SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

Crystalline structure and related physical properties of graphene layers synthesized on SiC polar surfaces

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Contents:

1. Personal data

Jolanta Agnieszka Borysiuk

2. Education and scientific degrees

Doctoral   2000 – Warsaw University of Technology, Faculty of Materials Science and Engineering
PhD thesis title: Investigations of structural defects in highly doped semiconductor GaAs:Te
Supervisor: Prof. Jan A. Kozubowski

Higher   1995 – Warsaw University of Technology, Faculty of Materials Science and Engineering
MSc thesis title: Investigations of surface of monocrystalline GaAs and $GaAs_{1-x}P_x$ substrates including defect created during growth of crystal and surface preparation
Supervisor: Prof. Roman Stępniewski

3. Information on previous employment

Since 2010 – present: Institute of Physics, Polish Academy of Sciences, physicist;

Since 2008 – present: Faculty of Physics, University of Warsaw, scientific technical specialist, senior scientific technical specialist;

2006 – 2010 Institute of Electronic Materials Technology, senior technical specialist, adjunct;

2002 – 2005 Institute of High Pressure Physics (Unipress), Polish Academy of Sciences, senior specialist, adjunct;

2000 – 2001 University Erlangen-Nürnberg, Department of Materials Science (Germany), post-doctoral researcher.

4. Scientific achievement being the basis of the habilitation procedure

The scientific achievement, in accordance with Article 16, Paragraph 2 of the Act of 14 March 2003 concerning the scientific degrees and titles (Journal of Laws No. 65, item 595, as amended), is the series of publications entitled:

4.1. Title of the scientific achievement:

Crystalline structure and related physical properties of graphene layers synthesized on SiC polar surfaces

4.2. The list of publications constituting the scientific achievement:

H1. J. Borysiuk, R. Bożek, W. Strupiński, A. Wysmołek, K. Grodecki, R. Stępniewski, J. M. Baranowski
"Transmission electron microscopy and scanning tunnelling microscopy investigations of graphene on 4H-SiC(0001)"
Journal of Applied Physics 105 (2009) 023503 -1-5

H2. M. Tokarczyk, G. Kowalski, M. Możdżonek, J. Borysiuk, R. Stępniewski, W. Strupiński, P. Ciepielowski, J. M. Baranowski
„Structural investigations of hydrogenated epitaxial graphene grown on 4H-SiC(0001)"
Applied Physics Letters 103 (2013) 241915 -1-5

H3. J. Borysiuk, R. Bożek, K. Grodecki, A. Wysmołek, W. Strupiński, R. Stępniewski, J. M. Baranowski
"Transmission electron microscopy investigations of epitaxial graphene on C-terminated 4H-SiC"
Journal of Applied Physics 108 (2010) 013518 -1-6

H4. J. Borysiuk, J. Sołtys, J. Piechota
„Stacking sequence dependence of graphene layers on SiC(000$\bar{1}$) – Experimental and theoretical investigation"
Journal of Applied Physics 109 (2011) 093523 -1-6

H5. J. Borysiuk, J. Sołtys, R. Bożek, J. Piechota, S. Krukowski, W. Strupiński, J. M. Baranowski, R. Stępniewski
„Role of structure of C-terminated 4H-SiC(000-1) surface in growth of graphene layers: Transmission electron microscopy and density functional theory studies"
Physical Review B 85 (2012) 045426 -1-7

H6. J. Sołtys, J. Borysiuk, J. Piechota, S. Krukowski
„Experimental and theoretical investigation of graphene layers on SiC(000$\bar{1}$) in different stacking arrangements"
Journal of Vacuum Science and Technology B 30 (2012) 03D117 -1-6

H7. J. Borysiuk, J. Sołtys, J. Piechota, S. Krukowski, J. M. Baranowski, R. Stępniewski
„Structural defects in epitaxial graphene layers synthesized on C-terminated 4H-SiC(000$\bar{1}$) surface - Transmission electron microscopy and density functional theory studies"
Journal of Applied Physics 115 (2014) 054310 -1-8

4.3. Description of the scientific discovery, selected publications and obtained results with their potential applications

