eV are observed in the spectrum of SWNTs samples (Fig. 5.2a). The Fe signal is due to the catalyst employed during the growth of the SWNTs, while the Cl signal most likely stems from residue after purification. For the SWNT and C_{60} samples, a small N 1s peak is observed at \sim 400 eV (Fig. 5.2b), which comes from residue of the DMF solvent used to disperse the SWNT and C_{60} molecules. As described in Section 5-2, vacuum drying and heat treatment efficiently removes most of the solvent residue. In contrast, the Cl 2p signal observed for the SWNT sample, was not reduced after heat treatment.

Individual peaks were extracted from the survey spectra and their integrated areas were used to estimate the relative concentration of the various elements according to the procedure described in Chapter III. The results are listed in Table 5.1.
Fig. 5.1: XPS survey spectra of HOPG, C\(_60\), and SWNT samples.

Table 5.1: Compositional analysis for HOPG, C\(_60\), and SWNT samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
<th>Other impurities (Cl, N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>99.3%</td>
<td>0.7%</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>C(_60)</td>
<td>98.8%</td>
<td>1.2%</td>
<td>&lt;0.1%</td>
<td></td>
</tr>
<tr>
<td>SWNT</td>
<td>96.6%</td>
<td>2.2%</td>
<td>1.17%</td>
<td>&lt;0.1%</td>
</tr>
</tbody>
</table>
Fig. 5.2: (a) Cl 2p and (b) N 1s spectral features extracted from the survey spectra of \( \text{C}_{60} \) and SWNT samples before heat treatment.

As can be seen from Tab. 5.1, the HOPG and \( \text{C}_{60} \) samples almost entirely consist of carbon, while a very small oxygen content probably comes from chemisorbed oxygen and adsorbed water molecules on the sample surface. A minor oxidation of the surface of HOPG after cleaving in the glove box may occur and may also contribute to the oxygen signal. The oxygen content of the SWNT sample, in contrast, is substantially higher, probably due to adsorbed water, oxides of the metal catalyst (Fe oxides), and/or oxygenated functional groups attached to the nanotube sidewalls during the purification process [122]. The concentration of other impurities (N, Cl) is estimated to be less than 0.1%. As mentioned above, Fe nanoparticles are often used as catalysts for SWNT production in the High Pressure CO gas combustion (HiPCO) process. The raw as-produced HiPCO SWNTs may contain up to 30% of Fe catalyst nanoparticles, usually
coated by amorphous carbon shells [123-125]. Various methods have been developed to remove the Fe nanoparticles and amorphous carbon from SWNTs. For example, heating SWNTs in air, followed by HCl acid oxidation treatment, has been used to purify HiPCO SWNTs [126-130]. The downside of such purification processes is that the acid oxidation treatment may create defects in the sidewall of the nanotubes and possibly adds oxygenated functional groups to the nanotubes. Our HiPCO SWNTs samples purchased from CNI are reported to have purity of 95% SWNTs. The impurities in our SWNT raw material are reported to include Fe catalyst nanoparticles and amorphous carbon [131]. Thus, it is not surprising to find Fe signals in the XPS survey spectrum and a higher concentration of oxygen species in the SWNT sample compared to C60 and HOPG. The presence of impurities in the form of Fe nanoparticles and amorphous carbon in the SWNT sample will be further discussed in conjunction with the microscopic investigation using STM.

Section 5-2

Effects of Heat Treatment

As described in Chapter III, DMF (C3H7NO) was used as a solvent to disperse C60 and SWNT molecules and to subsequently prepare thin films of C60 and SWNT samples. The solvent is supposedly evaporated while samples are “dried” in vacuum. Clearly, the presence of residual solvent may affect the interaction of deposited metal with carbon-based structures. As can be seen in Fig. 5.2b, the observation of a N 1s signal indicates that the solvent is still present in SWNT and C60 samples dried under vacuum. Thus, an additional heat treatment in the preparation chamber (200°C, 30 minutes) was employed
to enhance the removal of solvent residue from the samples before Ti and Li deposition (described in Chapter VI and VII). XPS measurements were used to check the effect of heating of samples dispersed by DMF, in comparison to samples without using DMF (i.e., the pristine SWNT powder pressed onto a Ta foil). Fig. 5.3 shows XPS survey spectra and Fig. 5.4 shows the N1s region of the pristine SWNT powder and a DMF-dispersed thin film of SWNTs on a Au substrate before and after heat treatment. It is clear that the residual DMF solvent induces a small, but significant N 1s peak and a slight increase of the O 1s signal. After heat treatment, the N and O signals are removed or largely reduced, respectively, and become comparable to those of the pristine SWNTs powder. This indicates that vacuum drying and subsequent heat treatment were sufficient to remove the solvent residue on SWNT and C60 samples. Thus, for all further experiments presented in this thesis, only results of C60 and SWNT samples after heat treatment will be discussed.

![XPS Mg Kα Survey](image)

Fig. 5.3: XPS survey spectra of pristine SWNT powder on Ta foil and a thin film of DMF-dispersed SWNTs on a Au substrate before and after heat treatment (200°C, 30 minutes) in vacuum.
Section 5-3

Spectroscopic Characterization of Carbon-based Materials

To understand the changes of the electronic structure of carbon-based materials induced by the deposition of metals on the surface, as seen in the core- and valence-level photoemission spectra, it is essential to characterize the atomic and electronic structure of carbon materials before any metal deposition experiments. A detailed analysis using XPS, XAES, and UPS was thus performed and will be presented here.

The C 1s spectra of HOPG, SWNT, and C\textsubscript{60} are shown in Fig. 5.5. All spectra were normalized to their maximal countrate. The main peaks of HOPG and SWNT are close to each other and centered at ~284.8 eV, while the C 1s peak of C\textsubscript{60} is found at about 285.3 eV, i.e., shifted by about +0.5 eV toward higher BE compared to the other two spectra. A
shift of +0.8 eV has been observed by Maxwell et al. [186] for C 1s peak of a thick C_{60} film compared to that of a 1 monolayer film (The C 1s position is at 285.2 eV and 284.4 eV for the films, respectively). The shift was ascribed to charging effect on the thick non-conductive C_{60} film. Similar behavior more likely occurs in our C_{60} sample and we ascribe this shift to charging effects due to non-conductive behavior of C_{60} film, rather than to a real difference in photoemission line position. To better observe the peak shape difference, the C_{60} spectrum was shifted by 0.5 eV to lower binding energy, such that all three spectra are aligned on a relative binding energy scale. The C 1s peaks of SWNT and HOPG have similar shape, suggesting a similarity of the carbon network structure. All spectra have a similar main peak, ascribed to photoelectrons from carbon atoms in sp^{2} configuration [3-5]. In contrast, variations in the tail at high BE of the main peak are observed for the three samples. The asymmetric broadening at the high BE side of the C 1s peak in both HOPG and SWNT suggests the presence of nonequivalent carbon sites in these structures. Defects, dangling bonds and disordered carbon atoms in an sp^{3}-hybridized configuration may contribute to a spectral feature at ~+0.9-1.0 eV from the main peak and cause the main peak broadened at the high BE side [135, 136]. In addition, several features at ~+1.5-4.0 eV from the main peak are usually attributed to carbon atoms in various bonding configurations with oxygen [122, 137-149]. Finally, both HOPG as well as the metallic components of the SWNT mixture could contribute to an asymmetric lineshape due to secondary electron creation by low-energy electronic excitations near the Fermi energy. It is evident from Fig. 5.5 that the relative intensity at high BE tail of the main peak in SWNT is higher than that in HOPG, indicating a larger contribution of respective spectral features in the SWNT case.
The main C 1s peak of C\textsubscript{60} is symmetric with shake-up satellites in the high BE tail (Fig. 5.5b), characteristic for shake-up excitations between molecular levels of the C\textsubscript{60} molecules [132-134]. The first satellite at about +1.8 eV relative to the main line is associated with an electron transition between the HOMO and the LUMO, i.e., it is indicative of the HOMO-LUMO gap. The second satellite is centered at +3.7 eV and corresponds to excitations from the HOMO-1 into the LUMO. The +5.8 eV satellite is attributed to a $\pi^* \leftrightarrow \pi$ plasmon.

Fig. 5.5: (a) C 1s XPS spectra of HOPG, SWNT, and C\textsubscript{60}. Peaks are normalized to the respective peak maxima; the C\textsubscript{60} was shifted by 0.5 eV to lower BE to align the peak with the HOPG and SWNT spectra for easier comparison. (b) Extended-scale of the high BE tail in (a).

As will be discussed in Chapters VI and VII, metal atoms deposited on HOPG, C\textsubscript{60}, and SWNT samples show different oxidation behaviors upon deposition. The oxygen
impurities on the sample surface could play a critical role in this oxidation process. Therefore, it is important to characterize the oxygen species on the sample surface before metal deposition. Detailed XPS O 1s spectra of the HOPG, C60, and SWNT samples are shown in Fig. 5.6. Different spectral shapes were observed for oxygen signals from HOPG, SWNT, and C60. The weak oxygen signal from HOPG centered at ~ 532.5 eV is attributed mostly to chemisorbed oxygen. As mentioned, a stronger O 1s signal is observed for SWNT and C60 samples. Compared to that of HOPG, the main O 1s peak of C60 is also shifted to higher BE by about ~0.5 eV. The shift is in accord with the observed shift of the C 1s peak, again indicating a possible charging effect of the C60 sample. As in the case of HOPG, the broadened O 1s peaks of C60 and SWNT are composed of several components, indicating the contribution of several oxygen species. Besides the chemisorbed oxygen component similar to that of HOPG, the low intensity and broad tail at the high BE side (536-538 eV) could be associated with water adsorbates. The feature is observed at the low BE side of the main peak in SWNT, centered at ~530.5 eV, probably originates from oxides of the residual metal catalyst particles (Fe oxides) [124, 125, 129]. In addition, oxygen-containing functional groups attached to the nanotube sidewalls as results of the purification process [122] may also add to the oxygen signal of the SWNT sample.

UPS valence band spectra using He I radiation (21.2 eV) are shown in Fig. 5.7 for HOPG, SWNT, and C60. A strong peak at about 13.7 eV below Fermi level is observed in spectrum of HOPG, which is due to a large density of states in the interlayer band between the carbon planes [152, 153]. The corresponding peak smears out in the SWNT
sample and disappears in C$_{60}$, which is due to the lack of the two-dimensional interlayer in SWNT and C$_{60}$ samples.

Fig. 5.6: O 1s XPS spectra of HOPG, SWNT, and C$_{60}$.

Fig. 5.7: UPS valence band spectra of HOPG, SWNT, and C$_{60}$, excited by He I radiation.
To determine the work function of the HOPG, SWNT and C\textsubscript{60} samples, the secondary electron cutoff was measured with He I radiation. The cutoffs and the corresponding work functions are shown in Fig. 5.8. The energy scale has been corrected for the applied sample bias (15 V) and displays the energy with respect to the Fermi level. Following the procedure described in Chapter III, the work function of the SWNT and HOPG samples were determined to be about 4.54 and 4.26 eV, respectively, in good agreement with literature [150, 152-154].

![Fig. 5.8: Work function of HOPG, SWNT and C\textsubscript{60} determined from low-energy valence band UPS He I spectra.](image)

The work function of the C\textsubscript{60} sample is 4.34 eV, which is different from literature values [152-154], where the work function of C\textsubscript{60} was reported to be larger than that of SWNT. As mentioned above, a shift of about 0.8 eV toward higher BE was observed in C 1s and O 1s XPS spectra of the C\textsubscript{60} sample, likely due to charging effects. Such charging effects would then also be expected in the UPS experiments, in particular for the
secondary electron cut-off. Note that the flux and energy of the excitation source are different, and thus the actual value is different from the XPS shift. As discussed below in conjunction with the HOMO position in the valence band, we estimate the shift to be 0.72 eV, leading to an estimated work function of 5.06 eV, in good agreement with literature.

Due to the reduced secondary electron background, the valence band structures of the HOPG, SWNT, and C_{60} samples are better visible using UPS excited by He II (40.8 eV), as seen in Fig. 5.9. The C_{60} spectrum is characterized by very sharp and distinct orbital features, typical for C_{60} molecules [132, 155]. The highest occupied orbital (HOMO) is located at 2.42 eV below Fermi level. As discussed in Ref [186], a shift of -0.9 eV in the position of HOMO level has been observed for a thick film of C_{60} compared to that of 1 monolayer (ML) thin film sample (2.6 eV and 1.7 eV below Fermi level, respectively). Charging on the thick C_{60} film is responsible for the observed shift. Similar charging likely occurs on our C_{60} sample, as observed for all core-level and valence-level spectra. Thus, we estimated a shift of 0.72 eV due to charging, applied to all valence spectral features, including the secondary electron cutoff. The features labeled 1 and 2 are from orbitals with pure $\pi$ character, with a separation of 1.33 eV [132, 154, 155]. States with binding energy > 4 eV exhibit a mixture of $\sigma$-$\pi$ character. In contrast to C_{60}, the spectra of HOPG and SWNT show broad band features. The spectra are almost identical and dominated by two features that are due to emission from a $\pi$-derived band at low binding energies (approx. 3 eV, band I) and emission from a $\sigma$-derived band at high binding energies (approx. 8 eV, band II) [154]. Fig. 5.10 shows the valence band spectra of HOPG and SWNT normalized to the integrated area to compare the relative intensity of the spectral features. The $\sigma$-derived band (II) is sharper for SWNT than for HOPG and
the maximum shifts to the higher BE side, possibly due to hybridization of C 2s states with impurity atoms, such as oxygen. It is interesting to note that the spectrum of SWNT near Fermi level is steeper than that of HOPG, suggesting that the density of states of the SWNT sample is larger in that energy region. The existence of metallic nanotubes or metal species such as the observed Fe catalyst nanoparticles in the SWNT samples may be responsible for this behavior.

