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Characterizations of as grown and functionalized epitaxial graphene grown on SiC surfaces

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Abstract

The superior electronic and mechanical properties of Graphene have promoted graphene to become one of the most promising candidates for next generation of electronic devices. Epitaxial growth of graphene by sublimation of Si from Silicon Carbide (SiC) substrates avoids the hazardous transfer process for large scale fabrication of graphene based electronic devices. Moreover, the operation conditions can potentially be extended to high temperatures, voltages and frequencies. This thesis is focused on characterizations of as grown and functionalized epitaxial graphene grown on both Si-face and C-face SiC. Synchrotron radiation-based techniques are employed for detailed investigations of the electronic properties and surface morphology of as grown and functionalized graphene.

Large area and homogeneous monolayer (ML) graphene has been possible to grow on SiC(0001) substrates by sublimation, but efforts to obtain multilayer graphene of similar quality have been in vain. A study of the transport behavior of silicon atoms through carbon layers was therefore performed for the purpose to gain a better understanding of the growth mechanism of graphene on Si-face SiC. It showed that a temperature of about 800 °C is required for Si intercalation into the interface to take place. Intercalation of Si was found to occur only via defects and domain boundaries which probably is the reason to the limited growth of multilayer graphene. Annealing at 1000-1100 °C induced formation of SiC on the surface and after annealing above 1200 °C Si started to de-intercalate and desorb/sublimate.

Different alkali metals were found to affect graphene grown in SiC quite differently. Li started to intercalate already at room temperature by creating cracks and defects, while K, Rb and Cs were found unable to intercalate into the graphene/SiC interface. Effects induced by the alkali metal Na on graphene grown on both Si-face and C-face SiC were therefore studied. For the Si-face, partial intercalation of Na through graphene was observed on both 1 ML and 2 ML areas directly after Na deposition. Annealing at a temperature of about 75 °C strongly promoted Na intercalation at the interface. The intercalation was confirmed to start at domain boundaries between 1 ML and 2 ML areas and at stripes/streaks on the 1 ML areas. Higher annealing temperature resulted in desorption of Na from the sample surface. Also for C-face graphene, a strong n-type doping was observed directly after Na deposition. Annealing at temperatures from around 120 to 300 °C was here found to result in a considerable π -band broadening, interpreted to indicate penetration of Na in between the graphene layers and at the graphene SiC interface.

The thermal stability of graphene based electronic devices can depend on the choice of contact material. Studies of the stability and effects induced by two commonly used metals (Pt and Al) on Si-face graphene were carried out after deposition and after subsequent annealing at different temperatures. Both Al and Pt were found to be good contact materials at room temperature. Annealing at respectively ~400 °C and ~800 °C was found to trigger intercalation of Al and Pt into the graphene/SiC interface, and

induce quasi-free-standing bilayer electronic properties. Contacts of Pt can thus withstand higher temperatures than Al contacts. For Al inhomogeneous islands of different ordered phases were observed to form on the surface during annealing, while this was not the case for Pt. The initial single π -band structure was in the Al case restored after annealing at $\sim 1200^\circ\text{C}$ although some Al remained detectable from the sample. For Pt, the bilayer graphene electronic properties induced by intercalation were thermally stable up to 1200°C . In the case of Al the stability and effects induced on C-face graphene were also investigated for comparison, and significant differences were revealed. An ordered Al-Si-C compound was found to form after annealing at temperatures between ca. 500°C and 700°C . Formation of this compound was accompanied with a large reduction of graphene in the surface region. Annealing at temperatures above 800°C resulted in a gradual decomposition of this compound and regrowth of graphene. No Al signal could be detected after annealing C-face graphene at 1000°C .

Graphene grown on C-face SiC has attracted high interest since its mobility has been reported to be one order of magnitude higher compared to Si-face graphene. C-face graphene has moreover been claimed to be fundamentally different compared to Si-face graphene. A rotational disorder between adjacent graphene layers has been suggested that effectively decouples the graphene layers and result in monolayer electronic properties of multilayer C-face graphene. The domain/grain size is typically much smaller for C-face graphene and the number of graphene layers less uniform than on Si-face graphene. Using LEEM and micro-LEED we showed that there is no rotational disorder between adjacent layers within the domains/grains but that they had different azimuthal orientations. Using nano-APRES, we recently also revealed that multilayer C-face graphene show multiple π -bands and Bernal stacking, similar to multilayer Si-face graphene.

Populärvetenskaplig Sammanfattning

Grafen, ett lager av grafit, är den första 2-dimensionella kristallen som framstälts experimentellt, och då först genom mekanisk exfoliering från grafit. De utmärkta elektroniska och mekaniska egenskaper som grafen uppvisade gjorde det till ett av de mest lovande materialen för tillverkning av nästa generation av elektroniska komponenter och apparater. Grafen kan väkas epitaxiellt på ytor av kiselkarbid (SiC) genom uppvärmning till så hög temperatur att Si sublimeras från substratet. På så vis erhållas grafen direkt på ett halvledande eller isolerande substrat och man undviker riskabla överföringsprocesser. Denna metod är dessutom lämplig för storskalig grafentillväxt och efterföljande processning för tillverkning av elektroniska komponenter baserade på grafen. Växt på substrat av SiC kan dessutom driftsförhållandena för komponenter utsträckas till höga temperaturer, spänningar och frekvenser. Denna avhandling fokuserar på karakterisering av grafen som växts på respektive Si- och C-ytan av SiC samt på funktionalisering av grafen. Funktionalisering har utförts genom deponering av ett ämne på grafenytan och efterföljande värmebehandling av provet. Några olika synkrotronljus-baserade tekniker har utnyttjats för detaljerade undersökningar av de elektroniska egenskaperna och av struktur och ytmorfologi av grafenprover efter tillväxt och efter funktionalisering.

Stora homogena prover med ett lager av grafen (1 ML) har producerats på SiC (0001) substrat, dvs på Si-ytan, genom sublimering, men arbeten med att få flerskiktiga prover av grafen med samma kvalitet hade inte alls lyckats. Därför utfördes en studie av kiselatomers transportbeteende genom kolskikt, i syfte att få en bättre förståelse av tillväxtmekanismen av grafen på Si-ytan av SiC. Den visade att en temperatur av ca 800 °C krävs för att kisel skall penetrera genom kollagren och interkalera i gränsytan mellan SiC och kollagren. Interkalering av kisel befanns ske enbart via defekter och domängränser och detta är förmodligen anledningen till att tillväxten av grafen blir begränsad så att homogena prover med flera lager grafen inte bildas. Värmebehandling vid 1000-1100 °C inducerade tillväxt av kiselkarbid på ytan av provet och vid temperaturer $\geq 1200^{\circ}\text{C}$ så började kisel sublimera/desorbera från provet.

Olika alkalimetaller hade befunnits ha helt olika påverkan på grafen växt på SiC. Li började interkalera redan vid rumstemperatur, genom att skapa sprickor och defekter i grafenlagren, medan K, Rb och Cs inte alls interkalerade in i grafen/SiC- gränsytan. Därför studerade vi påverkan som alkalimetallen natrium (Na) har på grafen som växts på både Si- och C-ytan av SiC. För Si-ytan observerades en delvis interkalering av natrium direkt efter deponeringen både på 1 ML och 2 ML områden av grafen. Värmebehandling vid en temperatur av ca 75 °C befanns starkt begränsa interkalering av Na i gränsytan. Interkaleringen påvisades börja vid domängränser mellan 1 ML och 2 ML områdena på provet samt vid ränder/defekter på 1 ML området. Värmebehandling vid högre temperaturer resulterade i gradvis desorption av Na från provet. Både för Si- och C-ytan så observerades en stark n-typ dopning efter deponering av Na. För Si-ytan så splittrades π -bandet till två klart separerade π -band efter värmning

till ca 100 °C är kol-buffertlagret transformerades till ett andra grafen-lager. För grafen på C-ytan så resulterade värmning till temperaturer mellan ca 120 till 300 °C i en avsevärd breddning av π -bandstrukturen, vilket tolkas att indikera penetrering av Na mellan grafensikten och i grafen/SiC-gränsytan, även om flera klart separerade π -band ej kunde urskiljas.