State of the art before the habilitation

Graphene is a material derived from graphite, a mineral known and used over several hundreds of years, accessible in natural deposits [1]. The special properties of graphene, a two-dimensional material, consisting of a single layer of carbon atoms, connected by sp^2

bonds were appropriately assessed after the investigations of Andre Geim and Konstantin Novoselov [2-6]. In 2010, both researchers awarded the Nobel Prize in Physics for separation and determination of the basic properties of graphene [4,5]. An immense increase of the interest in this material occurred after publication of Geim's and Novoselov's results in 2004, much before the 2010 Nobel Prize was awarded. The stimulus for the development of graphene research arise from the experimental determination of linear dispersion relations, indicating the carrier velocity (electrons and holes) close to 1/300 of the velocity of light (c/300 ~ $1×10^3$ km/s) [6]. It was expected that the discovery would lead to fabrication of superfast processors and other electronic devices [7]. A dynamic increase of graphene research led to the determination of other properties of this material allowing a potential application of graphene as a superhard material [7,8], and also in transparent electrodes in touch screens [9], supercapacitors [10], terahertz generators [11] or in molecular sensors [12].

Graphene identification as a material different from well known graphite was a stepwise process in which these two materials were not separated for many years, which is exemplified by the early works devoted to a single layer of graphite [13,14]. At present, graphene is defined as a two-dimensional material, consisting of a single atomic layer, graphite is a bulk material. The most important feature that distinguishes graphite from graphene is a parabolic dispersion relation in the vicinity of the K-point, standard for typical semiconductors or metals. The properties of graphene permitting its application in superfast electronic devices induced a huge interest in this material and the avalanche of papers devoted to investigations of graphene properties. The number of papers devoted to graphene reached an impressive level of several thousands per year, as a lot of are published in the most renowned journals of the highest impact factor [15]. Physical properties of single-layer graphene were exceptionally well investigated both by experimental techniques and theoretical modelling [16].

The application of single-layer graphene is technically difficult and requires its deposition on a solid substrate. Alternative methods of synthesis of this material were therefore sought. The deposition of single graphene layers were not possible in a mass production scale, therefore the methods were developed that deposited graphene layers on substrate during the synthesis. Two basic synthesis methods were developed - deposition from the vapour and hydrocarbon pyrolisis on substrates, e.g. on metals [6, 17-19] and sublimation of silicon from SiC in the high temperature annealing, first used by Walter de Heer [20]. Concerning graphene deposition on metal surfaces, separation and subsequent deposition on insulating support is necessary, such as SiO_2 [21,22]. The deposition on metal surfaces leads to technical difficulties and low crystalline quality of the obtained layers of a limited size. The deposition on a silicon carbide substrate seems to be the optimal technological solution [7]. Silicon sublimation from a SiC surface of different polarity leads to the creation of graphene layers of considerably different properties. Such carbon systems are subject of the investigations reported in the presented set of articles.

In the period before start of the habilitation, the basic properties of surface morphology and the crystalline structure of graphene obtained on silicon and carbon surfaces of SiC were determined [20,23]. It was shown that sublimation of silicon from a silicon surface SiC(0001) leads to coverage of the SiC surface by three to four carbon layers of hexagonal stacking known as AB stacking (Bernal stacking) [24], after which the growth is terminated, independent of the thermodynamic conditions of the process, such as temperature, gas pressure and flow. The graphene structures at a SiC(0001) surface are tightly bound to the SiC substrate. At a SiC surface, a buffer layer is created, called also the zero layer, consisting of carbon atoms with some admixture of silicon atoms. The covalent bond is strong; its influence is observed in scanning tunnelling microscopy (STM) investigations. At the graphene surface, a characteristic 6 x 6 pattern is observed of the lattice vector equal to 18 Å