**Fig. 5.9: UPS valence band spectra measured by He II radiation (40.8 eV) for HOPG, SWNT, and C_{60}.**
Section 5-4

Scanning Tunneling Microscopy Experiments on Single-walled Carbon Nanotubes

The investigation on nanostructures, in particular carbon nanotubes, requires access to the local atomic arrangement on the nanoscale. At present, the most commonly used techniques to obtain atomic resolution images of nanotubes are high-resolution transmission electron microscopy (HR-TEM) and scanning probe microscopy (SPM) [25, 156, 157]. While it is easier to prepare carbon nanotube samples for TEM, beam damage due to interaction of the highly energetic electron beam with the sample can induce defects and possibly even alter the local atomic arrangement. In contrast, SPM techniques can provide direct access to the atomic arrangement at the sample surface. In Scanning Tunneling Microscopy (STM), the non-contact nature of the interaction between the STM tip and the sample surface keeps the local atomic structure intact (provided sufficiently
low tunneling currents are used) and thus induces no damage to investigated samples. Furthermore, STM also allows obtaining local spectroscopic information (scanning tunneling spectroscopy – STS). One drawback, however, is that mechanical and thermal drifts on the nanometer scale may cause image distortions that make it difficult to obtain stable and reproducible images.

The perhaps greatest challenge in STM investigations of SWNTs is sample preparation, in particular if individual tubes are to be investigated. STM with atomic resolution requires a sufficiently flat and homogeneous surface. HOPG is often used as substrate for STM experiment because of its cleavability, flat surface, and the fact that it is conductive. For the study of carbon nanotubes, however, it is not suitable due to the similar atomic arrangement and chemical/electronic environments. In our case, we have therefore used the earlier-described Au-coated Si wafers.

Other challenges for STM of SWNTs exist. SWNTs generally aggregate in bundles, which makes it difficult to maintain the condition of a flat and uniform sample surface, and which may lead to characteristics that are different from individual tubes. Furthermore, as described earlier, carbon nanotubes can behave as a metal or a semiconductor, depending on their atomic arrangement (chirality), which consequently leads to different electronic interactions with the STM tip. This requires a fine tuning of the STM imaging parameters for each particular investigation (i.e., for large nanotube bundles or individual tubes, and for metallic or semiconducting tubes).

Several sample preparation methods for STM studies of carbon nanotubes are reported in literature: (1) dry contact transfer (DTC) to directly deposit nanotubes on the substrate surface [158, 159]; (2) SAM (Self-Assembled Monolayer) growth of carbon
nanotubes on the substrate surface, which usually involves cutting or functionalizing of the nanotube sidewalls [160, 161]; (3) electric-field deposition based on electrophoresis and charging nanotubes by solutes [162-167]; (4) deposition of nanotubes suspended in solution with surfactants [168-172]. Several promising results have been reported for separation of individual nanotubes from bundles and separation of metallic and semiconducting tubes by functionalization [173, 174].

Of these methods, we have evaluated methods (2), (3), and (4). We obtained best results with the dispersion and separation technique (method 4), which is easy to control and which has shown to be an effective way to obtain separated individual nanotubes, as will be discussed below. In this section we will present STM results that illustrate the separation of individual SWNT and that also give additional insight into the structural characteristics of carbon nanotubes. These will also be of relevance for the metal deposition experiments described in Chapters VI and VII.

The technical aspects of the dispersion and separation techniques have been described in Chapter III. In the following, we will present STM results obtained for various (partial) steps of the preparation procedure in order to illustrate the impact of the different steps on the separation and morphology of the SWNT on the Au/Si substrate.

5.4.1. STM images after dispersion of SWNTs in DMF in an ultra-sonic bath

SWNTs are reportedly dispersed well in DMF [168-172]. Figs. 5.11 and 5.12 show STM images of a SWNT sample, dispersed in DMF after applying a mild ultrasonication. No centrifugation of the dispersion was performed before deposition on the Au/Si substrate. It can be observed that SWNTs bundle into ropes of tens or hundreds of individual tubes. Occasionally, however, long and small bundles or pairs of tubes can be
observed, as seen in Fig. 5.11b. The ends of the tubes are usually decorated with nanoparticles, presumably Fe catalyst nanoparticles, possibly coated by amorphous carbon (Fig. 5.13a). In some instances, defect can be observed on the sidewalls of SWNTs (Fig. 5.13b). Since nanotubes experienced only mild ultra-sonication, the observed defect may stem from the original growth of the SWNT. It is also possible that some forms of adsorbates or functional groups attached to the nanotube sidewall as a result of purification and dispersion.

With a high-resolution STM, local spectroscopic measurements (STS) can be performed on individual tubes in a bundle, as seen at high resolution in Fig. 5.14a. The dI/dV(V) spectrum shows a semiconducting characteristic of the tube at the location marked with a circle, with a bandgap ~0.8 eV. However, because the tubes are still bound in bundle, the local spectroscopic results are expected to be influenced by the other (nearby) tubes in bundle.

Fig. 5.11: (a) STM image of SWNT bundles, observed after dispersion in DMF in an ultra-sonic bath; (b) Occasionally, long individual tubes can be observed.
Fig. 5.12: High-resolution STM images of SWNT bundles, observed after dispersion in DMF in an ultra-sonic bath. Scale bar (a) 20 nm; (b) 10 nm.

Fig. 5.13: (a) Carbon nanotubes exhibit nanoparticles at their ends, presumably Fe catalyst particles, possibly coated with amorphous carbon; (b) A defect is observed on the sidewall of the tubes.
Fig. 5.14: (a) High-resolution STM image of a SWNT bundle, showing atomic structure tunneling current variations on the atomic scale (scale bar: 5 nm). Local spectroscopy was measured by STS at the point in (a) marked with a circle. The dI/dV(V) spectrum (b) shows a semiconducting characteristic of the tube with a bandgap ~0.8 eV.

V-4.2. Influence of centrifugation and decantation

Gradual gravity centrifugation plays a critical role in the separation of small bundles and individual tubes from large nanotube aggregates after dispersion. Figs. 5.15 and 5.16 show STM images of nanotube samples after dispersion in DMF using ultra-sonication and subsequent separation by centrifugation. The STM sample was prepared from top layer (visually clear portion) of the centrifuged solution. Although bundles of nanotubes are still dominant on the sample surface, it is observed that the bundle sizes (diameters) are smaller and that, overall, the sample surface is more uniform. More straight and long (>500 nm) small bundle of tubes are observed. Nanoparticles are still evident at the end of the tube. STS measurements were performed on one of the nanotubes on top of the bundle in Fig. 5.16b (position denoted by the white circle). The I(V) curve, together with derived dI/dV(V) spectrum are presented in Fig. 5.17, which shows semiconducting characteristics of the measured tube.
Fig. 5.15: STM images of a nanotube sample prepared from the top layer of the dispersed solution after centrifugation. The scale bar is (a) 100 nm and (b) 50 nm. Compared to the non-centrifuged sample, the diameter of the nanotube bundles is smaller.

Fig. 5.16: STM images of the nanotube sample from Fig. 5.15 with higher spatial resolution. Individual tubes can easily be observed in (b). The white circle indicates the position for the STS measurement in Fig. 5.17.
Fig. 5.17: STS measurement in the nanotube shown Fig. 5.16b (position indicated by white circle). Left: I(V) curve; Right: dI/dV(V) curve, indicating a semiconducting character with a band gap of 0.8 eV.

V-4.3. Influence of repeated sonication, centrifugation, and decantation steps

In order to assert the important role of centrifugation and decantation in the STM sample preparation, a SWNT sample dispersed in DMF was sonicated, centrifuged, and decanted twice. A sample was prepared from the (clear) top layer of the solution and investigated by STM. Much smaller bundles (~5 tubes) now dominate the sample surface. It becomes easier to identify individual tubes. Figs. 5.18-5.21 show a series of STM experiments in which an individual nanotube was tracked from low to high (atomic) resolution, as indicated by the white arrows. The raw STM image of the individual tube was processed with SPIP image analysis software [101] and shown in Fig. 5.21b. As seen from Fig. 5.21b, the honeycomb hexagonal structure, characteristic for the carbon network of the nanotube sidewall can be easily observed. In difference to the ideal models of nanotubes in Chapter II, the actual STM image shows a somewhat distorted and twisted hexagonal network. The distortion may arise from bending or twisting of the
nanotube itself or an imperfect contact with the substrate along the tube. In addition, as mentioned earlier, vibration and drift of the STM scanner in this high resolution regime, which was experienced in this particular imaging process, also contribute to blur or ghost features on the image. Nevertheless, a contour of the hexagonal cells can be easily constructed, which can be fit with a model of the hexagonal network of carbon atoms as seen in Fig. 5.21b. Comparing with the carbon nanotube models in Chapter II, the image resembles the structure of an armchair tube. The average diameter of the tube, as determined from the line profile shown in Fig. 5.22, is about 15 Å; this suggests that the chiral index of the tube is (11, 11). According to the theoretical model, the tube with this index would show a metallic property. Indeed, the local STS measurement, presented in Fig. 5.23, shows a metallic behavior of the I(V) curve.

Fig. 5.18: STM images of a SWNT sample dispersed in DMF after repeated bath sonication, centrifugation, and decantation. The scale bars are (a) 100 nm and (b) 50 nm. The arrow indicates an individual nanotube that is imaged with increasing (and ultimately atomic) resolution in the subsequent figures.
Fig. 5.19: STM images of the SWNT sample in Fig. 5.18 at higher resolution. The scale bars are (a) 20 nm and (b) 10 nm. The arrow indicates the individual nanotube mentioned in the caption of Fig. 5.18.

Fig. 5.20: STM images of the SWNT sample in Fig. 5.19 at higher resolution, showing (a) an individual tube (left, indicated by the arrow) and a group of 3-4 tubes (right); (b) High-resolution image of the individual tube indicated by the arrow in the previous images. The scale bars are 5 nm.
Fig. 5.21: (a) Atomic resolution STM image of the individual nanotube; (b) The raw STM image of the tube is filtered (flattened) by analysis software [101]. The honeycomb structure of the hexagonal network is easily identifiable. For analysis, a model structure was constructed to fit to the image of the nanotube along the tube diameter. The chirality of the tube is determined to be (14,14).

Fig. 5.22: 2-D cross-section profile of the individual tube in Figs. 5.21.
V-4.4. Impact of water-based solutions and pulsed sonication

During the research work for this thesis, our lab acquired a pulsed sonicator to replace the ultra-sonic bath set-up that was employed for all previous results in this chapter. The pulsed energy transfer of this sonicator (sonotrode), is supposed to enhance the separation of individual tubes from bundles. As mentioned earlier, the application of a pulsed sonicator to dispersions of nanotubes, however, should be conducted with care. The strong pulsed force could shorten the tubes or create additional defects on the tube sidewalls. Although SWNTs are not dispersed as well as in DMF, water would be expected to have less impact on the characteristics of nanotubes in this environment. Therefore, the dispersion of SWNTs using the pulsed sonicator was performed in deionized water, as described in Chapter III. Fig. 5.24 shows a STM image of a SWNT sample dispersed in water after 5 pulses of 0.5 sec at 40% power of the sonicator, followed by 30 min of bath sonication. Centrifugation and decantation were also employed, as in the previous preparations.
With this approach, it can be observed that more individual tubes and fewer bundles are present on the Au substrate. However, it is also obvious that the tubes are shortened (from more than 500 nm to ~50-100 nm). Nanoparticles are also observed, mostly at the end of the tubes, again presumably originating from Fe catalyst nanoparticles. The tube sidewalls seem not smooth as previously observed (Fig. 5.25). Formation of water vapor nano-droplets on the sidewall may be responsible for that observation (?). Additional heat treatment may be used to improve the quality of STM imaging measurements. Fig. 5.26 shows STM image of this water-dispersed SWNTs sample after repeated centrifugation and decantation (without additional pulsed sonication). Small bundles (3-5 individual tubes) of short tubes (20-50 nm) can be clearly seen. Defect sites on the nanotube sidewalls, possibly due to pulsed ultrasonic force in sample preparation are also evident. In addition, the tube ends with nanoparticles and carbon impurity in amorphous form are also observed.