Den termiska stabiliteten av grafenbaserade elektroniska komponenter och apparater kan bero på valet av kontaktmaterialet. Studier av påverkan och stabilitet av två vanliga metaller platina (Pt) och aluminium (Al) på grafen växt på Si-ytan utfördes därför, dels direkt efter deponering av metallen och efter värmning av provet vid olika temperaturer. Både Al och Pt befanns vara goda kontaktmaterial vid rumstemperatur. Värmning vid respektive ~ 400 °C och ~ 800 °C befanns resultera i interkalering av Al och Pt in i grafen/SiC-gränsytan, och därvid också förändra de elektroniska egenskaperna från enkel-lager till kvasi-fristående två-lager grafen. Kontakter av Pt kan således motstå högre temperaturer än Al kontakter. För Al observerades att inhomogena fär av olika ordnade faser bildades på ytan vid värmebehandling, medan detta inte var fallet för Pt. Efter värmning vid ~ 1200 °C så observerades för Al åter enkel-lager elektroniska egenskaper även om lite Al fortfarande var detekterbart från provet. För Pt däremot så förblev de elektroniska egenskaperna för två-lager grafen stabila upp till 1200 °C. Effekter och stabilitet av Al på grafen växt på C-ytan undersöktes också för jämförelse, och signifikanta skillnader avslöjades. En ordnad Al-Si-C-förening visade sig bildas på C-ytan efter värmning vid temperaturer mellan ca 500 °C och 700 °C. Vid bildandet av denna förening så reducerades mängden grafen i ytlagren drastiskt, något som inte observerades på Si-ytan. Värmning vid temperaturer över 800 °C resulterade i en gradvis nedbrytning av denna förening och återväxt av grafen i ytlagren. Efter värmning vid 1000 °C så kunde inte längre någon Al signal detekteras på C-ytan.

Grafen tillväxt på C-ytan av SiC väckte stort intresse sedan dess mobilitet rapporterades vara en storleksordning högre jämfört med den för grafen på Si-ytan. Grafen på C-ytan hävdades dessutom vara fundamentalt annorlunda jämfört med grafen på Si-ytan. Grafenlagren föreslogs vara staplade på ett annat sätt på C-ytan och att uppvisa en ordning i rotationsvinkeln mellan näraliggande grafenlager som effektivt frikopplade lagren elektroniskt och resulterade i enkel-lager elektroniska egenskaperna för fler-lager grafen på denna yta. Storlek av domäner/kristallkornen som bildas vid tillväxt är vanligen mycket mindre på C-ytan och antalet grafen lager som bildas mindre enhetligt än på Si-ytan. Genom LEEM och mikro LEED experiment visade vi att det inte finns någon ordning i rotationsvinkeln mellan näraliggande grafenlager inom domäner/kristallkornen, men att näraliggande domäner/korn ofta har olika orientering azimuthalt. Genom nano-APRES studier kunde vi nyligen avslöja att fler-lager grafen på C-ytan uppvisar samma π -band struktur och därmed också samma stapling av grafenlagren, Bernal stapling, som fler-lager grafen på Si-ytan.

Preface

This Ph.D thesis is the result of my doctoral studies at the Semiconductor Materials Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden, during the time period 2010-2015. The experimental work has been carried out mainly at beamlines I4 and I311 of the MAX-lab synchrotron radiation national laboratory, Lund, Sweden. The micro- and nano-ARPES experiments were performed at the ANTARES beamline of the SOLEIL laboratory, Paris, France.

The thesis consists of two parts. The first part introduces the background of graphene grown on SiC, characterization techniques and a summary of the scientific work. The second part includes 9 scientific papers.

Publication List

Publications INCLUDED in this thesis

Paper I

Si intercalation/deintercalation of graphene on 6H-SiC(0001)

C. Xia, S. Watcharinyanon, A.A. Zakharov, R. Yakimova, L. Hultman, L. I. Johansson, and C. Virojanadara
Phys. Rev. B **85**, 45418 (2012).

Paper II

Changes in structural and electronic properties of graphene grown on 6H-SiC(0001) induced by Na deposition.

S. Watcharinyanon, L.I. Johansson, **C. Xia**, and C. Virojanadara
J. Appl. Phys. **111**, 083711 (2012).

Paper III

Detailed studies of Na intercalation on furnace-grown graphene on 6H-SiC(0001)

C. Xia, S. Watcharinyanon, A.A. Zakharov, L.I. Johansson, R. Yakimova, and C. Virojanadara
Surf. Sci. **613**, 88 (2013).

Paper IV

High thermal stability quasi-free-standing bilayer graphene formed on 4H-SiC(0001) via platinum intercalation

C. Xia, L.I. Johansson, Y. Niu, A. A. Zakharov, E. Janz n, and C. Virojanadara
Carbon **79**, 631 (2014).

Paper V

Effects of Al on epitaxial graphene grown on 6H-SiC(0001)

C. Xia, L.I. Johansson, A.A. Zakharov, L. Hultman, and C. Virojanadara
Mater. Res. Express **1**, 015606 (2014).

Paper VI

Effects of aluminum on epitaxial graphene grown on C-face SiC

C.Xia, L. I. Johansson, Y. Niu, L. Hultman, and C. Virojanadara

J. Appl. Phys. **117**, 195306 (2015).

Paper VII

Na induced changes in the electronic band structure of graphene grown on C-face SiC

L.I. Johansson, **C. Xia**, and C. Virojanadara

Graphene **02**, 1 (2013).

Paper VIII

Is the registry between adjacent graphene layers grown on C-face SiC different compared to that on Si-face SiC

L. I. Johansson, **C. Xia**, J. Hassan, T. Iakimov, A. A. Zakharov, S. Watcharinyanon, R. Yakimova, E. Janz n, and C. Virojanadara

Crystals **3**, 1 (2013).

Paper IX

Multiple π -bands and Bernal stacking of multilayer graphene on C-face SiC, revealed by nano-Angle Resolved Photoemission

L.I. Johansson, R. Armiento, J. Avila, **C. Xia**, S. Lorcy, I. A. Abrikosov, M.C. Asensio, and C. Virojanadara

Sci. Rep. **4**, 4157 (2014).

My contributions to the included papers

Paper I, III-VI:

I have planned and performed the experimental work, data analysis and interpretation, as well as the writing of the paper.

Paper II, VII-IX:

I have participated in the planning, the experimental work, data analysis and interpretation, as well as the writing of the paper.

Publications NOT INCLUDED in this thesis

Paper I.

Ytterbium intercalation of epitaxial graphene grown on Si-face SiC

S. Watcharinyanon, L. I. Johansson, **C. Xia**, J. Ingo Flege, A. Meyer, J. Falta, and C. Virojanadara
Graphene **02**, 66 (2013).

Paper II.

Ytterbium oxide formation at the graphene–SiC interface studied by photoemission

S. Watcharinyanon, L.I. Johansson, **C. Xia**, and C. Virojanadara
J. Vac. Sci. Technol. A **31**, 020606 (2013).

Paper III

Low thermal resistance of a GaN-on-SiC transistor structure with improved structural properties at the interface

J. Chen, J.W. Pomeroy, N. Rorsman, **C. Xia**, C. Virojanadara, U. Forsberg, M. Kuball, and E. Janzén
Accepted for publication in Journal of Crystal Growth (2015).

Paper IV

Li induced effects in the core level and π -band electronic structure of graphene grown on C-face SiC.

L.I. Johanssona, **C. Xia**, and C. Virojanadara
Accepted for publication in Journal of Vacuum Science and Technology (2015).

Paper V

Soft X-ray exposures promotes Na intercalation in graphene grown on Si-face SiC

S. Watcharinyanon, **C. Xia**, Y. Niu, A.A. Zakharov, L.I. Johansson, R. Yakimova, C. Virojanadara
Materials **8(8)**, 4768 (2015).