[20,25,26]. The graphene layers, up to three atomic layers thick are of good crystalline quality; thicker layers have a considerable defect density [23]. Defect generation is enhanced by initial roughness of the SiC surface [23]. It was assumed that graphene is nucleated at SiC steps after which the growth proceeds by a collapse of the surface layers. The collapse results due to a structural condition requiring decay of the three SiC atomic layers (double Si-C atomic layers) in which the number of carbon atoms is sufficient to create a single graphene layer [27]. The basic properties of graphene synthesized on a carbon SiC surface SiC(000$\bar{1}$) [20,23] are completely different. The growth of carbon layers is faster, without termination after the creation of any finite number of layers. The synthesis rate depends strongly on the applied temperatures and the pressure of neutral gas (Ar). The coverage of a thickness of tens carbon layers could be obtained. These layers easily detach from the substrate even after the use of a relatively minor force, e.g. during a cooling process. This favours the creation of corrugations (puckers, wrinkles) creating a dense network of defects observed on the surface. The detachment is partially caused by the absence of a buffer layer and covalent bonding between the first carbon layer and the SiC(000$\bar{1}$) substrate. The structural quality of such layers is very low and therefore, in the early period of investigations of graphene on SiC substrate, the carbon face was avoided assuming that the quality of such layers is too low for electronic applications. A fundamental change brought a discovery of the carrier mobility on the carbon side that was several orders of magnitude higher than the one obtained on the silicon side, despite a higher density of defects on the SiC(000$\bar{1}$) surface [24]. The magnetic measurements of absorption proved the existence of a linear dispersion relation in thick graphene layers on the SiC(000$\bar{1}$) side [28]. These investigations induced a hope that the synthesis of graphene on the carbon side may be useful for electronic applications [29-31]. Various methods of opening the energy gaps in graphene systems were tested which should close the transistor. In the transistor design, the gap dependence on the width and termination of graphene ribbons was used [30-33]. Another interesting solution was a single electron transistor [34,35]. In addition, the double carbon layer electronic properties were also employed in the transistor design [36,37]. The possibility of adsorption of gases on a graphene surface, such as hydrogen or oxygen, leading to the creation of graphane [38,39] or graphene oxide [40]. Such phenomena led to the emergence of the bandgap but neither method led to opening the gap for more than 360 meV, which is necessary for integration with silicon based electronics [41]. The application of chemical methods allowed some progress [42,43], similar to doping or other elements solid solution creation [44,45]. It is worth noting that these solutions were in the *ab initio* modelling level, without any indication of their application in technology. That raised well based doubts about their practical applications.

The above described attempts of technical realization of transistors and other devices based on graphene indicate the fundamental character of dispersion relations and relation to their structure. The influence of a SiC substrate on which graphene is deposited is also of importance. Another important aspect is the defect structure of the deposited graphene layers. Contrary to the predictions of K. A. Novoselov in the early period [5], graphene layers contain a large number of various structural defects. As it was shown by the investigations described below, the connection between the defect structure, especially on the SiC(000$\bar{1}$) side and the dispersion relations, is much stronger than in typical semiconductors and it is related to the two-dimensional structure obtained in the synthesized layered material. Therefore my research reported in the habilitation was devoted to these issues in a dominating part. Before the investigations reported in my habilitation, the transmission electron microscopy (TEM) observations describing the crystalline structure of thin graphene layers were scarce.

In my investigations, the electron microscopy techniques were used to determine the properties of various samples synthesized on SiC substrates. Therefore I would like to express my gratitude to dr. Włodzimierz Strupiński from the Institute of Electronic Materials Technology for delivery of the majority of the investigated samples. The research work was conducted in collaboration with dr. Jakub Sołtys and dr. Jacek Piechota, being members of the group of Professor Stanisław Krukowski from the Interdisciplinary Centre of Computational and Mathematical Modelling of University of Warsaw, responsible for the theoretical part of the work, based on density functional theory (DFT) simulations. The theoretical results were part of the PhD thesis of Jakub Sołtys [46]. Microscopic TEM investigations were made using the transmission electron microscope JEOL JEM 3010 at the Faculty of Materials Science and Engineering of Warsaw University of Technology; TEM group lead by dr. Elżbieta Jezierska, prof. PW.

Most important scientific results - subject of habilitation

According to the general direction of the investigation of epitaxial graphene on a SiC substrate, the first paper of the series [**H1**] is devoted to investigations of carbon layers obtained via silicon sublimation from a *4H*-SiC(0001) surface. The process was conducted in Epigress VP508 reactor according to a modified Wu et al. method [47,48]. Structural investigations by atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) were conducted in the Solid State Physics Division of University of Warsaw by Rafał Bożek, MSc from Professor Roman Stępniewski's group. The measurement of the *4H*-SiC(0001) surface morphology demonstrated the presence of the steps before and after the annealing. The presence of graphene layers was discerned by the characteristic 6 x 6 periodic structure, visible in STM results. The graphene layer was strained to the substrate and the corrugation of the surface was present in the 6 x 6 surface reconstruction of the lattice vector of 17.5 ±1.5 Å. These results confirmed a possibility of synthesis of standard graphene on a silicon SiC surface. My TEM observations indicated the presence of the first carbon layer at 2 ±0.2 Å above the SiC surface. The carbon buffer layer, covalently bound to the SiC surface, was identified. The presence of the covalent bond was confirmed by the distance 2 Å similar to the length of the Si-C bond in SiC equal to 1.89 Å. The distances between other carbon layers were 3.3 ±0.2 Å. These distances are close to the distances between the layers in layered graphite equal to 3.35 Å [49]. After these observations, it was concluded that the layers were determined by the sp^2 bonds within the layer and Van der Waals forces between the layers, in analogy to the graphite crystals, but the properties of the buffer layer's are derived from sp^3 covalent bonds.