Fig. 5.24: STM images of a SWNT sample dispersed in deionized water using a pulsed sonicator, followed by centrifugation and decantation. The scale bars are (a) 100 nm and (b) 50 nm. Short individual tubes are observed.
Fig. 5.25: High resolution STM images of the SWNT sample in Fig. 5.24. The scale bars are (a) 20 nm and (b) 10 nm. The surface of the tubes appears less smooth compared to the DMF-dispersed sample.

Fig. 5.26: High resolution STM images of this SWNT sample dispersed in water using pulsed sonication, followed by repeated centrifugation and decantation, show sidewall defects, Fe nanoparticles, and a kink-like defect. The scale bars are (a) 20 nm and (b) 10 nm.

Clearly, more work is needed to search for “perfection” in the process of preparation, identification, imaging, and quantification of single individual SWNTs. Nevertheless, the results in this research can serve as a foundation for a reliable and reproducible separation
of various different SWNTs on a single substrate. This is particularly important for STM investigations of the structural and electronic characteristics of SWNTs in the metal deposition experiments described in the following chapters. Information on the presence of Fe nanoparticles, defects, amorphous carbon, functional groups, etc. in SWNTs sample, observed by STM, help to interpret spectroscopic results in this “apparently simple” but “actually complex” materials system.

CHAPTER V SUMMARY

In this chapter, we have investigated the basic properties of the carbon-based materials HOPG, SWNT and C60. All samples are of high carbon purity, and adsorbed oxygen is identified as the only significant impurity found on the HOPG and C60 samples. Fe catalyst nanoparticles and oxygen-containing functional groups are the main impurities found in SWNT samples. STM experiments indicate that pristine SWNTs exist in bundles and ropes of hundreds of individual nanotubes. Nanoparticles (presumably Fe catalyst particles), possibly coated with amorphous carbon, are found primarily at the end of individual tubes.

DMF solvent was used to prepare thin films of SWNT and C60 on Au substrate for laterally-integrating spectroscopic investigation. Vacuum-drying removes most of the DMF solvent, and an additional heat treatment in vacuum minimizes possible effects of residual solvent. The heating has no effect on the integrity of the carbon structures under study.

XPS results show that oxygen adsorbates are detected on all sample surfaces of HOPG, C60, and SWNT. The oxygen content on SWNT is higher than that of C60 and
HOPG. The presence of metal oxides and possibly oxygen-containing functional groups contribute significantly to the oxygen signal of the SWNT samples.

C 1s XPS core level spectra of carbon materials show a similar main feature, characterized by an sp$^2$ configuration of the carbon atoms. A difference in spectral shape is found at higher binding energies, indicating slightly different configurations of the carbon network in HOPG, C$_{60}$, and SWNTs. Defects, dangling bonds, and carbon atoms in the tetragonal sp$^3$ configuration induce a broadening of the main peak, most prominently for SWNTs.

Valence band spectra show discrete molecular levels for C$_{60}$, while HOPG and SWNT show broader bands, as expected. The work function of the SWNTs is larger than that of HOPG. A positive shift in both core-level and valence-level spectra of C$_{60}$ was observed, probably due to charging effect. In particular, the work function estimated from secondary electron cut off for C$_{60}$ is off due to this charging effect.

A detailed study of the impact of sonication, centrifugation, and separation on the dispersion of SWNTs in DMF was conducted to optimize the preparation of samples with individual SWNTs on the surface. Parameters were found that unbundle nanotubes into smaller bundles and individual tubes, and atomic resolution STM/STS experiments on individual nanotubes could be performed that reveal the hexagonal lattice structure on the sidewalls of the tubes and derive the electronic structure of the individual tubes (metallic vs. semiconducting). Finally, we found that carbon nanotubes can also be dispersed in water using a pulsed sonicator. The application of pulsed ultrasonic energy, however, must be performed with caution – we observe significant shortening of the SWNT and the formation of defects.
CHAPTER VI

Ti DEPOSITION ON CARBON-BASED NANOMATERIALS

In this chapter, spectroscopic and microscopic investigations of the deposition of Ti on carbon-based materials will be presented. Photoelectron spectroscopy was used to examine the interaction of Ti with different atomic arrangements of carbon atoms in the materials under study (Section 6.1). The formation and morphology of the deposited Ti overlayer were studied using STM and the results will be presented in Section 6.2. The observed oxidation behavior of Ti-deposited carbon-based materials in ultra-high vacuum will be described in Section 6.3.

HOPG, used as substrate for this set of samples, was freshly cleaved in the glovebox (i.e., under dry nitrogen conditions) before introduction into ultra-high vacuum. XPS measurements were performed to record the initial state of the HOPG sample before Ti deposition. Ti was then deposited using an e-beam evaporator and the formation and time-dependent behavior of the Ti layer on the HOPG surface were investigated by a series of XPS measurements, in which the time-dependent evolution of the most important spectral features was monitored. “Fast series”, consisting of 20 single 1-minute-long scans for Ti 2p, O 1s, and C 1s, were measured to monitor the “fast and continuous” change in chemical state of the sample surface in the first hour after Ti deposition. In addition, single scans were also taken after 2 and 16 hours for reference. A
detailed (more comprehensive) set of XPS and XAES spectra was recorded after 1 hour, 15 hours, and 4 days after Ti deposition. During these measurements, the Ti-deposited sample was kept under ultra-high vacuum conditions (~ $2 \times 10^{-10}$ mbar) in the analysis and preparation chamber. Table 6.1 summarizes the sample details.

Table 6.1: List of samples in the Ti/HOPG XPS series.

<table>
<thead>
<tr>
<th>Sample/Spectra</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>Freshly cleaved HOPG</td>
</tr>
<tr>
<td>Ti/HOPG-(1-20)</td>
<td>2 min-100 nA Ti deposition on HOPG 20 1-min single scans during the first hour after deposition</td>
</tr>
<tr>
<td>Ti/HOPG-(21)</td>
<td>Single scan measured after 2 hours</td>
</tr>
<tr>
<td>Ti/HOPG-(22)</td>
<td>Single scan measured after 16 hours</td>
</tr>
<tr>
<td>Ti/HOPG-1h</td>
<td>Detail spectra measured after 1 hour</td>
</tr>
<tr>
<td>Ti/HOPG-15h</td>
<td>Detail spectra measured after 15 hours</td>
</tr>
<tr>
<td>Ti/HOPG-4d</td>
<td>Detail spectra measured after 4 days</td>
</tr>
</tbody>
</table>

The C$_{60}$ and SWNT samples were prepared as described in detail in Chapter III, i.e., by forming thin films of C$_{60}$ and SWNT from dispersed solutions in DMF on Au substrates. The films were heated in vacuum at 200°C for 30 minutes before Ti deposition in order to completely remove the solvent residue, as asserted previously in Chapter V. Depositions of Ti were performed with the same parameters as for the Ti/HOPG series (2 minutes at 100 nA flux current as described in Chapter III). Immediately after Ti deposition, UPS experiments were carried out to investigate changes of the valence band structure. XPS and XAES measurements, performed after 2 hours, 6 hours, and 17 hours for Ti-deposited C$_{60}$ sample, and after 2 hours, 18 hours and 40 hours for Ti-deposited SWNT sample allow a systematic investigation of the Ti layer formation, the Ti-C interactions and their evolution, and, in particular, the oxidation behavior of the Ti-deposited sample surface in UHV. Another SWNT sample of small bundles and
individual SWNTs was prepared following the procedure described in Chapter III. The presence of individual SWNTs was confirmed by STM, and a subsequent Ti deposition was performed for 30 seconds at a flux current of 100 nA. The morphology of the sample surface and the atomic structure of the Ti-deposited individual SWNTs were then investigated by STM. Details of the samples and the time-dependent measurements for Ti-deposited C\textsubscript{60} and SWNT samples are summarized in Table 6.2 and 6.3, respectively.

Table 6.2: List of depositions and time-dependent measurements on a Ti-deposited C\textsubscript{60} sample.

<table>
<thead>
<tr>
<th>Sample/Spectra</th>
<th>XPS</th>
<th>UPS</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{60}</td>
<td>X</td>
<td>X</td>
<td>Heated C\textsubscript{60} film deposited on Au substrate</td>
</tr>
<tr>
<td>Ti/ C\textsubscript{60}</td>
<td></td>
<td></td>
<td>Measured immediately after deposition</td>
</tr>
<tr>
<td>Ti/ C\textsubscript{60}-2h</td>
<td>X</td>
<td></td>
<td>Detail spectra measured at 2 hours after deposition</td>
</tr>
<tr>
<td>Ti/ C\textsubscript{60}-6h</td>
<td></td>
<td>X</td>
<td>Detail spectra measured at 6 hours after deposition</td>
</tr>
<tr>
<td>Ti/ C\textsubscript{60}-17h</td>
<td></td>
<td>X</td>
<td>Detail spectra measured at 17 hours after deposition</td>
</tr>
</tbody>
</table>

Table 6.3: List of depositions and time-dependent measurements on a Ti-deposited SWNT sample.

<table>
<thead>
<tr>
<th>Sample/Spectra</th>
<th>XPS</th>
<th>UPS</th>
<th>STM</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>X</td>
<td>X</td>
<td>STM</td>
<td>Heated SWNT film deposited on Au substrate</td>
</tr>
<tr>
<td>Ti/SWNT</td>
<td></td>
<td></td>
<td></td>
<td>Measured right after deposition</td>
</tr>
<tr>
<td>Ti/SWNT-2h</td>
<td>X</td>
<td></td>
<td></td>
<td>Detail spectra measured at 2 hours after deposition</td>
</tr>
<tr>
<td>Ti/SWNT-18h</td>
<td>X</td>
<td></td>
<td></td>
<td>Detail spectra measured at 18 hours after deposition</td>
</tr>
<tr>
<td>Ti/SWNT-40h</td>
<td>X</td>
<td></td>
<td></td>
<td>Detail spectra measured at 40 hours after deposition</td>
</tr>
<tr>
<td>SWNT</td>
<td></td>
<td>X</td>
<td></td>
<td>Film of top layer SWNT solution deposited on Au substrate (chapter 5)</td>
</tr>
<tr>
<td>Ti/SWNT</td>
<td></td>
<td>X</td>
<td></td>
<td>Measured immediately after deposition</td>
</tr>
</tbody>
</table>
Survey spectra measured on the cleaved HOPG sample before and one hour after Ti deposition are shown in Fig. 6.1. The spectra were normalized to the intensity of the C 1s lines and offset vertically for comparison. The dominant spectral features were assigned by comparing their BE to reference values [77]. The most prominent peak at ~284.5 eV corresponds to photoelectrons emitted from the C 1s core level. After Ti deposition, the intensity of the C 1s photoemission line decreases (as expected) due to the attenuation of corresponding photoelectrons in the deposited Ti layer. The presence of Ti on the surface of HOPG is observed by the emergence of Ti peaks, with the most prominent feature of Ti 2p between 455 and 465 eV. The corresponding Auger line (Ti LMM) can be found in the binding energy range between 800 and 900 eV. The feature at approximately 531.5 eV, which is ascribed to photoelectrons emitted from the O 1s core level, increases after Ti deposition. While we attribute the presence of the O 1s line in the XPS survey spectrum of the bare (uncovered) HOPG substrate to surface adsorbates, such as hydroxide and water, the increasing oxygen-related features after Ti-deposition are primarily indicative for oxygen species adsorbed on the deposited Ti. The relative ratios of the spectral features of O 1s (Ti 2p) to C 1s were deduced from the survey spectra of sample before and after Ti deposition, taking into account the respective photoionization cross-sections [72]. The results are listed in Table 6.4.
Fig. 6.1: Survey spectra of a HOPG sample measured before and one hour after Ti deposition.

Table 6.4: Relative O 1s/C 1s and Ti 2p/C 1s ratios of an HOPG sample before and after Ti deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 1s/C 1s</th>
<th>Ti 2p/C 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>6.94E-03</td>
<td></td>
</tr>
<tr>
<td>Ti/HOPG</td>
<td>2.55E-02</td>
<td>4.27E-02</td>
</tr>
</tbody>
</table>

Survey spectra of C_{60} and SWNT samples before and 2 hours after Ti deposition are shown in Figs. 6.2 and 6.3, respectively. The presence of Ti features and the increase of the oxygen signals after Ti deposition can be easily derived from the spectra. It also can be observed that, compared to the C 1s signal, the Ti and O signals are higher for the Ti-deposited SWNT sample compared to the C_{60} sample.
Fig. 6.2: Survey spectra of a C₆₀ sample measured before and 2 hours after Ti deposition.