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Chapter 1: Introduction of Graphene

Graphene, one monoatomic sheet of graphite (see Fig. 1(a)), as the first experimentally available two-dimensional crystal [1], has attracted great attention and interest in the past decade. The carbon–carbon bond length in graphene is 0.142 nm, while the interplanar spacing between graphene layers when stacked in graphite is 0.335 nm. The experimental realization of graphene not only falsified Mermin-Wager’s theorem that “a strictly 2D lattice could not exist at nonzero temperatures”, but also confirmed those remarkable properties of graphene which were predicted long time before [2]. The discovery of graphene opened a new era of two-deminsional crystalline materials.

Figure 1: (a) Hexagonal arranged carbon atoms in graphene. (b) Schematic of in plane σ bonds and out of plane π bonds in graphene. (From Fig. 1(b) in Ref [3].) (c) Calculated π -band energy dispersion of monolayer graphene, around the six K points in the Brillouin zone, from a tight-binding approach. The inset shows the linear dispersion near a Dirac point. (From Fig. 3(c) in Ref [3].)

1.1 Electronic structure of graphene

Carbon atoms in graphene are arranged in a hexagonal lattice which results in sp^2 hybridization with three linear combinations of the s , p_x and p_y orbitals, as displayed in Fig. 1(b). Strong σ bonds are formed due to the overlapping of these three sp^2 hybridized orbitals with their neighboring C atoms. Weak overlapping of remaining unmixed p_z orbital among neighboring C atoms form π bonds perpendicular to the

honeycomb lattice, as illustrated in Fig. 1(b). The dispersion relation $E(k)$ of the π -bands in the vicinity of the Fermi level (E_F) is linear and without a band gap, see Fig. 1(c). $E(k) = \hbar k v_F$ where v_F is the Fermi velocity. Therefore the effective mass calculated by expression $m^* = \frac{\hbar^2}{\partial^2 E / \partial k^2}$ is invalid in the case of linear $E(k)$ relationship. The effective mass in graphene should be calculated from equation $m^*(E, k) = \frac{p}{v_g} = \hbar^2 k \left(\frac{\partial E}{\partial k} \right)^{-1}$, where p is particle momentum and v_g is the group velocity [4]. This expression is generally valid for any $E(k)$ relationship including non-parabolic solid state materials. The Fermi velocity at the K point is around 1×10^6 m/s which is comparable to the speed of light, as a result, charge carriers behave like relativistic particles in graphene, i.e. massless Dirac fermions. The kinetic energy of electrons in graphene should follow the relativistic expression $E = \sqrt{p^2 c^2 + m_e^2 c^4}$ instead of the classic kinetic energy of free electrons $E = \frac{\hbar^2 k^2}{2m}$. This is the most striking feature of graphene's band structure which leads to a charge carrier mobility of 15,000 cm²/Vs even under ambient conditions [5]. This is noteworthy in comparison to free electron metals, where electrons close to E_F follow a parabolic energy dispersion relation which result in massive carriers.

Moreover, the measured charge carrier mean free path in graphene is $\sim 0.4 \mu\text{m}$ [1]. This means that charge carriers in graphene can travel on average thousands of interatomic distances before scattering. This phenomenon is called ballistic transport. Furthermore, temperature is found to have limited impact on these aforementioned outstanding properties [5].

1.2 Physical properties of graphene

Besides those superior electronic characteristics, graphene is known to be simultaneously the thinnest and strongest crystalline material ever tested. Graphene exhibits an ultimate Young's modulus around 1.0 TPa [6] which is similar to that of diamond [7]. The breaking strength is reported to be record high, 42 N/m [6], which is close to the theoretical limit. This makes graphene more elastically stretchable than any other crystal.

Furthermore, a superb thermal conductivity of graphene is reported to be as high as 5 kW/mK [8] which is more than 10 times better than that of copper or silver [9]. This makes it a good candidate for electronic devices.

Finally, the optical absorption rate of graphene for the electromagnetic spectrum from the near infrared to visible region is measured to be low and constant, 2.3% per monolayer [10] which is comparable to that of indium–tin–oxide (ITO) [11]. By coupling with the exceptional conductivity and mobility, graphene is a potential substitute for transparent conductive oxides.

Chapter 2: Graphene synthesis

There are numerous methods to synthesize graphene. Among them, three are addressed in this section and have been reported able to fabricate relative high quality graphene: mechanical cleavage of highly oriented pyrolytic graphite (HOPG), chemical vapor deposition (CVD) growth of graphene on metals, and sublimation growth of graphene on surfaces of SiC.

2.1 Mechanically Cleaved Graphene

Mechanical exfoliation of HOPG is the first successful method used to produce suspended graphene sheets [1]. The most appealing aspect of this technique is its simple production process, to peel off the top layers of HOPG by using scotch tape and to thin down the thickness by repeating this process a couple of times. A few layers of graphene (FLG) and even single layer graphene can be produced using this method. The number of graphene layers obtained can be distinguished in an optical microscope, utilizing for example the light interference between graphene flakes and a SiO₂ substrate. The high carrier mobility and low defect density obtained by this method [5], indicates that high quality graphene can be produced by mechanical exfoliation of HOPG.

However, the size of the graphene flake produced is typically no more than about hundred micrometers [12]. Due to the limited yield and the cumbersome identification process, this method is not suitable for large scale fabrication, let alone scalable commercial production.

2.2 CVD growth of graphene on metals

In contrast to the mechanical exfoliation method, large scale graphene can be fabricated by CVD and at low cost. Graphene sheets up to 30 inches large [13] can be produced, which promotes this technique for potential commercial use. One other advantage is that the metal plays the role as catalyst, making CVD growth a self-limiting process. Only monolayer graphene can therefore in many cases be grown using CVD.

There are mainly two mechanisms for CVD growth of graphene on metals [14]: direct decomposition of carbon-containing molecules (mostly ethylene) on the metal surface and, segregation of carbon dissolved in the bulk to the metal surface at high temperature.

Different metal substrates will interact differently with graphene. For example, Ni [15], Co [16], and Ru [17] substrates are found to exhibit strong interaction with graphene, which distort the π band and opens a gap in the vicinity of the Dirac point. Strong interaction also results in formation of a single graphene domain. Weak interaction with graphene is observed on Cu [18], Ir [19], Pt [20], and Au [21] substrates, and there the π -band dispersion of free standing graphene is preserved around the K point and no gap

appears at the Dirac point. However, rotational disorder is commonly observed for graphene grown on weak interacting metals, i.e. graphene domains with different azimuthal orientations are observed. For those metals who have a relatively large lattice mismatch with graphene, such as Ru [22], Pd [23] and Re [24], distinct moiré patterns are present in scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) data collected.

Despite all these advantages, the typical charge carrier mobility of CVD grown graphene is a few orders of magnitude lower compared to that of exfoliated graphene [5], only 100 - 4000 cm²/Vs [25,26]. The reason for this is not point defects or surface contaminations, but the line defects induced by grain boundaries [27]. The transfer process required for CVD grown graphene is another obstacle. Metal substrates are conductors that have to be etched away before the graphene can be used for device fabrication. During the substrate etching and graphene transfer process, a lot of defects, for example, cracks, folds and wrinkles [28], can be created which substantially degrade the quality of graphene.

2.3 Sublimation growth of graphene on SiC

At high temperature annealing of a Silicon Carbide (SiC) substrate, silicon starts to evaporate away due to its higher vapor pressure and left on the substrate is carbon that can result in epitaxial growth of graphene layers on the SiC substrate [29]. The advantage of using a wide band gap semiconductor SiC as substrate is that hazardous transfer process to another insulating substrate can be avoided. Furthermore, SiC has a high breakdown electric field strength, high saturation electron drift velocity, high thermal conductivity and is commercially available in wafer size. For these reasons, sublimation grown graphene on SiC substrate is considered one of the most promising routes for wafer-scale fabrication of graphene based fast electronic devices with potential applications in high temperature, high frequency and high voltage environments.