In addition, the structure of carbon layers on SiC surfaces misoriented by 4° from the [0001] axis was investigated. It was shown that the carbon layers are continuous on steps and terraces that demonstrate considerable uniformity of the SiC surface by carbon layers. The paper [**H1**] obtained a considerable insight into the microscopic picture of the structure of graphene layers, synthesized on the silicon face.

The second paper [**H2**] is also devoted to graphene layers on a silicon SiC(0001) surface. The paper was prepared much later and was related to hydrogenation of epitaxial graphene on a SiC(0001) surface that leads to the transformation of the buffer layer and a considerable increase of carriers in carbon layers [50-53]. The samples for structural investigations were obtained by sublimation of silicon [47,48] and by pyrolitic deposition of carbon from the vapour on a SiC(0001) surface [54]. Some samples were prepared similarly to these presented in the publication [**H1**]. The samples were hydrogenated in the same epitaxial reactor at the temperature of 1100°C and the hydrogen pressure of 900 mbar. Subsequently, the layers were dehydrogenated by annealing at the temperatures of 1000-

1050°C, at the atmospheric pressure of argon. The investigated properties include Raman scattering measured by dr. Kacper Grodecki, under supervision of dr. Andrzej Wysmołek, Prof. UW and dr. Paweł Ciepielewski from the Institute of Electronic Materials Technology (ITME). Structural investigations were made by Mateusz Tokarczyk, MSc under supervision of dr. Grzegorz Kowalski, Prof. UW. FTIR measurements were made by Małgorzata Możdżonek, MSc from the Institute of Electronic Materials Technology (ITME). Raman and Fourier spectroscopy investigations proved the presence of strained graphene layers and hydrogen after the hydrogenation procedure. The results indicated that Si-H bonds are parallel to the [0001] axis, i.e. they are perpendicular to the SiC(0001) surface. From X-ray measurements, the distance between graphene layers were 3.400 ± 0.025 Å and after hydrogenation, they were 3.600 ± 0.025 Å, and after dehydrogenation, they were 3.35 ± 0.025 Å. Thus the graphene interplanar distances d_{0002} were increased in the results of hydrogenation.

TEM investigations provided a microscopic scenario of the process. It was proved that the buffer layer disappears, probably due to reconstruction. In addition, the distance between carbon layers was increased from 3.4 Å to 3.8-3.9 ±0.2 Å. These data indicate intercalation of hydrogen in between the carbon layers. The disappearance of the buffer layer was related to saturation of bonds by attachment of hydrogen atoms to carbon atoms and transformation of the buffer layer to sp^2 bonds.

Additional Raman measurements showed that in the hydrogen removal, the breaking of hydrogen-carbon bonds leads to a considerable increase of defect density in the graphene layers. This was observed by the D band intensity increase. The dehydrogenation annealing decreases the distance between graphene layers to the typical value of graphite in AB stacking (d_{0002}=3.35 Å). Low-energy electron diffraction (LEED) results [55] and STM data [24, 56] are coherent, graphene layers synthesized on the Si face are characterized by hexagonal AB stacking, typical for graphite [1, 23]. The stacking is not changed by the hydrogenation and dehydrogenation processes at high temperatures.

The results of paper [**H2**] provided a microscopic picture of the changes in graphene layers on the silicon surface SiC(0001) under the influence of hydrogen and contributed to the explanation of the atomic mechanism of the process.

A subsequent paper in the habilitation [**H3**] is the first paper devoted to TEM investigations of carbon layers, synthesized in a carbon surface SiC(000$\bar{1}$). The carbon layers were synthesized due to silicon sublimation from the surface of a *4H*-SiC crystal of the orientation close to the [000$\bar{1}$] axis and from the surface misoriented by 8° from the [000$\bar{1}$] axis. The structural research allowed us to determine the influence of atomic steps on a misoriented surface on the course and the results of sublimation synthesis of graphene. Structural characterization employed microscopic AFM and TEM techniques and Raman scattering measurements.

The compared graphene layers were obtained in the two different temperatures, equal to 1425°C and 1600°C, with the same annealing time of 30-40 min. SiC annealing led to the creation of carbon layers of much different morphology. The layers obtained at a lower temperature of 1425°C were thin and discontinuous in some locations while those in the higher temperature 1600°C were thick and covered whole SiC surface. The influence of orientation on the thickness of the deposited layers was not observed.