Fig. 6.3: Survey spectra of a SWNT sample measured before and 2 hours after Ti deposition.
The relative O 1s/C 1s and Ti 2p/C 1s ratios of the C_{60} and SWNT samples before and after Ti deposition were estimated from the respective spectral features of the survey spectra. The results are listed in Table 6.5 and 6.6 for the C_{60} and the SWNT sample, respectively.

Table 6.5: Relative O 1s/C 1s and Ti 2p/C 1s ratios of the C_{60} sample before and after Ti deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 1s/C 1s</th>
<th>Ti 2p/C 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}</td>
<td>1.19E-02</td>
<td>7.72E-02</td>
</tr>
<tr>
<td>Ti/C_{60}</td>
<td>4.00E-02</td>
<td>7.72E-02</td>
</tr>
</tbody>
</table>

Table 6.6: Relative O 1s/C 1s and Ti 2p/C 1s ratios of SWNT sample before and after Ti deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 1s/C 1s</th>
<th>Ti 2p/C 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>2.28E-02</td>
<td>1.94E-01</td>
</tr>
<tr>
<td>Ti/SWNT</td>
<td>9.97E-02</td>
<td>1.94E-01</td>
</tr>
</tbody>
</table>

Note that the Ti 2p/C 1s ratio increases from HOPG (Table 6.4) to C_{60} (Table 6.5) and to SWNT (Table 6.6), even though they were prepared under the same deposition condition, in particular the same deposition time and ion flux. Thus, it is reasonable to assume that the sample surfaces were exposed to the same amount of Ti in each case. We tentatively associate this behavior with the different morphology of the carbon nanomaterials, which (among others) influences the surface area, electronic surface structure, sticking coefficient, surface diffusion coefficients, etc.

The oxygen signal also increases proportionally with the Ti concentration. Since the increase of the oxygen signal is attributed to the adsorption of oxygen species from the residual gas due to the presence of Ti on the sample surface, the results are indicative for
larger coverage of Ti on SWNT sample compared to that on HOPG and C\textsubscript{60} sample. Consequently, the larger Ti-covered area on the SWNT sample leads to more oxygen adsorption and to a higher attenuation of the carbon photoemission signals.

Detail C 1s and C KVV spectra taken from the HOPG sample before and one hour after Ti deposition are shown in Fig. 6.4. The intensity of the C 1s peak decreases due to the attenuation of the C 1s photoelectrons by the deposited Ti and the increasing oxygen-containing adsorbate layer on the surface after Ti deposition. A similar attenuation is observed for the C KVV XAES feature. If we (incorrectly) assume a uniform layer growth of Ti on the HOPG surface, the effective thickness of the deposited Ti layer can be estimated using the attenuation of the C 1s signal (as described in Chapter III) and an inelastic mean free path of \( \lambda = 20.89 \, \text{Å} \) for photoelectrons at KE = 970 eV in the Ti layer [73]. The effective thickness of Ti on HOPG is thus found to be approximately 2.5 Å, i.e., much less than the thickness estimated for the Ti deposition on the Au substrate using the same deposition conditions (~ 4 Å, Chapter IV). This indicates that the Ti layer formation on HOPG surface is far from uniform; instead, an island growth of Ti, i.e, the formation of clusters and nanoparticles is a more likely scenario and, indeed, found by the STM investigation to be described later.
Fig. 6.4: Detail spectra of (a) the C 1s XPS and (b) the C KVV Auger feature of a HOPG samples before and one hour after Ti deposition.

The C 1s spectra consist of the main peak at approx. 284.4 eV and satellites at the high BE side. In order to show the spectral structure change of the C 1s features, the normalized spectra in Fig. 6.4 were renormalized such that the main peak has the same height, as shown in Fig. 6.5 (a). In addition, an expanded scale is plotted in Fig. 6.5 (b) to better show the change of the spectral features upon Ti deposition. The main peak slightly shifts (~ 0.1 eV) to higher BE and the intensity of the shoulder at high BE (around 286 eV) increases, indicating an interaction of Ti with the network of carbon atoms. The FWHM of the main peak increases from 1.15 eV to 1.20 eV after Ti deposition. The high BE shoulder of the main peak is usually attributed to disordered carbon atoms on the surface of HOPG [135, 136, 175-178]. Furthermore, we observe a small feature emerging upon Ti deposition at approximately 282 eV. A similar feature
was also observed for Ti deposited on Au (Chapter IV) and is attributed to Ti-C bonding of Ti adatoms with adventitious carbon via a charge transfer mechanism [113,178]. This interface interaction was observed for a Ti layer on a diamond substrate [179], for a thin carbon film on a titanium substrate, and a thin Ti film on graphite [180, 181]. In contrast, Ma and Rosenberg [41] found that Ti does not chemically bond to HOPG, but only interacts through the Van der Waals force with a pristine HOPG surface. They attributed a small Ti-C bonding formation to interaction of Ti adatoms with partially oxidized carbon or defect sites on the HOPG surface [42]. The Ti-C feature observed in our experiment is rather small and may indeed be formed due to interaction of Ti with carbon dangling bonds and defects.

Fig. 6.5: (a) C 1s XPS detail spectra (normalized to the peak maxima) of an HOPG sample before and one hour after Ti deposition; (b) magnified plot of (a).
The detail C 1s core level and Auger C KVV spectra of C\textsubscript{60} and SWNT samples after Ti deposition are presented in Fig. 6.6 and 6.7, respectively. As is evident, the Ti deposition leads to a reduction of the overall intensity of the carbon features. Furthermore, shifts and line shape modifications are observed in the XPS spectra, which will be discussed below.

Fig. 6.6: (a) C 1s XPS and (b) C KVV XAES spectra before and after Ti deposition on C\textsubscript{60}, illustrating the attenuation of the C 1s photoemission line due to the Ti overlayer.
Fig. 6.7: (a) C 1s XPS and (b) C KVV XAES spectra before and after Ti deposition on SWNTs, illustrating the attenuation of the C 1s photoemission line due to the Ti overlayer.

The effective thickness of the Ti overlayer, estimated from the attenuation of the C 1s signal, is approximately 3.7 Å for Ti-deposited C60 and 7.6 Å for Ti-deposited SWNT sample. As mentioned earlier, this estimation is based on the assumption of a uniform growth of Ti on the sample surface.

The formation behavior of the Ti layer on the here-investigated carbon-based materials can also be derived by examining the relative change of the C 1s/C KVV intensity ratios before and after Ti deposition. Table 6.7 lists these ratios for the HOPG, C60, and SWNT samples. The integrated areas under the C 1s and the C KVV peaks after linear background subtraction were taken as the intensity of the respective spectral features.
Table 6.7: Relative change of the C 1s/C KVV ratio for HOPG, C$_{60}$, and SWNT samples before and after Ti deposition.

<table>
<thead>
<tr>
<th>Ratio C 1s/C KVV</th>
<th>HOPG</th>
<th>C$_{60}$</th>
<th>SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Ti deposition</td>
<td>0.58</td>
<td>0.545</td>
<td>0.58</td>
</tr>
<tr>
<td>After Ti deposition</td>
<td>0.61</td>
<td>0.583</td>
<td>0.70</td>
</tr>
<tr>
<td>Relative change</td>
<td>5.2%</td>
<td>7%</td>
<td>20.7%</td>
</tr>
</tbody>
</table>

Since the C 1s photoelectrons and corresponding Auger electrons, which contribute to C KVV feature, have different kinetic energies (~970 eV and ~260 eV with Mg K$_\alpha$ X-ray excitation, respectively), their inelastic mean free paths (IMFP) are quite different: $\lambda_{C-KVV} < \lambda_{C-1s}$ (for a Ti layer, the respective IMFP values are 8.3Å and 20.9Å [73]). Consequently, their respective information depths are also different. While both C 1s and C KVV signals decrease upon Ti deposition, the increase of the C 1s/C KVV ratios indicates that the C KVV signal decreases faster than the C 1s. The relative change of the C 1s/C KVV ratios for Ti-deposited SWNT sample is about 3 times and 4 times larger than that of the Ti-deposited C$_{60}$ and Ti-deposited HOPG samples, respectively. While a small change of C 1s/C KVV ratio (as in Ti-deposited HOPG or Ti-deposited C$_{60}$) is indicative for a low coverage of Ti on the surface, a large increase of this ratio in Ti-deposited SWNT suggests that the Ti deposition covers a much larger area on the SWNT sample. Together with the above-discussed estimation of the effective Ti layer thickness, we suggest that the formation of Ti on C$_{60}$ (more precisely: its coverage behavior) is likely similar to that on Au and on HOPG, i.e., as shown earlier, with preferred nanoparticle formation. A closer look at the detail C 1s spectra of C$_{60}$ before and after Ti deposition also supports the cluster formation of Ti on C$_{60}$, as will be discussed below. In
contrast, the findings for the SWNT sample suggest that the Ti cluster formation is less pronounced, at least in the monolayer regime.

As we have seen in Chapter V, the different atomic carbon arrangements in HOPG, C₆₀, and SWNT lead to different characteristics, in particular in view of their electronic structures. Thus, it is not unlikely that the detailed Ti-C interaction for these structures could also be quite different. To further investigate this concept, detail C 1s spectra of the SWNT sample before and 2 hours after Ti deposition are shown in Fig. 6.8. The spectra were normalized to constant peak height to observe shape changes due to Ti deposition.

![C 1s XPS detail spectra before and after Ti deposition on SWNTs.](image)

Fig. 6.8: C 1s XPS detail spectra before and after Ti deposition on SWNTs.

The evolution of C 1s peak after Ti deposition on the SWNT sample is qualitatively similar to that of HOPG (see Fig. 6.5). The main C 1s peak shifts about 0.1 eV to higher BE side and broadens at the high BE shoulder. The similarity, again, indicates a
resemblance of the carbon network in SWNT and HOPG. However, the degree of Ti-C interaction for the SWNT sample is much stronger than that for HOPG. The evidence of that can be seen in the larger broadening of the main peak at the high BE shoulder and a stronger Ti-C bonding feature at low BE (around 282.5 eV). The FWHM of the main peak increases from 1.1 eV to 1.3 eV after Ti deposition. The small Ti-C bonding formation in Ti/HOPG is attributed to disorder carbon network, defects and assisted by partially oxidized carbon on the surface [41, 42]. The presence of more defects and oxygenated functional groups in SWNT, as seen in Chapter V, can lead to stronger Ti-C bonding formation for Ti/SWNT sample. In addition, as mentioned above, the larger coverage of Ti on SWNT probably also increases the number of Ti adatoms in contact with the carbon network, which increases the probability of Ti-C bond formation. This, in turn, increases the number of carbon atoms in a new chemical environment (i.e., the presence of a Ti atom), which leads to an increase of the sp³ feature at the high BE shoulder of the main C 1s peak.

The change of the C 1s peak for the Ti/C₆₀ sample is quite different from that of Ti/HOPG and Ti/SWNT samples. Fig. 6.9 and 6.10 show the shape change of the C 1s peak of the C₆₀ sample after Ti deposition. The main peak broadens (FWHM increases from 1.0 eV to 1.3 eV after Ti deposition), and shifts almost 0.5 eV to lower BE (Fig. 6.9a). As previously mentioned in Chapter V, a charging effect on the non-conductive film of C₆₀ is probably responsible for shifting of all spectral features of the C₆₀ sample (to higher BE). The deposition of Ti on the sample surface may make it more conductive, effectively reducing the charging effects. It is thus not clear whether the observed shift of 0.5 eV to lower BE is due to a chemical shift, due to a reduction of the charging effect, or
both. A similar behavior of the C 1s peak was observed by Norin et al. [37] and Qian et al. [38] on thin films of co-evaporated Ti and C₆₀ samples. The authors attribute the chemical shift and shape change of the C 1s peak to a newly formed compound of TiₓC₆₀. The chemical shifts of 0.35 eV and 0.42 eV to lower BE were reported for Ti₂.₁C₆₀ and Ti₃.₆C₆₀ [37, 38] compounds, respectively, compared with pure C₆₀, where the authors checked and found no charging effect of C₆₀ film. Due to charging effects we cannot rely only on the shift of C 1s spectra to identify the chemical shift induced by charge transfer in our experiment. A relative distance between C 1s and Ti 2p peaks was used instead to compare with the same parameter in Ti/HOPG and Ti/SWNT sample. The results will be presented below.

![Graph showing spectral changes](image)

Fig. 6.9: Spectral changes of the C 1s core level due to Ti deposition on a C₆₀ sample; (a) the main peak shifts 0.5 eV to lower BE; (b) Shake-up satellites at the high BE tail of the main peak.
The high BE tail of the C 1s peak was magnified in Fig. 6.9b to accentuate the changes. The high BE shake-up satellites, characteristic for shake-up excitations in the $\text{C}_{60}$ molecular electronic structure, are broadened due to Ti deposition. However, the characteristics of the spectral features are still preserved. This is interpreted such that $\text{C}_{60}$ molecules not covered by Ti also contribute to the spectrum, again suggesting evidence of Ti clustering on the $\text{C}_{60}$ sample.