Nevertheless, the high cost of SiC wafers and relative high growth temperature may limit this technique to be widely used in industry. It has moreover to be considered that the quality of the graphene obtained on different surfaces of SiC do vary a lot. The growth condition needs to be optimized for each specific surface and polytype of SiC. The vast majority of research to date, concerning graphene growth on SiC, have focused on graphene growth on polar Si-face (0001) and C-face (000 $\bar{1}$) of hexagonal polytypes (4H- and 6H-) of SiC [3,30,31]. In this thesis work, all graphene samples investigated were prepared on these two polar surfaces using the sublimation growth technique. The rest of this section is devoted to a more detailed introduction of the graphene obtained on these two polar faces.

2.3.1 Graphene grown on Si-face SiC

Prior to the formation of graphene, the Si-terminated surface can undergo a number of stable surface reconstructions during thermal annealing. When annealing at around 1050 °C, the initial (1×1) Low Energy Electron Diffraction (LEED) pattern (Fig. 2(a)) transforms into a ($\sqrt{3}\times\sqrt{3}$) R30° phase [32–35], as shown in Fig. 2(b). Further annealing between ca. 1100-1200°C results in a ($6\sqrt{3}\times6\sqrt{3}$) R30° reconstruction (see Fig. 2(c)) [32,34,36–38]. This ($6\sqrt{3}\times6\sqrt{3}$) R30° reconstruction originates from the first carbon layer formed, called the buffer layer [39,40]. This carbon precursor is carbon atoms arranged in a honeycomb structure like graphene but where the π -bands at the K points are quite different than for free standing graphene [41,42]. This is ascribed to the fact that the buffer layer is partially covalently bonded with Si atoms in the layer underneath [42], as demonstrated in Fig. 3(a). This covalent bonding has a dramatic effect on the π -bands and destroys their linear dispersion around the K-points. Upon annealing at temperatures around 1250-1350 °C [34,43] graphene starts to form on top of this carbon buffer layer. The buffer layer actually serves as a template for the growth of graphene on Si-face SiC and aligns the graphene layers to be azimuthally rotated by 30 ° with respect to the underlying SiC substrate.

Figure 2: Evolution of LEED patterns from SiC(0001). (a) before thermal annealing and (b) after annealing at around 1050 °C. (c) after annealing at around 1150 °C and (d) after Si intercalation at 800 °C. (Fig. 2(a) and (b) from Ref [47] and collected at 80 eV, Fig. 2(c) and (d) from Ref [48] and collected at 45 eV.)

The carbon buffer layer can be decoupled from the substrate via intercalation of atoms, such as H [42,44], F [45], O [46], at the interface. The linear dispersion of the π -bands is found to recover after intercalation, which indicates that the buffer layer is transformed into a quasi-free-standing graphene layer (see μ -LEED pattern in Fig. 2(d) and the model in Fig. 3(b)).

Figure 3: (a) A schematic structural model for carbon buffer layer on the SiC(0001) substrate, (b) a structural model for atoms intercalated at the interface which can passivate the dangling bonds in the Si layer.

Angle resolved photoemission spectroscopy (ARPES) provides detailed information about the electron band structure of epitaxial graphene, and thereby also about the stacking of the graphene layers. When comparing experimental ARPES results for graphene samples with different number of layers to the theoretical band structure calculated using a tight binding (TB) method, it is unambiguous that Bernal stacking models the experimental π -band dispersions much better than rhombohedral (ABC) or AA stacking [49], as demonstrated in Fig. 4. For monolayer graphene grown on SiC(0001) the Dirac point is typically located ~ 0.4 eV below the Fermi level, as displayed in Fig. 4(a). This has been ascribed to electron transfer from Si dangling bonds at the interface [50,51] that produces an intrinsic n-doping of the graphene, and this corresponds to a doping concentration of $\sim 1 \times 10^{13} \text{ cm}^{-2}$, if a linear π -band dispersion is assumed close to Dirac point. This doping concentration is found to decrease with increasing number of graphene layers, due to screening effects. Another thing to notice is that only one branch of the π -bands is visible in Fig. 4. The reason is that the other branch is largely suppressed in the experimental geometry utilized, due to the so called dark corridor. That is an interference effect from the two equivalent hexagonal sublattices in the graphene honeycomb [52,53].

If the graphene is grown in ultra-high vacuum (UHV), a high Si sublimation rate results which leads to formation of deep pits and steps and thus a significant deterioration of the quality of the graphene film [54]. Moreover, graphene multilayers form easily in the pits while only monolayer graphene typically nucleates on the terraces. Graphene grown this way on Si-face SiC form fairly small domains/grains and can as well suffer from non-uniformity. In order to suppress the silicon desorption rate, the silicon vapor pressure in the growth environment needs to be increased. This can be achieved either by introducing an inert argon gas [55,56] or silane [57] so as to increase base pressure, or by putting the sample in a graphite enclosure which allows the surface to be in a

more equilibrated state [58]. As a consequence, a higher graphitization temperature is required which enhances the diffusion of carbon atoms on the surface and thereby provides a sufficient carbon source to both form graphene and repair surface vacancies [56]. This result in a much better uniformity and morphology of the graphene, i.e. in much larger domains and much smaller variations in the graphene thickness, as illustrated in Fig.5.

Figure 4: The π -bands around the K point recorded from 1 – 4 layers of graphene were displayed in (a) – (d), respectively. Dashed lines are theoretical calculation of band structure by applying tight binding model. Red and orange lines stand for Bernal (AB and ABAC) stacking, and blue lines stand for rhombohedral (ABC) stacking (modified from Fig. 2 in Ref [49].)

Figure 5: (a) A typical LEEM image from an *ex-situ* (under 1atm Ar) prepared graphene sample. The field of view is 50 μm . (From Fig. 1(a) in Ref.[59]). (b) A typical LEEM image from an *in-situ* (under UHV) prepared graphene sample. The field of view is 20 μm . (From Fig. 4(b) in Ref. [55].)

2.3.2 Graphene grown on C-face SiC

The graphitization behavior on C-face SiC was already in one of the earliest investigations reported to differ appreciably compared to the Si-face [32].

Graphitization of SiC started at a lower temperature, $\sim 800^\circ\text{C}$, was more rapid, and the thin graphite layers on the C-face were suggested to be mostly polycrystalline, since the LEED pattern showed a diffraction ring instead of the (1×1) mono-crystalline pattern observed on the Si-face [32]. Formation of C-rich (2×2) and (3×3) surface reconstructions prior to graphitization, was also reported. Pretreatment of the SiC substrate in a Si flux, during annealing at $\leq 800^\circ\text{C}$, was later established as an effective way to remove the surface oxide before graphene growth. This resulted in a Si-rich (3×3) reconstruction [60–62], as illustrated by the LEED pattern in Fig. 6(a). This (3×3) pattern disappeared upon annealing at around $\sim 1050^\circ\text{C}$, when a C-rich (2×2) pattern instead developed [60,63], as shown in Fig. 6(b). Graphene started to form at $\sim 1100^\circ\text{C}$, and after annealing at $\sim 1200^\circ\text{C}$ the ring like graphene diffraction pattern shown in Fig. 6(c) was observed [60,63]. The appearance of this strongly modulated diffraction ring was suggested to indicate either the presence of graphene domains/grains of different azimuthal orientations or the presence of graphene layers with different azimuthal orientations, i.e. the existence a rotational disorder between adjacent layers. Several later investigation [64–69] favored the latter explanation, i.e. existence of rotational disorder between adjacent layers in the domains/grains. By using micro-LEED, we recently unambiguously showed [66,67] that there is no rotational disorder between adjacent layers within the graphene grains/domains forming on C-face SiC. The diffraction ring observed in macro-LEED could be attributed to the summation of graphene spots from adjacent grains [66,67], i.e. that adjacent grains had different azimuthal orientations. Another difference between graphene on Si-face and C-face concerns the carbon buffer layer. So far, no one has reported C-face graphene samples to contain an ordered carbon buffer layer like on the Si-face. PES studies did not find any trace of such a carbon interface layer [41,70,71]. Only some TEM and LEEM studies have reported the presence of a disordered carbon interface layer [67–69]. The lack of a carbon buffer layer that couples strongly to the SiC substrate has been suggested to explain why graphene nucleates on the C-face in grains/domains having different azimuthal orientations.