AFM measurements of the surface of graphene layers, obtained at the lower temperature indicated the coexistence of an atomic steps picture of the height equal to the lattice constant c (c_{SiC} = 1.0053 nm). In the case of thick graphene layers synthesized in high temperature, AFM pictures showed that the surface structure consisted of a dense network of wrinkles (corrugations) of a various height, in which the domains intersected by the dense network or smaller structures. The difference in Raman scattering, visible as a shift in 2D

band energy, indicated a relationship between the surface structure and the existing strains in graphene layers. In thick graphene layers, higher relaxation may be observed comparing to the thin layers, more strongly connected to the substrate.

TEM observations provided a microscopic picture of the carbon layers. These results indicate that the first graphene layer is located at a large distance from the SiC surface, i.e. at the distance $3.0 \div 3.2$ Å. This distance excludes the existence of a covalent bond between the graphene layer and the SiC surface that explains a weak coupling between the layers and the substrate. In the case of thick graphene layers, the corrugation regions, the several nanometre detachments of the layers from the SiC surface are observed. The distances between subsequent carbon layers are about $3.3 \div 3.6$ Å and are identical for the layers attached to the surface or for corrugations. These results indicate a stronger coupling between the carbon layer and their weaker bonding to the surface. Additional TEM observations are related to the carbon layer structure on the surface misoriented by 8° to the $[000\bar{1}]$ axis. On such surfaces, the coverage by the carbon layer is thick in which the number of carbon layers is changed in the vicinity of the atomic and macro steps, and the discontinuity of the layers emerges. TEM electron diffraction indicates a high disorientation degree in the layers. Such phenomena occur independent of the surface orientation which indicates that the effect is typical for the layers themselves. This is correlated with the increase of the distance between carbon layers to about 3.7 Å, which is caused by the separation of the carbon layers.

The results in paper [**H3**] allowed us to determine the basic features of graphene structures synthesized on a carbon $4H$-SiC$(000\bar{1})$ surface.

The subsequent [**H4**] paper is devoted to the explanation of the connection between the crystallographic structure of thick carbon layers on a SiC$(000\bar{1})$ surface and their electronic properties, showing linear dispersion relations in magnetic measurements [28]. In [**H3**] paper, it was shown that small changes in the interlayer distances are caused by some disorientation degree, which is signed by the existence of different structure types. High-resolution TEM (HRTEM) observations revealed that independently of the hexagonal AB stacking, in the layers simple hexagonal AA and trigonal ABC stacking is present. The computer simulations HRTEM pictures obtained using JEMS program [57] showed a good agreement between theoretical and experimental results. TEM observations indicated a technological possibility of the synthesis of a stable AB hexagonal form and also metastable AA and ABC forms. The possibility of the existence of AA stacking in graphene was first proposed by Norimatsu and Kusunoki [58] but their results were obtained for small size graphene layers close to the steps on the SiC surface.

For a different graphene layer stacking sequence density functional simulations were also made with their results published in the paper [**H4**]. From these calculations, it follows that a linear dispersion relation in the vicinity of the K point is related to the hexagonal symmetry of the layers in AA stacking. These results are in agreement with other authors' calculations which postulated that AA stacking leads to closing of the gap and emergence of linear dispersion relations [59-61]. Such dependence is observed also in the case of adsorption of hydrogen atoms on a graphene structure in which the hexagonal symmetry of the system is preserved, i.e. at each carbon atom, a hydrogen atom is attached. If the hydrogen atom adsorption breaks the hexagonal symmetry of the system or the neighbouring carbon layers in AB or ABC sequences are present, then such changes open the bandgap and transformation to a nonlinear dispersion relation and emergence of the carrier mass. In the [**H4**] paper, it was shown that the presence of the SiC surface does not change dispersion relations of the graphene layers.

The results published in the [**H4**] paper, related to thick graphene layers on the $(000\bar{1})$ side of silicon carbide indicate a possibility of the synthesis of layers with AA stacking having linear dispersion relations.

The paper [**H5**] is devoted to investigations of graphene layers on a carbon $SiC(000\bar{1})$ surface and modelling of the kinetic processes on this surface. The paper characterizes the obtained carbon structures and demonstrates a thermodynamic mechanism of graphene layer synthesis, obtained during silicon sublimation from the SiC surface. A large-scale picture of these layers, obtained by optical microscopy and AFM, presents a considerable degree of corrugation of the surface, already described in the papers [**H3**, 62].