To further examine the shape change of C 1s peak for the Ti/$\text{C}_{60}$ sample, the spectra were shifted in energy to align at the position of maximal intensity, as shown in Fig. 6.10. It is evident that the main peak is broadened asymmetrically at the high BE side.

Furthermore, a shoulder emerges at the C 1s position of C-Ti bonding $\sim 2.5$ eV below the main peak, as is best seen on the magnified scale in Fig. 6.10(b).

![Fig. 6.10: Spectral changes of the C 1s core level due to Ti deposition on a $\text{C}_{60}$ sample; (a) main peaks, aligned at the energy of maximal intensity; (b) large scale of the Ti-C bonding feature at the low BE tail of the main peak.](image-url)
The broadening of the main C1s peak suggests a contribution of carbon atoms in a new chemical environment. Hybridization between the highest occupied molecular orbital (HOMO) of the C₆₀ molecule and the Ti 3d states was suggested based on DFT calculation [39] and asserted by examining symmetry-selective resonant x-ray inelastic scattering (RIXS) [40]. A simplified scheme of the bond formation between Ti and the C₆₀ molecule [39] is shown in Fig. 6.11. In this scheme, the Ti 3d states interact with the HOMO and LUMO of the C₆₀ molecule to form four states, two of which are occupied and two of which are unoccupied.

![Fig. 6.11: Simplified schematic bond formation between Ti and a C₆₀ molecule [39].](image)

Fig. 6.12 shows Ti 2p detail spectra of HOPG, SWNT and C₆₀ samples, each measured 2 hours after Ti deposition. The Ti 2p features on the C₆₀ sample shift to higher BE compared with that on HOPG and SWNT. Again, this could be due to a charging effect, as described above. However, the relative distance between the main peak C 1s and the Ti 2p₃/₂ line increases from 170.02 eV for Ti/HOPG to 170.06 eV for Ti/SWNT and 170.38 eV for Ti/C₆₀. Another “double check” can be performed by determining the
relative distance between the Au 4f\textsubscript{7/2} and Ti 2p\textsubscript{3/2} lines of the Ti/SWNT and Ti/C\textsubscript{60} samples (using the Au signal from the sample substrate). These numbers can then be compared with the value found in the Ti/Au experiments. The results also indicate a shift of \( \sim +0.3 \) eV for the Ti 2p peaks in Ti/C\textsubscript{60} (Au 4f-Ti 2p distance: 371.13 eV) relatively to that of Ti/SWNT (Au 4f-Ti 2p distance: 370.88 eV) and Ti/Au (Au 4f-Ti 2p distance: 370.7 eV). The positive shift of Ti 2p in Ti/C\textsubscript{60} is consistent with the negative shift of the C 1s, which could suggest a charge transfer from Ti to C\textsubscript{60} in the formation of a Ti\textsubscript{x}C\textsubscript{60} phase \[37\]. A (charging-corrected) chemical shift of \( \sim 0.3 \) eV is then close to the value reported for the formation of a Ti\textsubscript{2.1}C\textsubscript{60} compound \[39\], which is equivalent to an atomic concentration of 3.5\% of Ti on the C\textsubscript{60} sample. However, the relative ratio of Ti to C atoms found on our Ti/C\textsubscript{60} sample is much higher (see Table 6.5), suggesting that not all deposited Ti atoms react with carbon atoms of the C\textsubscript{60} molecules. This is particularly true for the Ti atoms bound inside the above-discussed Ti clusters.

Compared with HOPG, it is reasonable to attribute the observed strong Ti-C interaction of the Ti/SWNT sample to defect- and/or oxygen-assisted sites found on surface of SWNT (as will be discussed below). The strong Ti-C interaction in C\textsubscript{60} molecule, on the other hand, may be driven by the more reactive nature of the C\textsubscript{60} molecule (note the presence of pentagons in the molecular structure as described in Chapter II). We have no experimental evidence, however, to identify and verify the interaction sites of Ti on the C\textsubscript{60} molecule. The chemical shifts generally observed for the Ti 2p peaks bonding with carbon atoms (compared to metallic Ti) are small [113] and cannot be resolved in our experiments.
Fig. 6.12: Ti 2p detail spectra of the Ti/HOPG, Ti/SWNT, and Ti/C₆₀ samples, measured 2 hours after Ti deposition.

Further details of the Ti layer formation on the surface and its possible reaction with carbon atoms of SWNTs and C₆₀ molecules can be derived from the evolution of the valence band after Ti deposition. The valence band spectra were measured using He II (40.8 eV) radiation on freshly Ti-deposited samples to minimize the effects of Ti oxidation. The respective spectra are shown in Fig. 6.13 for the Ti/C₆₀ sample and in Fig. 6.14 for the Ti/SWNT sample. In addition, spectra of the Ti/SWNT and Ti/C₆₀ samples are plotted together in Fig. 6.15 for easy comparison. All spectra were normalized to the integrated intensity to show the change of constituted components and are vertically offset.
A pronounced maximum just below the Fermi energy is observed for both the Ti/C\textsubscript{60} and the Ti/SWNT sample, which is derived mainly from Ti 3d states [109, 112, 184, 185]. This feature is more evident for Ti/SWNT, indicating a larger spectral contribution of Ti on the surface of SWNT compared to that on C\textsubscript{60}. Unlike the sharp structure of the Ti 3d band in pure Ti [185], the structure at \( \sim 1.0 \) eV below the Fermi energy is broadened, which is more pronounced for Ti/SWNT sample compared to that of Ti/C\textsubscript{60} sample (Fig. 6.15). The stronger appearance of this feature in Ti/SWNT is consistent with larger Ti-C bonding feature found in the core-level spectra of Ti/SWNT compared with that of Ti/C\textsubscript{60}. We thus attributed this feature to Ti chemically bound with carbon atoms. The work function decreases from 4.35 eV to 4.25 eV for the C\textsubscript{60} sample (which might be obscured by the reduction or removal of the charging effect; if so, the work function would reduction would be larger), and from 4.5 eV to 3.85 eV for the SWNT sample after Ti deposition. While the work function of pure C\textsubscript{60} and pristine SWNT samples are close to each other in our measurements, the small work function of the Ti/SWNT sample is also indicative for a larger coverage of Ti on the SWNTs.

All molecular-type spectral features of the pure C\textsubscript{60} are smeared out due to attenuation of their signals in the deposited Ti as well as due to chemical interactions in forming the Ti-C\textsubscript{60} compound mentioned above. The broadening of the valence levels is consistent with the broadening of the shake-up satellites of C 1s core levels observed above. On the other hand, the appearance of Ti 3d-derived feature in spectrum of Ti/C\textsubscript{60} supports the model of hybridization between Ti 3d and molecular orbital of C\textsubscript{60} (Fig. 6.11).
Fig. 6.13: (a) HeII UPS spectra of $C_{60}$ sample before and after Ti deposition; (b) Work function of SWNT sample change due to Ti formation.

Attenuation of the intensity of both $\pi$-band and $\sigma$-band of SWNT is observed due to Ti layer formation on Ti/SWNT sample. There is an enhancement of a feature at about 6-7 eV below the Fermi level. This new feature is probably associated with O 2p states [109, 184], which indicates adsorption of oxygen-containing species from the residual gas due to the gettering effect of Ti (as will be discussed in the following).
Fig. 6.14: (a) HeII UPS spectra of SWNT sample before and after Ti deposition; (b) Secondary electron cut-off and work function of the SWNT sample before and after Ti deposition.

Fig. 6.15: Comparison between HeII UPS spectra of Ti/SWNT and Ti/C_{60} samples.
Section 6-2

Morphology of Ti Deposition on Carbon-based Materials

STM experiments were performed on the Ti-deposited HOPG sample discussed in Section 6-1 after 6 weeks after Ti deposition. During that time, the Ti deposited sample was stored in ultra-high vacuum in the preparation chamber and exposed to H$_2$ gas and atomic hydrogen for 10 minutes each to investigate the hydrogen storage effects. The latter preparation steps were conducted using the Atomic Hydrogen Source (AHS) constructed by Roberto Félix in the framework of his Master’s thesis [187]. To prepare the sample for the STM investigation, it was then transferred to the N$_2$-filled glove box and mounted on an STM sample holder without any exposure to ambient air. Even though the exposure to H$_2$ gas and atomic hydrogen, as well as the contamination by adsorbates from the residual gas during the 6-week storage could change the detailed morphology of sample surface, the STM investigations may give additional insights into the Ti/HOPG interaction and this particular Ti/HOPG sample. Figs. 6.16 – 6.18 show typical STM images obtained for this Ti/HOPG sample. Nanoparticles of Ti can be observed as bright spots, which are randomly distributed on the HOPG surface (Fig. 6.16). The average size of Ti nanoparticle is approximately 5 nm in diameter (Fig. 6.17). We notice that the Ti/HOPG nanoparticles have a size comparable to that of the Ti nanoparticles formed on the Au substrate (~5 nm) (Chapter IV), but with significantly lower density. We have tried to observe the atomic structure of the Ti nanoparticles by high resolution STM imaging of the Ti nanoparticles. Fig. 6.18 shows STM images of the Ti-deposited HOPG sample, obtained at the atomic resolution scale. While atomic resolution of the HOPG substrate can be observed, the areas of the Ti nanoparticles are
"blurry". This may be due to the less-conductive oxide layer on the Ti nanoparticles found in the XPS investigations earlier in this thesis.

Fig. 6.16: STM images of the Ti/HOPG sample. The scale bar is (a) 100 nm and (b) 20 nm.

Fig. 6.17: STM image of the Ti/HOPG nanoparticles. The scale bar is 5 nm.
STM experiments were also performed to examine the morphology of the Ti layer deposited on individual carbon nanotubes. The sample preparation and the observation of the atomic structure of an individual nanotube were described previously (Chapters III and V). After checking for the presence of individual or small bundles of nanotubes on the surface of the Au substrate, as seen in Fig. 6.19, the sample was transferred under vacuum to the preparation chamber for Ti deposition. Ti was deposited at a flux current of 100 nA for 30 seconds and the sample was transferred back to the STM chamber for imaging. Fig. 6.20 shows STM images of Ti deposited on an individual nanotube. Before Ti deposition, atomic resolution images can be achieved for the individual nanotubes on the Au surface (Fig. 6.19). However, Ti deposition creates a rough surface, which is unfavorable for high resolution STM imaging. The deposited Ti atoms form nanoparticles on the surface of the Au particles, as described in Chapter IV and also observed in Fig 6.20. The images of the individual nanotubes are “blurry” after Ti deposition and no
atomic resolution image of the Ti-deposited nanotubes could be obtained. Therefore, we are unable to ascertain the concrete morphology of the Ti layer on the surface of the nanotubes. The deposition of Ti on the surface and the observed Ti-C interaction may substantially change the local electronic properties of the nanotubes, in particular the local density of states, which affects the tunneling current that forms the STM images. It thus may require better fine-tuning and optimization to obtain appropriate parameters for high resolution STM imaging of Ti-decorated nanotubes. It may also require choosing appropriate substrates for the deposition of individual nanotubes and subsequent Ti deposition, because the formation of Ti nanoparticles on the surface would downgrade the high resolution imaging. Furthermore, in-situ Ti deposition would be desirable. All of these aspects are listed here as goals for future work.

Fig. 6.19: STM image of individual nanotubes on the surface of a Au substrate before Ti deposition. The scale bars are (a) 50 nm and (b) 20 nm.
Section 6-3

Oxidation Behavior of Ti on Carbon-based Materials

The oxidation behavior of Ti on HOPG was investigated by two “time-dependent” measurement series. The “fast-series” Ti 2p and O 1s spectra are shown in Fig. 6.21 for the first 10 consecutive 1-minute-long scans, measured right after deposition, with an increment of 3 minutes between scans. In Fig. 6.22, the single scans measured after 2 hours and 16 hours are also included for comparison with the single scans measured in the first hour after Ti deposition. It is clear from Figs. 6.21 and 6.22 that the Ti 2p features gradually shift to higher BE. The main Ti 2p_{3/2} peak shifts from 454 eV to 454.4 eV after the first 30 minutes, and the additional shift after the first hour is much smaller (to 454.5 eV and 454.6 eV after 2 and 16 hours, respectively). The Ti 2p feature broadens as time increases. The relative intensity of the spectral region at the high BE shoulder of the Ti 2p doublet (indicated by an arrow in Fig. 6.21) increases. At the same time, a gradual increase of the O 1s signal is observed. A shoulder at the low BE side of the O 1s

Fig. 6.20: STM image of individual nanotubes on the surface of a Au substrate after Ti deposition. The scale bars are (a) 100 nm and (b) 50 nm.
peak becomes more and more pronounced as time increases. The O 1s spectrum measured after 16 hours shows contributions of several oxygen species. The results indicate a continuous adsorption of oxygen-containing species from the residual gas on the sample surface. The shift of the Ti 2p peaks to higher BE is attributed to the transformation from metallic Ti to Ti oxide as a result of the reaction between Ti and the oxygen-containing species (in particular water molecules). The transformation begins immediately after Ti deposition and slows down as time increases, suggesting that the oxidation becomes less efficient after the outermost layer of metallic Ti is completely transformed into Ti oxide.