(a) (3×3) : Si + $\sim 950^\circ\text{C}$, 150eV (b) (2×2) : $\sim 1050^\circ\text{C}$, 90eV (c) Gr ring: $\sim 1200^\circ\text{C}$, 100eV

Figure 6: evolution of LEED patterns from SiC(000 $\bar{1}$) under thermal annealing (a) under Si flux and annealing at $\sim 950^\circ\text{C}$ (b) annealing at 1050°C (c) annealing above 1200°C (From Fig. 1 in Ref [60].)

It was puzzling that only a single linearly dispersing π -band was first observed on multilayer graphene grown on SiC(000 $\bar{1}$) in conventional APRES [65]. Rotational disorder between the graphene layers was proposed to be the explanation [64,67]. This was suggested to effectively decouple the graphene layers and result in monolayer electronic properties for multilayer graphene samples, i.e. to preserve the single linearly dispersing π -band. In a recent nano-ARPES investigation [68] we, however, unambiguously revealed the fact that multilayer graphene on C-face SiC do exhibit multiple π -bands and Bernal stacking, as on Si-face SiC. By applying nano-APRES we could map the band structure of individual graphene grains [72] on C-face SiC, while conventional ARPES provides an averaging over many graphene grains.

Graphene on SiC(000 $\bar{1}$) form considerably smaller domains/grains (down to tens of nanometers) and with a larger spread in the number of graphene layers than on the Si-face, which makes it difficult to control its thickness and homogeneity [3, 66–69]. Despite this, the electron mobility was reported to be an order of magnitude higher than on the Si-face [36,74]. Therefore, graphene grown on C-face appeared more promising for certain electronics applications if its thickness and uniformity could be controlled/improved. Also for the C-face growth in an Ar ambient, and/or in a graphite confinement, has been reported [66,70,71,75] to provide considerable improvement in the graphene quality but similar uniformity and large domain/grain sizes as on Si-face SiC has so far not been possible to accomplish.

2.4 Aim of the thesis work

The scope of this thesis was to characterize the electronic properties of as grown and of functionalized epitaxial graphene grown on Si-face and C-face SiC. Surface functionalization is regarded as one effective way to tune the electronic properties of graphene.

So far, only large and homogeneous monolayer graphene has been possible to grow on Si-face SiC substrates, using the sublimation method. The reason why bi-, tri- and multilayer graphene could not be grown in a controlled way was not well understood. Therefore, a study of the transport behavior of Si atoms through carbon layers was conducted for the purpose to gain a better understanding of the growth mechanism of graphene on Si-face SiC. These results are presented and discussed in paper I.

The effects induced by different alkali metals on graphene grown on SiC(0001) have been found to be quite different. Li could intercalate at room temperature while K, Rb and Cs did not intercalate at all. Studies of the effects induced by the alkali metal Na were performed both for Si-face and C-face graphene. These results are presented and compared in papers II, III and VII.

The choice of contact material for graphene based electronic devices is important since it affects the performance and thermal stability of the device. Moreover, the reactivity of graphene has been predicted to be improved by decorating or doping it with Al or Pt [76–78], which can be utilized in gas sensor applications. Studies of the thermal stability of two commonly used contact materials (Al and Pt) on Si-face graphene are presented in papers IV and V. A comparative study of the effects induced by Al on C-face graphene is presented in paper VI, and show significant differences.

The existence of rotational disorder between adjacent layers for C-face graphene has been a controversial issue, since the domain/grain size for C-face graphene typically is much smaller than the probing area in conventional LEED and ARPES, so such experimental results represents an integration over many graphene domains/grains. Utilizing LEEM and micro-LEED, on C-face graphene samples having domain/grain sizes of up to several micrometers, we could unambiguously determine that there was no rotational disorder within the domains/grains but that they had different azimuthal orientations, see paper VIII. In a micro- and nano-ARPES investigation we recently also revealed that multilayer C-face graphene show multiple π -bands and Bernal stacking, similar to multilayer Si-face graphene, see paper IX.

Chapter 3: Characterization techniques

3.1 Photoelectron Spectroscopy (PES)

PES is a highly surface sensitive technique that can be used to quantitatively analyze elemental composition, electronic structure and chemical state of surfaces of solids.

The basic principle of PES is the photoelectric effect. The sample surface is illuminated by photons of known energy. Photoelectrons are generated due to the photoelectric effect. The energy of the radiation used is typically from 10 – 2000 eV which results in an electron mean free path of 5 - 20 Å. The mean free path λ describes the average distance an electron travels within a material between two collisions. The mean free path is relatively independent of the selected sample material, but depends strongly on the electron energy and follows the well-known ‘universal curve’, which is shown in Fig. 7. Therefore, only electrons from a thin layer at the surface of the sample are able to escape and be collected by the detector. Since the surface is vulnerable to adsorption and contamination, UHV environment is required for this technique.

If the photon energy can be changed, the electron mean free path can be varied by selecting different electron kinetic energies. By this procedure, the surface sensitivity of the technique can be tuned. This is easily achieved when using a synchrotron radiation source. Changing the incident photon beam angle or electron emission angle are other options to tune the surface sensitivity. The effective penetration depth/effective escape depth under grazing incidence angle/grazing electron emission angle is much smaller compared to that at normal incident/emission.

Figure 7: The so called “universal curve” of the electron mean free path in solids. From Zangwill’s *Physics at surfaces*, theoretical curve shown by solid line is from Penn [79], experimental data from Rhodin [80], and Somorjai [81].

The photoemission process can be described to occur in three steps [82]. First, the electron is excited above the Fermi level by obtaining the energy of an incoming photon. Second, the photoelectron with large enough mean free path can be transported to the surface without being scattered or suffer any energy loss. Third, the photoelectron overcomes the potential barrier at the surface, the work function, and escapes into the vacuum. Then the kinetic energy E_{kin} of the emitted electron can be measured in a spectrometer. The binding energy E_B of the initial state can be calculated from the photoelectric equation: $E_B = h\nu - E_{kin} - \Phi$ where $h\nu$ is the photon energy and Φ the work function of the spectrometer, as illustrated in Fig. 8.

Figure 8: Schematic illustration of the photoemission process.

Non-scattered, and also elastically scattered, photoelectrons contribute to the characteristic peaks in the spectrum while in-elastically scattered electrons will produce either a continuous background, an asymmetry on the characteristic peak (from electron-hole excitations) or a specific loss peak (for example from bulk and surface plasmon excitations). The emitted photoelectron will leave a core-hole vacancy behind. This can be filled by an electron from an outer shell which might induce the liberation of an Auger electron. It is quite easy to distinguish an Auger peak from a photoemission peak, since an Auger peak has a fixed electron kinetic energy while a photoemission peak has a fixed binding energy.

There are mainly three sources used to generate soft X-rays for PES experiments: laboratory X-ray sources, gas-Discharge Lamps and Synchrotron radiation sources.

Laboratory sources generally produce X-rays by bombarding an anode material with high energy electrons. The most commonly used anode materials are magnesium and aluminum. A monochromator is often used to extract only the characteristic $K\alpha$ X-rays from Al (1486.6 eV) or Mg (1253.6 eV) and filter away satellites and the continue Bremsstrahlung radiation.

Helium Gas-Discharge Lamps are commonly employed to generate ultra-violet (UV) radiation, and yield the He I line (21.2 eV) and He II line (40.8 eV) used for ultraviolet photoelectron spectroscopy (UPS) investigation of the valence band of solids.