TEM results confirmed the earlier observed structure of carbon layers on the $SiC(000\bar{1})$ surface, both their mutual positions and their distances [**H4**, **H3**]. The influence of $4H$-$SiC(000\bar{1})$ surface morphology on the structure of graphene layers, synthesized due to sublimation of Si atoms was identified. The relation between the state of the SiC surface (the presence of single atomic steps, multisteps and macrosteps) and the emergence of structural defects in graphene. The most characteristic defects are detachments and breaks of the graphene layers, emerging at the SiC surface. Other defects are the dislocations emerging at the interfaces where the transition form SiC to C structure occurs. An example of the position of graphene layers with respect to the SiC surface, parallel to the macrostep edge and parallel to the (0001)SiC planes, are presented in the paper [**H5**] (Fig. 7). In addition, the schemes are presented, showing mutual relations of graphene and SiC planes in the investigated systems. The images of defects are presented in the paper [**H5**] indicating a considerable variety of defects depending on the structure of the steps on the SiC surface.

The calculations using the DFT method for the carbon SiC side showed that adsorption (attachment) of additional excess carbon atoms transforms the upper surface layer of carbon atoms of the SiC crystal into a flat configuration, typical for sp^2 bonded systems. In the outcome of the barrierless adsorption process, an Si atom is simultaneously liberated. The nucleus of the new graphene phase emerges. Such a process may occur in any location on a C-polar SiC surface. From DFT calculations, it also follows that diffusion of carbon atoms is basically impossible on a carbon polar SiC surface as such a process causes strong bonding of carbon surface atoms. These results also indicate that diffusion of Si atoms may occur at a relatively high temperature of ~1600°C. Excess carbon atoms behave as nucleation centres for a newly created graphene layer. On a carbon polar SiC surface, the buffer (zero) layer is not created. Due to a large distance between the graphene layer and the SiC substrate, a channel is created allowing fast horizontal diffusion of silicon atoms below the graphene layer. Such liberated Si atoms outdiffuse from the terraces; the phenomenon may be more robust along the defects created by corrugations of graphene layers. Sp^2 bonds of carbon atoms are created gradually in the growing graphene layers and contribute to the incorporation of stress into the growing graphene layers detaching them from the SiC substrate and partially causing the creation of corrugations. Alternative direct sublimation of Si atoms from the surface layer of silicon carbide requires breaking of three Si-C bonds in SiC and overcome of a high energy barrier (above 6 eV). That makes this channel ineffective and does not play an important role in silicon sublimation and the formation of graphene layers. A DFT calculated atomic structure of the surface and energy of adsorbed Si and C atoms is presented in Fig. 3 of the paper [**H5**].

The results published in the paper [**H5**] allowed us to create a coherent picture of the growth of graphene layers on a carbon $SiC(000\bar{1})$ surface. It was shown that nucleation of graphene layers occur under the excess of carbon, i.e. due to the escape of silicon, without the presence of the steps. Basically, graphene nucleation may occur on the terraces. Si liberation leads to lowering of the SiC surface, as a single carbon layer requires disintegration of three

SiC atomic layers. The process prefers the creation of the channels, by which silicon escapes. Effective channels are folds and detachments of carbon layers. Silicon diffusion proceeds independently of the number of the existing carbon layers that leads to formation of thick, tens layer wide graphene layers. The nucleation of the sp^2 bonded graphene occurs in the excess of carbon without any energy barrier leading to the creation of numerous growth centres of the graphene SiC($000\bar{1}$) surface. The growth and coalescence of the islands creates a large number of domain boundaries and the defects related to rotation of the layers [63-66].

The paper [**H7**] is devoted to a further analysis of the properties of graphene epitaxial layers on a carbon polar *4H*-SiC surface formed in the silicon sublimation process. In the analysis, similar to the preceding paper, TEM and *ab initio* calculations were used.

The TEM results show that stacking sequence of carbon layers on the SiC($000\bar{1}$) surface is predominantly hexagonal AB or trigonal ABC type. In addition, in planar TEM pictures, the rotation of carbons layers is observed around the [0001] axis by an angle close to 30°. In the recorded cases, the graphene layers are mutually rotated planes in the AB stacking sequence. The rotations of single graphene layers are also possible. The rotation of the planes indicates a strongly different overlap of wavefunctions of atoms in the neighbouring planes in the multilayer graphene structure. The twist of single layers leads to the creation of additional turbostratic AA' stacking described theoretically [67-69] and confirmed experimentally [28,70]. The bandgap for AA' stacking is closed and linear dispersion exists in the vicinity of the K point.