Fig. 6.21: Time-dependent single scans of (a) Ti 2p and (b) O 1s measured immediately of Ti deposition HOPG (1 minute per scan, separated by 3 minutes).
Fig. 6.22: Time-dependent single scans of (a) Ti 2p and (b) O 1s measured on Ti/HOPG in the first hour, after 2 hours, and 16 hours after deposition.

The time-dependent intensity variations of the C 1s, Ti 2p, and O 1s peaks for Ti/HOPG in the first hour after Ti deposition are shown in Fig. 6.23. Their relative ratios are shown in Fig. 6.24. The O 1s signal increases sharply in the early stage (20-30 min) after Ti deposition, indicating a significant adsorption of oxygen species on the sample surface due to the gettering effect of the Ti adatoms (again, it should be noted that this is reason for the widespread use of Ti-sublimation pumps to achieve UHV conditions). The adsorbate layer is also responsible for a decrease in intensity of the C 1s signal, which is already decreased due to attenuation in the deposited Ti. At the same time, a transformation of Ti from metallic Ti to titanium oxide is observed. As described above, we interpret the relative “speed” of oxidation with the formation of an outer Ti oxide layer (shell) around a metallic core. The formed Ti oxide layer is expected to reduce the reactivity of Ti adatoms, in particular for the adsorption of other gaseous species (e.g.,
other oxygen-containing species or hydrogen). Thus, at a later stage after Ti deposition (30-60 min), the oxygen signal increases more slowly.

Fig. 6.23: Time-dependent variation in intensity of (a) C 1s, (b) Ti 2p and (c) O 1s peaks for Ti/HOPG in the first hour after Ti deposition.

Fig. 6.24: Intensity ratios (a) O 1s/Ti 2p, (b) Ti 2p/C 1s and (c) O 1s/C 1s as function of time for Ti/HOPG during the first hour after Ti deposition.

The "time-dependent" series of detailed measurements were performed to record C 1s, O 1s, and Ti 2p spectra at 1 hour, 15 hours, and 4 days after Ti deposition on HOPG. No major change of the C 1s shape of the Ti/HOPG sample is found after storage in
vacuum up to 4 days. We find that the C 1s peak intensity continuously decreases with increasing storage time up to 15 hours, similar to the trend shown in Fig. 6.23a for the first hour after Ti deposition. An exponential increase of the O 1s signal is also observed. The decrease of C 1s can be explained by the continuous adsorption of oxygen species on the Ti-deposited surface and the corresponding attenuation of the photoemission signal from the “buried” carbon atoms. After 4 days of storage, we observe an intensity increase of the C 1s XPS peak, presumably due to the adsorption of carbon-containing species from the residual gas. The time-dependent intensity variation of C 1s, Ti 2p, and O 1s is shown in Fig. 6.25 and the relative ratios of O 1s/Ti 2p, Ti 2p/C 1s, and O 1s/C 1s are shown in Fig. 6.26. The Ti 2p intensity also increases after 15 hours of storage, but the Ti 2p/C 1s ratio steadily decreases as the storage time increases, indicating that the C 1s signal increases faster than the Ti 2p signal. As mentioned, the increase of the C 1s signal is expected to be due to an increase of adventitious carbon and accompanying oxygen species that are adsorbed on the sample surface during storage. An interesting additional effect is described by Ma and Rosenberg [41, 42]. In their experiment of a one-monolayer (1.8 Å) deposition of Ti on HOPG, they found that the C 1s intensity substantially increases with time after Ti deposition, and attributed that to a “recovery” of the sample surface. Assuming a uniform distribution of Ti for the initial deposition, it was estimated that the Ti coverage decreased by a factor of 5 at 126 minutes after deposition. The surface “recovery” process implies diffusion and clustering of Ti on the HOPG surface as a function of elapsed time after deposition. In our experiment, it appears reasonable to ascribe the decrease of the carbon signal up to 15 hours after deposition to the adsorption of oxygen species on the Ti-coated sample surface. Furthermore, the diffusion of Ti
adatoms, as described by Ma and Rosenberg, might indeed contribute to the increase of the C 1s intensity observed after 4 day of storage. However, the more likely source of the increased carbon signal is the adsorption of adventitious carbon over the course of the 4-day storage.

![Graphs showing time-dependent variation of C 1s, Ti 2p, and O 1s intensity of Ti-deposited HOPG.](image)

Fig. 6.25: Time-dependent variation of (a) C 1s; (b) Ti 2p; and (c) O 1s intensity of Ti-deposited HOPG.

![Graphs showing time-dependent variation of O 1s/Ti 2p, Ti 2p/C 1s, and O 1s/C 1s intensity ratios of Ti-deposited HOPG.](image)

Fig. 6.26: Time-dependent variation of (a) O 1s/Ti 2p; (b) Ti 2p/C 1s; and (c) O 1s/C 1s intensity ratios of Ti-deposited HOPG.
The oxygen signals on the sample surface increase sharply (Fig. 6.27) after Ti deposition, probably because Ti atoms absorb water and other oxygen species from the residual gas in the vacuum system. The O 1s spectral intensity also increases with storage time, providing additional confirmation for the suggested oxygen adsorption process of the Ti layer. A similar behavior was also observed for the O KLL signals (Fig. 6.27b), confirming the increase of oxygen species concentration on the surface of the sample. The small O 1s signal before Ti deposition can be represented by two broad components, which are characterized as oxygen and hydroxides [144, 177] on the HOPG sample surface. After Ti deposition, it is evident that the O 1s peak is a superposition of at least three oxygen species. The main component, centered at around 531.5 eV, is characteristic for chemisorbed oxygen. The high BE shoulder of the main peak is a contribution of hydroxides or water, while the low BE shoulder is characteristic for Ti oxides [109-114].

Fig. 6.27: (a) O 1s XPS and (b) O KLL XAES detail spectra of the HOPG sample before and after Ti deposition as well as after 15 hours and 4 days of storage in UHV.
The oxidation of Ti on the HOPG surface can also be asserted by examining the Ti 2p XPS spectra. Fig. 6.28 shows the change in the Ti 2p spectra for the Ti/HOPG sample, measured at 1 hour, 15 hours, and 4 days after Ti deposition. A Shirley background, which accounts for the background of inelastic electron scattering, was subtracted from the Ti 2p spectra shown in Fig. 6.28. The spectra were then normalized to their integrated areas and plotted together with their respective “difference spectrum” (to be discussed below). As already observed in the “fast series” single-scans (Fig. 6.21a), Ti oxidizes immediately after deposition, which is indicated by a shift of the Ti 2p lines from a BE characteristic for metallic Ti to a BE characteristic for titanium oxides. The oxidation process continues as the storage time increases. The detail Ti 2p spectra measured at 1 hour after Ti deposition is still dominated by the metallic peaks, characterized by an asymmetric spin-orbit doublet (Ti 2p$_{3/2}$ at $-454.5$ eV and Ti 2p$_{1/2}$ at $460.4$ eV) [77]. After 15 hours of storage, however, the Ti 2p peaks decrease in intensity and the maxima shift $\sim 0.2$ eV to higher BE (clearly seen in Fig. 6.28a for Ti 2p$_{3/2}$). At the same time, new spectral weight emerges in the valley between the Ti 2p doublets and at the high BE shoulder, which is shown as a broad feature in the difference spectrum. The new broaden features are ascribed to contribution of Ti in higher oxidation states, such as TiO, $T_2O_3$, and TiO$_2$. A similar tendency is observed for the spectrum measured at 4 days after deposition (Fig. 6.28b). However, the shift and decrease of the Ti 2p peaks are smaller.

The shift of Ti 2p peaks to higher BE clearly indicates a continuous oxidation and transformation of Ti from its metallic state to an oxidized state. This transformation occurs faster in the early stage after Ti deposition and slows down as the storage time increases. As mentioned earlier, this decrease of the transformation rate is probably
related to the oxidation of the outermost layer(s) (shell), which reduces the accessibility of the more reactive Ti metal atoms in the core.

![Graph](image)

**Fig. 6.28:** Evolution of Ti 2p spectra measured at (a) 1 hour and 15 hours and (b) at 15 hours and 4 days after Ti deposition. The respective difference spectra are also shown.

The detailed C 1s, O 1s, and Ti 2p XPS spectra of Ti/SWNT and Ti/C_{60} samples were recorded after first performing UPS measurements for 2 hours (as discussed in Section 6-1). The time-dependent evolution of the three core level features was monitored as listed in Tables 6.2 and 6.3. After Ti deposition, a sharp increase of the O 1s signal on the surface of the Ti/SWNT and Ti/C_{60} samples is found. Figs. 6.29 and 6.30 show O 1s and O KLL spectra of the Ti/SWNT and Ti/C_{60} samples, respectively, measured at different times of sample storage in UHV. It is suggested that oxygen species from the residual gas are adsorbed on the surface of the sample due to the gettering ability of the Ti adatoms. The evolution of the oxygen signal on the Ti/C_{60} sample is similar to that of the Ti/HOPG...
sample (Fig. 6.27). Strong oxygen absorption occurs in the early stage after Ti deposition (spectra measured at 2 hours), but the oxygen uptake slows down as the vacuum storage time increases. The decrease in the oxygen adsorption rate is again attributed to the less reactive property of the oxidized outermost Ti layer, which is observed in Ti/C\textsubscript{60} after 2 hours. In stark contrast, the oxygen adsorption on the Ti/SWNT sample does not appear to slow down until after 18 hours. While clustering of Ti adatoms reduces the surface area and thus the number of potential oxygen adsorption sites, a larger or more homogeneous coverage of Ti on the SWNT sample (as observed in this thesis) would maintain the high reactivity of the Ti layer for a longer time (analogous to a Ti sublimation pump with larger surface area; in fact, one could argue that a SWNT surface would make a very efficient Ti sublimation pump). The results thus give additional evidence for the more homogeneous layer formation of Ti on SWNT, as compared to the predominant formation of clusters on C\textsubscript{60} and HOPG.

Fig. 6.29: Increase of (a) O 1s and (b) O KLL signals from the Ti/SWNT sample before and after Ti deposition and after storage in UHV.
The adsorption of oxygen species on the sample surface is accompanied by an oxidation of the deposited Ti, as can be seen from the evolution of the Ti 2p spectra from both Ti/C\textsubscript{60} and Ti/SWNT samples (Fig. 6.31). A Shirley background was subtracted, and the spectra were normalized to the integrated area in the range of 450-470 eV (covering the Ti 2p peaks). In the early stage after Ti deposition, the Ti 2p peak positions indicate the presence of metallic Ti with a strong spin-orbit doublet at around 455 and 461 eV, characteristic for Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2}, respectively [77]. As the vacuum storage time increases, the Ti 2p metallic features decrease, broaden and shift to higher BE. New features emerge in the valley between the metallic peaks and at the high BE side of the doublet, best resolved in the spectra of the Ti/SWNT sample (Fig. 6.31a). In the latter case, the observed peaks are characteristic for Ti oxide in the form of TiO\textsubscript{2} (doublet approx. 459.0 and 465.0 eV [77]). With increasing storage time in UHV, the intensity
decreases and the doublet shifts to higher BE. Furthermore, the TiO$_2$ features increase. This clearly indicates an oxidation of the Ti overlayer, where Ti metal transforms to TiO$_2$. Again, the time behavior is such that the oxidation process initially occurs quickly and then slows down due to the less-reactive nature of the oxide shell (TiO$_2$) that is formed. Compared to the Ti/C$_{60}$ sample, the oxidation of the Ti/SWNT sample is significantly more pronounced, with more reliable evidence for TiO$_2$ formation. The oxidation rate of Ti on C$_{60}$ is also slower than on SWNT (by comparing attenuation and transformation of Ti metallic features measured at 17 hours for Ti/C$_{60}$ and at 18 hours for Ti/SWNT sample, respectively). In accord with the behavior of oxygen adsorption observed above (Fig. 6.29 and 6.30), the slower oxidation of Ti on C$_{60}$ adds further evidence for a cluster formation of Ti on C$_{60}$. The stronger oxidation of the Ti/SWNT sample can be interpreted as a result of two effects. On one hand, the larger coverage of Ti on the SWNTs increases the surface area of the deposited Ti, which in turn increases the number of Ti adatoms available for a reaction with oxygen species from the residual gas. On the other hand, Ti adatoms could also react with oxygen species already incorporated in the SWNTs (recall that the initial oxygen concentration in the SWNT sample is higher than that of C$_{60}$ and HOPG, as discussed in Chapter V). The continuous increase of adsorbed oxygen on the sample surface with increasing storage time suggests that the oxygen source comes mostly from residual gas (Tables 6.5, 6.6). However, we cannot rule out a Ti oxidation contribution of oxygen species previously adsorbed on (or attached to) the SWNTs. By strong interaction with Ti, oxygen species can serve as a bridge between Ti adatoms and the nanotube sidewalls and can thus potentially provide
more nucleation sites for a continuous layer formation of Ti on the surface of SWNTs [33, 41-42].