Synchrotron radiation sources have much higher brightness and brilliance compared to laboratory X-ray sources. Moreover, unlike the discrete laboratory X-ray and UV sources, a synchrotron or storage ring produces radiation over quite a large energy range. Then by utilizing a monochromator the photon energy becomes tunable over the energy range of interest. This provides also the possibility to vary the surface sensitivity in PES experiments. Most experiments in this thesis were carried out at beamlines I311 and I4 at the Swedish National Synchrotron Laboratory MAX-lab. I311 covers an energy range from 43 to 1500 eV and provides light for two end-stations. The first station is equipped with a large hemispherical Scienta electron analyzer where high resolution Core Level Photoelectron Spectroscopy (CLPES) experiments were performed. A total energy resolution, determined by the operating parameters, of <10 to 100 meV at photon energies from 43 to 450 eV and of < 300 meV at energies from 600 to 750 eV was typically utilized. The second end-station is equipped with a spectroscopic photoemission and low-energy electron microscope (SPELEEM) instrument, which is briefly described below. This microscope has a spatial resolution better than 10 nm in the LEEM mode. Angle Resolved Photoelectron Spectroscopy experiments (ARPES) were performed at beamline I4, which covers the energy range 14 to 160 eV. Micro- and nano-ARPES experiments were carried out at the ANTARES beamline [83,84] at the SOLEIL laboratory in France. This instrument allowed ARPES spectra to be collected from selected micro- or nano-sized areas on the surface, compared to the almost mm-sized probing area obtained at beamline I4.

3.1.1 Core level photoelectron Spectroscopy (CLPES)

CLPES can be employed to identify the chemical elements present, and determine the chemical composition, in the near surface region. The set of core level binding energies represents a ‘fingerprint’ of an element, but often also of the chemical state of this element. The binding energy will exhibit a chemical shift depending on the chemical environment in the sample for this element. By CLPES one can, for example, differentiate between a physisorbed and chemisorbed element, and even differentiate between adsorption sites (top, hollow or bridge sites) [85]. In principle, bonds with more electronegative atoms will generate larger chemical shifts towards higher binding energy.

In reality, a peak fit procedure [86] is often necessary to apply in order to understand a complicated core level spectrum. A core level peak is usually fitted using a Voigt line shape, which is a convolution of Gaussian and Lorentzian functions, and an asymmetry parameter. The Gaussian broadening comes mainly from broadening of the electron analyzer and radiation source used. The Lorentzian broadening arises from the finite

core-hole lifetime and the peak asymmetry from electron hole pair excitations near the Fermi level [87]. Integrated peak areas can be extracted in the fit procedure. They represent quantitative information about the chemical composition in surface region of the sample, since the recorded peak intensity is proportional to the number of atoms within the detected volume.

A typical C 1s spectrum from a 1ML graphene sample grown on Si-face SiC is shown in Fig.9. Three components, labeled B, G and SiC are commonly required to achieve a good fit. Peaks B, G and SiC represent signals from carbon buffer layer, graphene, and SiC substrate, respectively. The graphene thickness can be estimated from the intensity ratios between the peaks, applying a simple layer attenuation model.

Figure 9: C 1s spectrum recorded from an *ex-situ* prepared 1ML graphene sample grown on SiC(0001) under Argon environment at a photon energy of 600 eV.

3.1.2 Angle Resolved Photoelectron Spectroscopy (ARPES)

ARPES is a technique to directly map the electron band structure of a solid, i.e. a method to experimentally determine the electron energy dispersion relation $E(\vec{k})$ for valence electron states, where $\vec{k}$ is the electron wave vector. While core level electrons are localized and the core level energies are discrete, valence electron states in a solid are often quite delocalized and their energy is dependent on their momentum, $\hbar\vec{k}$, and form energy bands. Since both high angular and energy resolution is required for a detailed mapping of the band structure, the photon energy range used for ARPES is typically 10 - 100 eV.

In ARPES, the energy conservation is still valid as in CLPES. Additionally, the momentum is conserved in APRES during the photoelectron excitation process, which means vertical transitions in the reduced band scheme when the momentum of the photon is small enough to be neglected. The following energy relations between the initial and final states are valid: $E_{final} = \hbar\nu + E_{initial}$ and $E_{kin} = E_{final} - \Phi = \hbar\nu + E_{initial} - \Phi$, see Fig.10(a). In reduced zone schema, $\vec{k}_{final} = \vec{k}_{initial} + \vec{G}$. The

photoelectron is then transported towards the surface and when it overcomes the surface potential barrier, i.e. the work function barrier, its momentum component perpendicular to the surface is not conserved. The momentum component parallel to the sample surface is, however, conserved since the translational symmetry along the crystal surface is preserved. Thus the momentum component of the photoelectron inside the solid equals the measured momentum component of the emitted free electron outside the solid. This is described by the following relation: $k_{\parallel} = \sqrt{\frac{2mE_{kin}}{\hbar}} \sin \theta$, where θ is the emission angle and E_{kin} the kinetic energy of the emitted electron (see Fig.10(b)).

The initial energy $E_{initial}$ and parallel momentum $k_{\parallel}$ of the electron in the crystal can be determined by measuring the kinetic energy (E_{kin}) and the emission angle θ of the emitted electron. At normal emission i.e. at $\theta = 0$ so $k_{\parallel} = 0$, then $E_i(k_{\perp})$ along a high symmetry direction can be acquired by varying $h\nu$. A calculated band structure is required in order to obtain $k_{\perp}$. Using these methods the electron energy band structure of the solid $E_i(k_i)$ can be mapped out. The possibility to use ARPES to identify the number of layers and the stacking order of the layers is actually unique for graphene, where these properties are directly reflected by the number of π -bands and their dispersions around the K-point, as shown in Fig. 4. ARPES can moreover be employed to investigate the doping concentration in graphene, which is directly reflected by the shift of the Dirac point with respect to the Fermi level, and to check how the π -bands are affected by interactions between graphene and adsorbed atoms. The electron carrier concentration can be estimated from equation: $N_e = \frac{(E_F - E_d)^2}{\pi(\hbar v_F)^2}$ [30,88], where N_e is the electron areal density, v_F is the Fermi velocity, $(E_F - E_d)$ is the relative energy difference between the Fermi energy and the Dirac point.

Figure 10: Sketch of (a) energy and momentum conservation and (b) the experimental geometry in ARPES.

3.2 Low Energy Electron Diffraction (LEED)

LEED is a standard technique to provide information about the symmetry of the atomic arrangement on surfaces of solids. A beam of low-energy electrons, in the range of 10 to 300 eV, is directed onto the sample surface and the diffraction spots formed by elastically backscattered electrons is detecting on a florescent screen.

The low energy limits the penetration depth of the electrons to a few surface layers of the sample, since the mean free path in this energy range is $\sim 5\text{-}10 \text{ \AA}$. LEED is therefore a surface sensitive technique.

For qualitative purposes it is sufficient to apply a kinematic theory, which considers only single elastic scattering events. Utilizing this the symmetry of surface atomic arrangements (of for example external adsorbate atoms or surface reconstructions) with respect to the substrate bulk truncated unit cell can be directly analyzed. The previous Figures 2 and 6 are good examples of surface reconstructions, identified this way, which provide information about the order and symmetry of the surface atomic arrangement with respect to the bulk truncated SiC surface.

Figure 11: Ewald's sphere construction in two dimensions for an electron, with wave vector $\vec{k}_0$, incident normal to the surface. Five backscattered beams, $\vec{k}'$, are drawn that fulfill the diffraction condition, which is seen to occur at the intersections between the Ewald's sphere/circle and the 2D reciprocal lattice rods. (Forward scattered beams are not shown.)

Constructive interference will occur only when the incident electron wave vector $\vec{k}_0 = \frac{2\pi}{\lambda}$ and scattered wave vector $\vec{k}'$ fulfill the Laue condition:

$\vec{k}'_{\parallel} - \vec{k}_{0\parallel} = \vec{G}_{hk}$ with $\vec{G}_{hk}$ being a reciprocal lattice vector parallel to surface of the 2D crystal. Since only elastic scattering is considered, the magnitude of wave vector will not change after scattering, i.e. $|\vec{k}'| = |\vec{k}_0|$. The reciprocal lattice of 2D solids consists of lattice rods oriented perpendicular to the sample surface, as illustrated in Fig. 11. The Ewald's sphere construction can be used to visualize the Laue condition, see Fig. 11. The backscattered beams that fulfill the Laue condition are those with a wave vector that originates from the center and terminates at an intersection between the Ewald's circle and a reciprocal lattice rod.