The modelling results published in the paper [**H6**] confirm the existence of a linear dispersion relation in the system composed of double AB stacking in which single carbon layers are rotated by the angle equal to 27.7° or 32.2°. The rotation of single carbon layers changes the dispersion relations in the neighbourhood of the K point from parabolic to linear which is related to restoration of the average hexagonal symmetry. In addition to rotation, the change of interlayer distances in AB and ABC stacking may also lead to the emergence of liner dispersion relations. Such an effect emerges after the layers move apart to a distance greater than 4.8 Å. In this case, the neighbouring planes may be treated as isolated and single. Contrary to the theoretical simulations, no such large distances were observed in TEM measurements. Usually, these distances were 3.3 ÷ 3.6 Å, thus close to the theoretical distance in graphite (d_{0002}= 3.35 Å).

The last paper from the series [**H7**] describes the crystallographic features of a random arrangement of carbon layers on a *4H*-SiC C-polar surface. The paper makes use of the two earlier publications [**H5**] and [**H6**], and, additionally, also of the work of other authors, dealing with the kinetic aspects of the growth of graphene layers, synthesized in silicon sublimation from a carbon SiC($000\bar{1}$) surface [71-76]. The obtained results indicate the presence of the rotations of many planes by large angles which depends on the coalescence of the segments of the layers. Such graphene layers consist of the domains of the size ranging from a dozen nanometres to a fraction of millimetre [63]. The complicated domain structure was identified, rotated by themselves by angles close to 30°. The HRTEM image of the boundary between two domains was shown and illustrated by the crystallographic analysis. From the analysis, it follows that the observed large angle boundary has a more complex crystallographic structure that the one proposed in other papers containing (5-7) pairs only. Similar boundaries were also observed by other authors and it was shown that on the boundaries of some type, the electric charge is accumulated [75,78].

In the paper [**H7**], HRTEM images presenting the arrangement of graphene layers in AB stacking with the corresponding computer simulation were demonstrated. The subsequent results illustrate the presence of edge dislocations of the Burgers vector $\vec{b}$=1/3<11$\bar{2}$0> in the layer of the AB stacking sequence. A relatively small distance between subsequent

dislocations of about 8 nm confirms the existence of a low angle boundary in the areas of a slightly different orientation. In addition to low- and large angle boundaries, in the domain body rotation, stacking faults are observed. Identification of such areas on TEM images is possible by observation of Moiré fringes, emerging by superposition of the atomic network rotated mutually by some angle. The crystallographic analysis of selected areas showed that the rotations are close to 5°, 10° and 30°, thus they are different from the translation rotation by 60°, typical for the $\{1\bar{1}00\}$ plane family in the basal plane (0001), i.e. around the [0001] axis.

In the paper [H7], in addition to microstructural examinations, DFT simulation results were also published in which dispersion relations of a double atomic carbon layer stacked in the AB+AB or AB+BA sequence, and rotated by 27.7° and 32.2° were specified. The results of the calculations indicate that rotations of double AB layers with respect of other AB (BA) layers by an angle equal to 27.7° and 32.2° lead to a nonlinear (parabolic) relation in the vicinity of the K point. In the case of AB layers, in which the rotations are limited to single (0001) planes, the linear dispersion relation is obtained [H6]. The calculations confirm the Sprinkle's hypothesis describing the linear dispersion relation concerning a large angle rotation [79]. The calculation results presented in the papers [H4, H6] and [H7] confirm also the hypothesis of a relation between the hexagonal symmetry and the absence of the bandgap and a linear dispersion relation in the vicinity of the K point.

The results described in papers [H4] and [H7] indicate a possibility of attaining linear dispersion relations in graphene layers only by the synthesis of carbon layers in AA or AA' stacking. The fabrication of such structures allows reaching high mobility of the carriers, which was reported for the layers grown on the carbon side. The application of graphene transistors in the cipher logic systems or processors requires the development of transistor opening and closing methodology. Traditional methods are based on a shift of the Fermi level. In graphene, with a linear dispersion relation and closed gap, the change of the Fermi level would not close the transistor. One of the proposed methods is the application of the electric field parallel to the graphene surface [80]. This is relatively difficult as the achievement the gap of an order of 300 meV requires the application of a strong electric field [41,80]. Such a solution still gives hope for attaining computer logics in the future.

The results described in the latter two papers [H6] and [H7] indicate that the electronic application of graphene grown on a polar SiC surface requires a series of research work and a considerable progress in technology of synthesis of this material. Turbostratic graphene of AA' stacking is a low quality material which could not be used for the construction of fast electronic devices. An improvement of quality by an increase of the size of domains will not improve its quality. A more perspective way is an attempt to obtain areas having AA stacking and the application of processing methods to use even small size areas. At present, these methods are already used but only in small-series production.