![Graph](image)

**Fig. 6.31:** Evolution of XPS Ti 2p spectrum of (a) Ti/SWNT and (b) Ti/C$_{60}$ samples measured at different times after Ti deposition.

### CHAPTER VI SUMMARY

In this chapter, the detailed interaction between Ti and the three carbon allotropes (HOPG, C$_{60}$, and SWNT) as well as the oxidation behavior of the three Ti-decorated systems was discussed.

Our STM experiments show a formation of Ti nanoparticles on the HOPG surface, similar to that on the Au substrate. Spectroscopic measurements provide multiple evidence for the formation of a Ti layer on SWNT and for Ti cluster formation on C$_{60}$ samples. The effective thickness of the Ti layer on SWNT is larger than that on HOPG and C$_{60}$ under the same deposition conditions, indicating a higher coverage of Ti on SWNT. The chemical interaction between Ti adatoms and the network carbon atoms in
HOPG and SWNT is characterized by the formation of Ti-C bonds, presumably via charge transfer from Ti to carbon atoms. The Ti-C interaction is weak for HOPG, but stronger for SWNTs, presumably due to the curvature of the tube, more defects, and oxygenated functional groups found on the surface of SWNT. The Ti-C interaction on C\textsubscript{60} agrees well with a model of hybridization of molecular orbitals of C\textsubscript{60} with Ti, which induces a newly formed Ti\textsubscript{x}C\textsubscript{60} compound. In addition, the deposition of Ti on the sample surface, either as a layer (on SWNT) or in form of clusters (on HOPG and C\textsubscript{60}), induces changes in the chemical environment of carbon atoms. On all investigated carbon-based samples, the deposited Ti reacts strongly with oxygen and adsorbs (getters) oxygen species on sample surface even under UHV condition. As a consequence, the deposited Ti atoms become quickly oxidized, which may have important impact on potential applications of Ti-decorated carbon nanostructures. The Ti layer formed on the SWNTs reacts more strongly and adsorbs more oxygen species on the sample surface, compared with that of Ti/HOPG and Ti/C\textsubscript{60}, again giving support to the model of a Ti layer formation on SWNTs.
CHAPTER VII

Li DEPOSITION ON CARBON-BASED MATERIALS

The interaction of Li with carbon-based materials has attracted considerable interests [43-45]. The intercalation of Li into graphite and carbon nanotubes has been studied to improve the capacity of lithium-ion batteries [45-50]. Li-doped C$_{60}$ has also been investigated for potential super-conducting behavior of alkali-doped fullerenes. Theoretical considerations recently have shown a great potential of Li-doped carbon-based materials as hydrogen storage matrices [66, 67]. Thus, reactions of Li with carbon surfaces and interactions with other adsorbate species on the carbon surface are important to study. In this chapter, the results of photoelectron spectroscopy and scanning tunneling microscopy investigations of Li-deposited carbon-based materials will be presented.

Section 7.1

Interaction between Li and Carbon-based Materials

As described in detail in Chapter III, Li was deposited from a Li getter element source onto HOPG, SWNT, and C$_{60}$ sample with standard deposition conditions (9A current for 2 min). The XPS survey spectra for all three types of carbon samples are very similar. As an example, Fig. 7.1 shows the survey spectra of a SWNT sample before and after Li deposition. The spectra were normalized to the C 1s lines and offset along the y-axis. The
Li 1s peak is weak and overlaps with the Fe 3p feature. Apart from the large C 1s peak, the most common characteristic for the three carbon-based materials is the increase of the oxygen signal after Li deposition, which indicates the adsorption of residual gas molecules on the surface. The attenuation of the C 1s peak was used to estimate the “effective” Li thickness, following the procedure described in Chapter III, and found to be 1.5 Å for Li on HOPG, and 1.65 Å (1.15 Å) for SWNT and C_{60} samples, respectively. Note that this estimation provides an average, effective thickness only. The actual morphology of Li on carbon-based samples depends on a variety of factors, such as diffusion and sticking coefficients of Li adatoms on the sample surface and the interaction energies between lithium and carbon atoms at the surface.

Fig. 7.1: XPS survey spectra of a SWNT sample before and after Li deposition.
The analysis of detailed XPS (C 1s and O 1s) and UPS spectra of Li-deposited samples reveals strikingly different behaviors for the three carbon materials. Fig. 7.2 shows C 1s XPS spectra of HOPG before and after Li deposition. The spectra were normalized to their maxima to observe possible chemical shifts and line shape changes. The position of the main C 1s peak of HOPG is unchanged, i.e., no chemical shift is observed. The peak asymmetrically broadens toward high BE after Li deposition; the FWHM of the main peak increases from 1.00 eV to 1.11 eV. As described in Chapter V, carbon atoms in sp\(^3\)-configuration are responsible for the high BE shoulder of the main C 1s peak in the sp\(^2\)-dominated structure of HOPG.

While the absence of a chemical shift suggests that Li does not interact with HOPG very strongly, the broadening indicates that the deposition of Li may induce a disruption of the planar network of HOPG. This would create more sp\(^3\)-like local structures of carbon atoms on the surface.

![XPS Mg K\(_{\alpha}\) C 1s](image)

Fig. 7.2: C 1s XPS spectra of an HOPG sample before and after Li deposition.
In contrast to the HOPG sample, the deposition of Li on a SWNT sample induces a large change of the C 1s peak, as shown in Fig. 7.3. A chemical shift of +0.35 eV to higher BE is found. In addition, the C 1s peak broadens, again by forming a shoulder at high BE, as seen in Fig. 7.3b (the spectra were aligned and centered at the maximum). The FWHM of the main peak increases from 1.20 to 1.30 eV. The observed chemical shift indicates a strong interaction between Li and the carbon atoms of SWNTs. A charge transfer, induced by the injection of Li 2s electrons into unoccupied molecular states of the SWNT could be responsible for the shift.

Fig. 7.3: C 1s XPS spectra of SWNT sample before and after Li deposition. A positive shift of 0.35 eV was observed in (a). Peak alignment and enlargement in (b) shows a broadening at the high BE shoulder.
The C 1s XPS spectra of Li-deposited C\textsubscript{60} are shown in Fig. 7.4. A very small shift of the main peak is observed in the raw data (+0.03 eV). However, as mentioned in Chapter V and VI, a charging effect is observed for the C\textsubscript{60} sample, which induces a shift of +0.80 eV for the pristine thick C\textsubscript{60} sample. The deposition of Li on the surface can potentially make the sample more conductive and can reduce or remove the charging effect, thereby shifting the main peak to lower BE. Therefore, the seemingly unchanged position of the C 1s peak may actually indicate a positive chemical shift (i.e., to higher BE) due to Li-C\textsubscript{60} interaction. In addition, the broadening is observed at both high and low BE sides of the main peak, as seen in Fig. 7.4a, indicating contributions of carbon atoms in different chemical environments. The FWHM increases from 1.02 to 1.12 eV after Li deposition. The features at the high BE shoulder become somewhat less pronounced, but are still clearly observed. In particular, the energy of the shake-up satellites associated with HOMO-LUMO and HOMO-1-LUMO transitions are unchanged, indicating no disruption to the cage-like structure of the C\textsubscript{60} molecules.

Further information on the deposition of Li on the surface of carbon samples was gained by examining XPS Li 1s spectra and UPS-derived work functions before and after Li deposition. As shown in Fig. 7.5 for Li/HOPG and in Fig. 7.6 for Li/C\textsubscript{60}, a broad Li 1s feature centered at 56.8 eV (FWHM=2.55 eV) and 56.6 eV, respectively. Compared with the reference value of ~55.0 eV for metallic Li [77], the shift to higher BE side might be due to the above-mentioned charging effects, a reduced screening compared to the metallic case, and/or contributions of Li atoms with higher oxidation states. In the latter case, the oxidation of Li is attributed to a reaction with adsorbed molecules from the residual gas.
Fig. 7.4: (a) C 1s XPS spectra of a C$_{60}$ sample before and after Li deposition; (b) Magnified view of the shake-up satellite region.

Fig. 7.5: Li 1s XPS spectra of an HOPG sample before and after Li deposition.
Fig. 7.6: Li 1s XPS spectra of a C$_{60}$ sample before and after Li deposition.

Fig. 7.7: Li 1s/Fe 3p XPS spectra of the SWNT sample before and after Li deposition. (a) The Li 1s peak overlaps with Fe 3p feature of SWNT; (b) Difference spectrum shows a broadened feature of Li 1s on SWNT.
As mentioned earlier, the intensity of Li 1s peak is weak due to its small cross-section. For the Li/SWNT sample, the Li 1s peak appears as a shoulder of the Fe 3p feature, as seen in Fig. 7.7a. (The photoionization cross-section of Li 1s is ~0.06 and Fe 3p is 0.54, compared to that of C 1s [72]).

The deposition of Li on the surface of carbon-based materials induces a change of the surface work function. Fig. 7.8 shows work functions of Li-deposited samples determined from the secondary electron cutoff of He I UPS spectra. The difference in the interaction between Li and carbon atoms may also be reflected in the difference of the work function of Li-deposited carbon-based samples. The weak interaction between Li and HOPG lead to the work function of Li/HOPG close to that of pure metallic Li (2.9 eV). On the other hand, interaction between Li and C60 (and SWNT) may lead to formation of Li-C compounds, which have sufficiently higher work functions.

Fig. 7.8: Secondary electron cutoff for carbon-based samples before and after Li deposition: (a) HOPG, (b) C60, and (c) SWNT. The work functions are also given.
The UPS valence spectra (He II excitation) of the HOPG sample before and after Li deposition are shown in Fig. 7.9. As already deduced from the C 1s core-level spectra, no indication of a strong chemical interaction between Li and HOPG is found. The deposition of Li on HOPG merely smears out the $\sigma$- and $\pi$-band structure of HOPG.

![Graph showing UPS spectra of HOPG and Li/HOPG](image)

Fig. 7.9: Evolution of valence band spectra of HOPG sample upon Li deposition.

The valence band structures of the C$_{60}$ sample before and after Li deposition were measured with He I UPS and are presented in Fig. 7.10. The feature-rich structure, characteristic for C$_{60}$ molecules, is clearly observed before and after Li deposition, again indicating that there is no significant structural modification of the C$_{60}$ molecules. All molecular orbitals are slightly broadened by the Li deposition. The interaction between Li and the C$_{60}$ molecules induces a downward shift of $\sim$0.1 eV for all molecular valence band features. As previously described, a charging effect on the thick C$_{60}$ sample causes a shift of all spectral features to high BEs. A shift of $\sim$0.90 eV induced by charging has been observed for the HOMO level of a thick C$_{60}$ layer compared to 1ML of C$_{60}$ on Au substrate [187]. A similar shift is likely applicable for our measurement of the pristine
C₆₀ sample, while the Li-deposited sample is expected to be more conductive and thus possibly exhibit a smaller (or no) charging-induced shift. Thus, the actual shift of the molecular orbitals is expected to be larger than the observed downward shift of 0.1 eV; in the extreme case of complete removal of charging effects in our sample, it would be ~0.72 eV. The chemical shift in valence band can be estimated and attributed to the interaction between Li and C₆₀ molecules.

Fig. 7.10: He I UPS valence band spectra of a C₆₀ sample before and after Li deposition.

The deposition of Li on a SWNT sample induces a shift of ~0.35 eV for both the σ-band and the π-band of the SWNTs, as shown in Fig. 7.11a. The shift is in agreement with the chemical shift observed for C 1s core-level, indicating a systematic shift of the electronic structure of the SWNT. Fig. 7.11b shows the change of the valence band in the
proximity of the Fermi energy. There is no Fermi edge formed by Li deposition, indicating that the deposited Li is not metallic, but "reacted" (e.g. oxidized due to reaction with oxygen or formation of Li-carbon compounds).

![Graph](image)

Fig. 7.11: (a) He I UPS valence band spectra of a SWNT sample before and after Li deposition; (b) Enlarged region near the Fermi energy.

Section 7.2

Morphology of Li Deposition on HOPG

In order to better understand the (laterally integrating) spectroscopic results in the previous section, it is necessary to understand the detailed morphology of the Li "layer" that is formed on the surface of the carbon-based materials. For this purpose, the formation and morphology of the Li layer on an HOPG sample were investigated by STM. An example of an HOPG surface after Li deposition is shown in Fig. 7.12. It can
be observed that Li forms nanoparticles with a broad size distribution around 5 nm on HOPG.