LEED experiments need to be performed in UHV so as to keep the sample clean from contaminations. A simplified diagram of an LEED apparatus is illustrated in figure 12. The electron beam emitted from the electron gun is accelerated towards the sample. The sample and also Grid 1 are grounded to earth so there the electrons move in a field free region. A retarding potential applied between Grid 2 and Grid 1 filters away inelastically scattered electrons and let only elastically backscattered electron pass through Grid 2. A large positive potential between the Fluorescent screen and Grid 2 then accelerates those electrons onto the screen where they produce a visible diffraction pattern. A CCD camera is often used to record the pattern on the screen, and in rear view as illustrated in the figure.

Figure 12: schematic view of an experimental LEED apparatus.

In order to obtain quantitative information about the exact positions of the atoms in the unit cell the intensity of the individual diffraction spots need to be recorded as a function

of the incident electron kinetic energy, i.e. the so-called $I(V)$ curves have to be recorded. A full dynamical theory then needs to be applied in the interpretation since multiple scattering effects have to be included for calculating the intensity of diffracted low energy electrons. The dynamical theory takes these and also a finite penetration depth into account.

3.3 Spectroscopic Photoemission Low Energy Electron Microscopy (SPELEEM)

SPELEEM integrates Low Energy Electron Microscopy (LEEM) and X-ray Photoelectron Microscopy (XPEEM) into one instrument. Moreover, it is a unique technique that can provide complementary information from both real-time imaging and diffraction.

The basic design of SPELEEM is shown in Fig. 13. Different beam source (X-ray or low energy electron) and different optical column configurations can be selected according to the technique or the mode used. The source beam will be guided towards the specimen surface by the illumination column. If the contrast aperture (CA) is positioned in the diffraction plane, the angular acceptance will be limited. As a result, the chromatic and spherical aberrations of the objective lens are reduced which leads to optimum resolution but less intensity. Emitted photoelectrons, or electrons elastically reflected from the surface, are extracted in the objective lens by a strong electric field. The real-time image of the specimen will be magnified after the imaging column of the instrument. By inserting a field-limiting aperture after the objective lens one can select the area to be probed. The hemispherical analyzer filters the image at the desired electron kinetic energy and then projects the energy-filtered image onto an imaging micro-channel plate (MCP) detector.

Figure 13: (a) Schematic view of a SPELEEM instrument: (1) electron gun, (2) image column, (3) magnetic beam separator, (4) specimen chamber, (5) magnetic objective lens, (6) sample manipulator, (7) preparation chamber, (8) air lock, (9) transfer rod, (10) illumination, selected area and contrast aperture, as well as energy slits, (11) analyzer, (15) soft X-ray refocusing mirror. (From Fig. 1 in Ref [89].) (b) The optical layout of the SPELEEM. (From Fig. 2 in Ref [90].)

3.3.1 Low Energy Electron Microscopy (LEEM)

In the LEEM mode (both image and diffraction mode), low energy electrons (typically 0-100 eV) are used and collimated onto the specimen and backscattered electrons are collected and analyzed. The outgoing electrons are separated from the incoming electrons by a magnetic beam separator in front of the specimen. In diffraction mode, the backscattered low energy electrons will form a LEED pattern at the back focal plane (BFP) of objective lens.

Different modes used in LEEM:

Bright field (BF) LEEM mode: is an image mode using the reflected normal incidence (0, 0) beam. Both the surface topography and the crystal structure of the specimen contribute to the contrast in the image. For instance, the improvement of the surface homogeneity by using argon assistant sublimation compared to *in-situ* growth was apparent as shown earlier in the LEEM images in Fig.5. Steps on the surface or different number of overlayers on a substrate material can for example give rise to significant variations in the contrast.

This phase contrast can for example be utilized to determine the number of graphene layers on SiC with high accuracy and reliability. The energy levels in the conduction bands of thin graphene films are discrete in the $k_{\perp}$ direction. Transmission through the graphene film into the SiC substrate will be enhanced when the incident electrons energy matches these quantized conduction band states which results in dips in the reflectivity. Therefore, the electron reflectivity curve versus electron kinetic energy, i.e. the $I(V)$ curve, exhibits a number of local minima, dips, that correspond to the number of graphene layers [91]. The curves in Fig. 14(b) extracted from areas (1)–(4) in the LEEM image in Fig. 14(a) exhibit 1-4 minima, dips, which correspond to 1–4 layers of graphene, respectively.

Figure 14: (a) A LEEM image from a graphene sample grown on Si-face SiC at a FOV of $20\mu\text{m}$ (b) The electron reflectivity curves extracted from areas (1) to (4) indicate 1-4 ML graphene areas, respectively (From Fig. 3 in Ref. [55]).

Dark field (DF) LEEM mode: is an image mode using some other beam than the $(0, 0)$ beam. This can be realized by tilting the sample so the other deflected beam instead becomes aligned close to the optical axis of the instrument. Typically a particular diffraction spot in a LEED image is selected by the contrast aperture, which means that only domains that contribute to this particular diffraction spot will contribute to the DF image. A distribution map of domains with the same structure but with for example different azimuthal orientations can therefore be obtained in the DF LEEM mode.

Mirror electron microscopy (MEM): is an image mode using nearly zero or negative starting voltages, which means that the incoming electrons are reflected back before penetrating into the sample. The contrast of the image in this mode is a convolution between the electrostatic field, magnetic field, work function and surface topography. Even non-crystalline samples are feasible to study using this mode.

Selected area Low Energy Electron Diffraction (μ -LEED): is a diffraction mode with a field-limiting aperture inserted in the illumination column which enables filtering of the signal coming from only a certain area on the sample surface. Different phases, domains and defects can be distinguished using the μ -LEED mode. This mode was found more profitable for graphene grown on C-face SiC since the grain size obtained is much smaller on that surface and neighboring grains were found to have different azimuthal orientations.

3.3.2 X-ray Photoelectron Microscopy (XPEEM)

In XPEEM either soft x-rays or ultra-violet (UV) radiation is used to illuminate the specimen, and the emitted photoelectrons are collected and analyzed.

Different modes used in XPEEM:

Secondary electron XPEEM: is an image mode where the secondary electrons emitted from the surface are collected. The contrast is then very sensitive to variations in the local work function. As a result, this mode is often employed to study dynamic processes such as adsorption and/or desorption of atoms/molecules on surfaces.

Selected area X-ray photoelectron spectroscopy (μ -XPS): is a PES mode using a selected area aperture to record XPS spectra from a small selected area on the sample.

Figure 15: XPEEM images recorded using (a) the Si 2p at a photon energy of 133 eV and electron energy of 29.3 eV, (b) the Al 2p at a photon energy of 133 eV and electron energy of 55.6 eV, and (c) the C 1s at a photon energy of 330 eV and electron energy of 41.0 eV. (From Fig. 4 in Ref.[92]).

Energy filtered XPEEM: is an image mode where the image is formed by photoelectrons emitted at a certain kinetic energy, i.e. from the core level of a selected element. This mode provides direct quantitative information about variations in the chemical composition over the surface, since the intensity in the image is proportional to the concentration of the selected element within the detection volume. Maps of the distribution of different elements on a surface can be constructed, as exemplified in Fig.15. The XPEEM images in (a) to (c) were acquired at the binding energy of the Si

2p, Al 2p and C 1s level, respectively. These maps show islands that are composed of Al and Si, that Si is located preferably at the edges of the islands, while the other areas on the surface are covered mainly by carbon.

This mode is often combined with the μ -XPS mode, so the kinetic energy is selected from μ -XPS results collected from the same sample. Tuning the kinetic energy can also provide the possibility to distinguish the signal from different chemical environments of the same element. For example, to distinguish the metal oxide from the pure metal, or even oxides with different oxidation states.