An atomic resolution image of the Li-deposited HOPG surface is shown in Fig. 7.13. While the atomic periodicity of the HOPG substrate can be observed, the structure on the surface of the Li nanoparticles cannot be resolved. High electron density on those Li
structures would require a different set of parameters, such as bias voltage and set current, to obtain an appropriate tunneling current for imaging. However, several interesting features related to Li formation on HOPG surface can be observed. The observation of an atomic arrangement of the substrate in areas not covered by the Li nanoparticles suggests that the surface is not covered by layer of Li. The feature at image center resembles a pit (or crater), possibly due to impact of Li during deposition, which creates damages to surface. Thus, a discontinuity of the atomic arrangement of HOPG surface can be observed. The damage of HOPG surface is probably correlated to the increase of $sp^3$-feature observed in the C 1s core-level spectra, described above.

The formation of Li nanoparticles on the surface of HOPG, observed by local microscopy, also supports the lateral spectroscopic results described above. A small sticky coefficient of Li on HOPG surface may lead to a strong Li-Li interaction (that forms Li clusters and nanoparticles). The formation of nanoparticles (clustering) also implicates a less-covered area of Li on the surface of HOPG, which again reduces the possibility of Li-C interaction. Based on this argument, the stronger interaction between Li and carbon atoms of C60 and SWNT sample may be interpreted as a result of larger coverage (in other word, layer formation) of Li on those samples. It is evident that there is a correlation between the formation of deposited metals on carbon-based materials (morphology) and the metal-carbon interaction. STM and STS, which provide access to atomic arrangement and local electronic structure, could help to reveal the local interaction mechanisms of the deposited metals.
Fig. 7.13: High resolution STM image after Li deposition on an HOPG surface. Crater, impact with Li cluster during deposition, can be observed which damages the atomic arrangement of HOPG surface. (the scale bar is 2 nm)
Section 7.3

Oxidation of Li on Carbon-based Materials

Li can react not only with carbon atoms of our carbon-based samples, but also with oxygen-containing species, either already adsorbed on the sample surface or present in the residual gas. To study the impact of the adsorption of such residual gas molecules, the oxidation behavior of Li-decorated carbon-based materials under ultra-high vacuum (~$5 \times 10^{-10}$ mbar) was investigated using photoelectron spectroscopy. For all Li-deposited sample, the O 1s and O KLL detail spectra were measured with better counting statistics (1 hour accumulation time, taken 2-3 hours after Li deposition). These spectra thus reflect an average evolution of oxygen signals for several hours after Li deposition. For Li-deposited C$_{60}$ sample, in addition, ten series of single scans (approx. 1 minute) were measured consecutively for the C 1s, O 1s, and Li 1s spectral regions in the first hour after Li deposition (single scans for each monitored elements are thus separated by ~ 5 minutes). Due to sample transfer, 5 minutes elapsed between the end of Li deposition and the start of the XPS measurements.

The O 1s and O KLL detail spectra before and after Li deposition on HOPG are shown in Fig. 7.14. The initial oxygen content on the surface of the HOPG sample is low and significantly increases after Li deposition. This increase is attributed to the adsorption of residual gas molecules on the sample surface, most likely on the Li nanoparticles and in their vicinity. Similar to the reaction found for Ti, the adsorption of oxygen-containing species on the sample surface of Li-deposited HOPG is not surprising. Even though the oxygen signals on the pristine HOPG sample have contributions from several oxygen species, as discussed in Chapter V, the signature of the Li-induced
oxygen adsorption is clear. There are at least two prominent features that can be resolved in the O 1s spectrum of Li-deposited HOPG. The main feature, centered at ~533.0 eV, can be ascribed to Li hydroxides due to the reaction of Li with water molecules from the residual gas. The low BE feature at ~530.0 eV, observed after Li deposition, has the same BE as reported for Li oxide in the form of Li$_2$O [103, 104, 114].

Fig. 7.14: (a) XPS O 1s and (b) XAES O KLL detail spectra of an HOPG sample before and after Li deposition.

A similar behavior of oxygen adsorption and oxidation of Li was observed after deposition on a SWNT and a C$_{60}$ sample. Fig. 7.15 shows the change of the oxygen signals (XPS O 1s and XAES O KLL) induced by Li deposition on the SWNT sample. The most prominent feature corresponds to adsorbed oxygen species in the form of Li hydroxides, centered at ~532.6 eV. It is again likely due to a reaction of Li with water molecules from the residual gas. The second species at ~530.7 eV is ascribed to Li oxide.
(Li₂O) with a possible contribution from oxides of the metallic catalyst (Fe₂O₃, Fe₃O₄). Note that the onset of the O 1s spectrum occurs at lower BE (~0.25 eV) compared to that of the pristine SWNT sample, indicating a metal oxide contribution after Li deposition that is not found on the pristine SWNT sample and hence that is ascribed to the formation of Li oxide. The more prominent Li hydroxides feature in O 1s spectra (about 2.0 eV from metal oxides) is accompanied by an emergence of a new feature in the O KLL spectra also at ~2.0 eV to lower kinetic energies.

Fig. 7.15: (a) XPS O 1s and (b) XAES O KLL spectra of a SWNT sample before and after Li deposition.

For our investigation of Li deposition on C₆₀, we again need to take into account the charging effect described earlier. The charging shifts all spectral features to higher BE, and thus the most prominent feature of the O 1s signal from the pristine C₆₀ sample appears at ~533.0 eV, as seen in Fig. 7.16. After Li deposition, an increase of the peak
indicates the formation of Li hydroxide (BE ~532.2 eV). Similar to the behavior of Li on HOPG and SWNT samples, the characteristic feature for Li oxide (Li_2O) is clearly observed as a shoulder at lower BE of the main O 1s peak.

![XPS O 1s spectra of the C_{60} sample before and after Li deposition](image)

Fig. 7.16: XPS O 1s spectra of the C_{60} sample before and after Li deposition.

The "fast evolution" of the Li 1s and O 1s spectral features in the first hour after Li deposition on C_{60} sample is shown in Fig. 7.17. No clear trend can be observed for the Li 1s spectra. The evolution of O 1s spectra is also slowly changed, indicating that there is only little oxygen adsorption right after Li deposition. The most prominent feature in the O 1s spectra is observed at ~532.2 eV, corresponding to Li hydroxides. The feature characteristic for Li oxides is not evident in the first hour after Li deposition.

The strong interaction of Li with C_{60} molecules (described in Section 7.1) can also be observed in the "fast scan" spectra after Li deposition. The evolution of the C 1s region of a Li-deposited C_{60} sample in the first hour after Li deposition is shown in Fig. 7.18. A clear shift of the main C 1s peak to higher BE is observed as the time increases. The trend
is indicative for the interaction of Li with carbon atoms of C₆₀ molecules, in which charge
transfer from Li to carbon atoms induces a chemical shift to higher BE.

Fig. 7.17: Evolution of (a) Li 1s and (b) O 1s spectra of the Li/ C₆₀ sample as a function
of time after Li deposition.

Fig. 7.18: Evolution of XPS C 1s spectra of C₆₀ sample before and after Li deposition.
CHAPTER VII SUMMARY

Using photoelectron spectroscopy, the interaction of Li with carbon atoms in different atomic arrangements was studied. The findings indicate that the Li-C interaction is quite different for the different materials under study. Despite its high reactivity, Li weakly interacts with HOPG. Microscopic investigations by STM reveal that Li forms nanoparticle clusters on the surface of HOPG. In contrast, Li reacts strongly with SWNT and HOPG. The strong interaction induces a positive chemical shift, observed for both core-level and valence level spectra - a shift of ~1.0 eV and ~0.35 eV is observed for Li-deposited C_{60} and SWNT samples, respectively, indicating that its magnitude depends on the local environment of the carbon atoms. In addition to a reaction with the carbon atoms, Li deposition also induces chemical environment changes to the carbon network of SWNTs that broadens C 1s peak. Similar changes are observed for C_{60}, but no evidence for a Li-induced disruption of the cage-like structure of the C_{60} molecules is found.

Li reacts strongly with oxygen species from the residual gas in ultra-high vacuum. The reaction leads to adsorption of oxygen species on the sample surface and formation of Li hydroxides and oxides. The oxidation behavior appears to depend on the interaction of Li with carbon substrate. For C_{60}, it is observed that Li reacts mostly and strongly with C_{60} molecule in the first hour after deposition, while the oxygen absorption is small. The latter processes are probably slow, which accumulates a large amount of oxygen species on the sample surface only after several hour of sample storage under UHV. The results may be related to Li-C interaction, formation and diffusion of Li on the carbon-based materials.
CHAPTER VIII

CONCLUSION AND OUTLOOK

While the here-studied carbon-based materials graphite, C₆₀, and SWNTs, are all based on similar building blocks, i.e., a flat or “rolled-up” carbon network, the experimental results presented in this thesis demonstrate that the metal-carbon interaction is very differently for each of these carbon allotropes.

To gain such insights into the metal-carbon nanotube interface formation, dedicated sample preparation procedures had to be established, in particular for obtaining individual nanotubes on a sufficiently flat and conducting substrate. After successful preparation, the arrangement of carbon atoms in the honeycomb structure of individual nanotubes could be observed with atomic resolution. The results lay a foundation for further studies of the local atomic and electronic structures of metal-deposited carbon-based materials. The possibilities of obtaining individual nanotubes by other methods need to be explored in order to develop a standardized sample preparation procedure, which could improve quality of the nanotube samples for microscopic and spectroscopic investigations. The “simplicity” of the “peel-off” technique in preparing graphene from layer-structured graphite intrigues a thought of sample preparation, which would employ a similar technique to peel off individual tubes from bundles. The technique could be readily
applicable to mats or "buckypaper" of carbon nanotubes, or better to vertically-aligned carbon nanotubes.

Microscopic and spectroscopic studies of thin layers of Ti and Li on carbon-based materials show that Ti interacts weakly with HOPG and forms nanoparticles on the surface. In contrast, a stronger Ti-carbon interaction, characterized by Ti-C bond formation, is observed for Ti deposited on SWNTs. The stronger interaction is attributed to the curvature of the tube and the presence of defects, dangling bonds, and oxygenated functional groups on the SWNTs. As a consequence, a larger coverage of Ti is observed in this case, compared to that on HOPG and $C_{60}$. Both Ti and $C_{60}$ are quite reactive, and readily interact with each other, possibly through a hybridization mechanism between Ti 3d states and $C_{60}$ molecular orbitals. The deposition of Ti on the surface of these carbon-based structures causes changes of the chemical environment of the carbon atoms in the network, which induces a chemical shift and a broadening of the C 1s XPS peak.

Li also reacts weakly with HOPG and forms nanoparticles on its surface. However, Li reacts strongly with $C_{60}$ and SWNTs. This is likely through injection of Li 2s electrons into unoccupied states of SWNT and $C_{60}$, which induces chemical shifts of the C 1s XPS peaks of $C_{60}$ and SWNTs.

The oxidation behavior of the deposited metals were studied with emphasis on potential issues related to using metal-decorated carbon-nanomaterials for hydrogen storage applications. Due to its reactivity, Ti readily oxidizes, even under ultra-high vacuum condition. This creates a great concern for potential applications of such systems as hydrogen storage materials, since potential hydrogen adsorption sites may be blocked. Li also reacts strongly with oxygen-containing species, and can even react with oxygen.
atoms originally bonded in a Ti oxide environment. The results thus demonstrate that Li can be used to reduce the oxidation of Ti. Thus, a co-evaporation of Ti and Li could be a solution for the decoration of carbon-based materials with metallic Ti. This requires further investigations to optimize the experimental procedure and to assert the interaction mechanisms.

Several avenues of research on metal-decorated carbon-nanomaterials remain open. While progress has been made in addressing the metal-carbon interaction, the roles of defects and oxygenated functional groups for the metal-carbon interaction and for the overlayer growth mode are still speculations and need to be asserted. STM and STS, which have proven to be effective techniques in elucidating the local atomic and electronic structures of carbon-based materials, would help to reveal the local interaction mechanisms of the deposited metals and potential adsorbate molecules. Especially for hydrogen storage applications, it is important to understand the metal-metal and metal-carbon interactions at the interface in a local fashion, to control the growth modes of the adsorbed metals, and tailor their oxidation behavior.

In summary, we have taken a first step towards the overarching goal of understanding the microscopic chemical and electronic interactions between adsorbates (in particular hydrogen), metal decoration layers, and carbon nanomaterials. Once such understanding is achieved, it will be possible to explain the discrepancy between the extremely promising theoretical predictions of high hydrogen storage capacity and the disappointing experimental (bulk) results. By pursuing a local approach, paired with the fundamental insight on chemical bonding and electronic structure offered by laterally integrating electron spectroscopies, it should be possible to not only understand the shortcomings of
the status-quo, but also to make predictions and give guidance to new directions that will help solve the hydrogen storage problem. Once solved, the international community will be one step closer to overcoming the fundamental problems associated with the looming global energy crisis and the ever-increasing energy demand of generations to come.

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