2-D $E_i(k_x, k_y)$ photoelectron angular distributions (PAD): is a mode to record the angular dispersion (k_x, k_y) of photoelectron from the valence bands at a selected initial state energy. A full band mapping over the whole Brillouin zone can be obtained in this mode by varying the selected initial state energy. An example is shown in Fig.16 from a graphene sample on SiC(0001) with both 1ML and 2ML domains. The PAD images in Figs. 16 b) and c) show Dirac cones centered around each of the six K points in the Brillouin zone, see Fig. 1 c) in Chapter 1. Since these PAD:s were recorded at an energy of about 2 eV below the Dirac point the trigonal warping effect [93] is clearly evident. However, the difference in thickness of the two graphene domains is still directly reflected in these images since two concentric Dirac cones are present at each K-point from the 2ML area while there is only one from the 1 ML area.

Figure 16: (a) A LEEM image of an *ex-situ* grown graphene sample on SiC(0001) with both 1ML and 2ML domains. PAD images from (b) 1ML and (c) 2ML areas recorded at 2.5 eV below the Fermi level and a photon energy of 35 eV. (From Fig. 1 in Ref.[88]).

Chapter 4: Summary of the results

Paper I: Si intercalation/deintercalation of graphene on 6H-SiC(0001)

The effects induced after Si deposition on monolayer graphene grown on SiC(0001) substrates and subsequent annealing are investigated by photoemission and SPEELEM. Small Si droplets are observed on the surface after Si deposition at room temperature. An elevated temperature of about 800 °C is found to be crucial for Si to intercalate into the interface. The intercalation of Si is possible only via defects and domain boundaries. These findings can explain the difficulty of growing homogeneous bi-/multilayer graphene on nearly perfect monolayer graphene samples prepared on SiC(0001). Formation of SiC on the surface is observed after annealing at 1000-1100 °C. At temperatures higher than 1200 °C the intercalated Si is found to leave the sample and the SiC formed on the surface to decompose.

Paper II: Changes in structural and electronic properties of graphene grown on 6H-SiC(0001) induced by Na deposition.

Synchrotron based photoelectron spectroscopies are utilized to investigate the effects of Na deposited on monolayer epitaxial graphene on SiC(0001). After deposition at room temperature, only a small fraction of the Na atoms are able to penetrate in between the graphene and the carbon buffer layer or into the substrate interface, while most of the Na stay on top of the graphene layer. Na intercalation is found to be promoted when increasing the sample temperature and to be completed at about 75 °C. The sample then exhibits two π -bands, appearing as a superposition of two linearly dispersing π -bands. The intercalated Na is found to be unstable at higher temperatures and to gradually desorb from the sample when annealing at temperatures above ca. 125 °C.

Paper III: Detailed studies of Na intercalation on furnace-grown graphene on 6H-SiC(0001)

The influences induced by Na deposited on furnace grown graphene on Si-face SiC and after subsequent annealing are investigated in detail using SPEELEM, which provides the possibility to study the surface morphology, and the uniformity in chemical composition on the sample surface. Partial intercalation of Na in between carbon layers and at the SiC interface is found to occur directly after Na deposition both on the 1 ML and 2 ML areas present on the surface. The XPEEM data show that the intercalation starts at domain boundaries between the 1 ML and 2 ML areas and also at stripes/streaks on the 1 ML areas. The intercalation is observed to be promoted by annealing at a temperature around 100 °C or by exposure to the electron/photon beam. Annealing at higher temperatures induce desorption of Na from the sample.

Paper IV: High thermal stability quasi-free-standing bilayer graphene formed on 4H-SiC(0001) via platinum intercalation

The carbon buffer layer present on graphene samples grown on SiC(0001) significantly reduces the carrier mobility of graphene. Intercalation that transforms this layer to a graphene layer is a way to increase the mobility. To date, however, none of the quasi-free-standing graphene samples achieved via intercalation is thermally stable above ca. 800 °C. Pt was considered as a good candidate to obtain a higher temperature limit. Our photoemission results indicate Pt to be a potentially good contact material for graphene at temperatures below 600 °C, since no chemical reactions are observed on the graphene surface. Annealing at above 600 °C induced Pt intercalation at the interface and silicide formation, and at 900 °C the sample was fully intercalated. The quasi-free standing bi-layer graphene sample obtained this way was of high quality and found to be stable up to an annealing temperature of 1200 °C.

Paper V: Effects of Al on epitaxial graphene grown on 6H-SiC(0001)

The interaction of Al deposited on monolayer graphene samples grown on SiC(0001) is investigated using photoemission and SPEELEM. Deposition of Al at room temperature results in a fairly uniform Al overlayer but no observable change in the graphene electronic properties. After annealing at a temperature of ~400 °C, Al islands or droplets are observed to form on the surface and the XPS data then indicate intercalation of Al at the interface. Annealing at temperatures from 700 to 1000 °C yield islands of ordered phases of Al, Si, and Al-Si on the surface. A single π -band structure is found to be restored after annealing at 1200 °C, although some Al is still observed to remain in/on the sample.

Paper VI: Effects of aluminum on epitaxial graphene grown on C-face SiC

The effects induced by Al layers on graphene grown on C-face SiC are investigated using photoemission and compared with those observed on Si-face graphene. Significant differences compared to Al on Si-face graphene are obtained when annealing at temperatures above 400 °C. Between 500 °C and 700 °C most of the graphene is found to be consumed by forming an ordered Al-Si-C compound, that produces a two domain $\sqrt{7} \times \sqrt{7} R19^\circ$ LEED pattern. This ternary Al-Si-C compound decomposes gradually at annealing temperatures of 800 °C and higher and at 1000 °C the initial graphene sample is essentially restored, and with no trace of Al in/on the sample.

Paper VII: Na induced changes in the electronic band structure of graphene grown on C-face SiC

Effects on the electron band structure induced by Na deposited on a C-face 2 ML graphene sample are studied using ARPES. Na deposition shifts the Dirac point downwards by 0.5 eV due to electron doping. After annealing at temperatures from around 120 to 300 °C, the π -band structure appears considerably broadened, and collected core level spectra then indicate Na intercalation in between the graphene

layers and at the graphene SiC interface. The broadening is therefore interpreted to arise from the presence of two slightly shifted, but not clearly resolved π -bands. Constant energy photoelectron distribution patterns extracted from the clean 2 ML sample look very similar to earlier calculated distribution patterns for monolayer graphene. After Na deposition the patterns extracted at energies above the Dirac point show the flipped, “mirrored”, intensity distribution predicted for monolayer graphene.

Paper VIII: Is the registry between adjacent graphene layers grown on C-face SiC different compared to that on Si-face SiC

Graphene samples grown on C-face SiC using two different growth conditions, high and low growth temperature and different ambients, are investigated using SPELEEM based techniques. Both type of samples show formation of μm -sized grains of graphene. The sharp (1×1) μ -LEED patterns and six Dirac cones observed in the photoelectron angular distribution patterns from a grain show that adjacent layers are not rotated relative to each other, but that adjacent grains in general have different azimuthal orientations.

For both types of samples, a hydrogen treatment is found to have a detrimental effect on the graphene quality since it drastically reduced the graphene grain/domain size. The LEED electron beam is found to induce local desorption of hydrogen. Heating a hydrogenated C-face graphene sample did not restore the quality of the original sample.

Paper IX: Multiple π -bands and Bernal stacking of multilayer graphene on C-face SiC, revealed by nano-Angle Resolved Photoemission

Only a single linearly dispersing π -band cone, characteristic of monolayer graphene, had been observed in ARPES experiments on multilayer graphene grown on C-face SiC. A rotational disorder that effectively decouples adjacent layers had been suggested to explain this. However, the co-existence of μm -sized grains of single and multilayer graphene with different azimuthal orientations and no rotational disorder within the grains was recently revealed for C-face graphene, but conventional ARPES still resolved only a single π -band. Here we report detailed nano-ARPES band mappings of individual graphene grains that unambiguously show that multilayer C-face graphene exhibits multiple π -bands. The band dispersions obtained close to the $\bar{K}$ -point moreover clearly indicate, when compared to theoretical band dispersion calculated in the framework of the density functional method, Bernal (AB) stacking within the grains. Thus, contrary to earlier claims, our findings imply a similar interaction between graphene layers on C-face and Si-face SiC.

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