Summarizing the results in the presented papers, we could conclude that they have contributed to an explanation of the crystalline structure of graphene layers synthesized on polar surfaces of silicon carbide in a high temperature sublimation process. Also an atomic picture of the hydrogen intercalation process of the layers deposited by pyrolisis on the silicon side SiC(0001) was obtained. In addition, the defect structure of the layers was determined indicating the possibility of obtaining of AA, AB and ABC stacking in the layers synthesized on the carbon side SiC(000$\bar{1}$). It was shown that linear dispersion may be obtained only for layers in the AA sequence which is related to the sixfold symmetry of such structures. The other two stackings AB and ABC are characterized by a nonlinear dispersion relation leading to the mass emergence and a decrease of carrier mobility. In the case of thick graphene layers obtained on the carbon side SiC(000$\bar{1}$), the results showed that these layers may have fragments of turbostratic stacking AA'. Such structures are related to the heavy defect

presence and mutual rotations of subsequent carbon layers. In the layers with rotation, the intra- and inter-domain boundaries are created. The crystallographic structure of the domain boundaries emerging due to the rotation of the carbon plane was determined. Theoretical modelling determined the dispersion relations for single and double carbon planes, excluding the contribution of double layers as they have nonlinear dispersion relations. Thus the phenomenon of linear dispersion relations, observed in magnetic measurements of thick graphene layers in the carbon side $SiC(000\bar{1})$ was elucidated. The structural investigations showed strong defectiveness and a low crystalline quality of such layers. Such a feature of graphene material is an immense barrier for the application in high speed electronics.

<u>Importance of these results for science and application of graphene</u>

The graphene research progress has led to the emergence of huge scientific literature in which the number of publications exceeded 10000 publications. Despite that, there still exist some relatively less explored areas. One of the important directions of the investigations both for graphene physics and applications is the molecular structure of the layers synthesized on the silicon carbide SiC. An essential issue is the relation between the structural and electronic properties, including dispersion of electronic states in the vicinity of the K point. The publications of the habilitation have contributed to some degree to elucidation of these issues. That was confirmed by the acceptance of these publications in leading scientific journals and in the citations and literature references in patents.

Another important aspect in the graphene application is the crystalline quality of carbon layers obtained on both polar SiC surfaces, i.e. silicon and carbon sides. The described results indicate different morphology of both surfaces of these layers and a different growth mechanism. The papers in the set have allowed us to elucidate the mechanism of numerous domain creations on the carbon side and related high defect density. This has considerable importance for technologically advanced applications of graphene, including numerical processing of data and fast signal processing. The presented publications have allowed us to elucidate the relationship between an atypical graphene structure on the carbon side and experimentally observed dispersion relations. The obtained crystallographic characteristics of graphene are of considerable importance for the development of the graphene technology on SiC substrates.

The confirmation of the importance of the presented results is an invitation of the author to contribute to a review paper in Graphene Science Handbook [81], devoted to the assessment of graphene properties in technological applications.

5. Description of other scientific achievements

5.1. Research done before obtaining the PhD degree

I was a postgraduate student in the Faculty of Materials Science and Engineering of Warsaw University of Technology in 1995-1999 under the supervision of Professor Jan Kozubowski. My research work was directed towards the characterization of structural defects in gallium arsenide highly doped by tellurium GaAs:Te, employing transmission electron microscopy TEM. The subject of my research was related to the investigations in dr. Tomasz Słupiński, research project within the group of Professor Roman Stępniewski from the Faculty of Physics of University of Warsaw. At the final stage of my postgraduate studies, I also employed TEM for investigations of structural defects in gallium nitride doped magnesium GaN:Mg obtained in the Institute of High Pressure Physics PAS within the group of dr. hab. Izabella Grzegory, Prof. of IWC PAN.

During my postgraduate studies, I participated in two scientific conferences - XVII Conference on Applied Crystallography and XXV International School on Physics of Semiconducting Compounds where I presented the posters [IIIB13, IIIB14]. During these studies, I was a co-author of three scientific publications [IIA63, IIA64, IIC19].

The publications and presentations from this period are listed in Appendix 4 "List of scientific publications and originative professional achievements"

5.2 Research done after obtaining the PhD degree

After getting my PhD degree, I was directed for a 1.5 year long scientific stage in the Department of Materials Science of University of Erlangen-Nürnberg Germany in Professor Horst Strunk's group (2000-2001). In the framework of European Project IPAM (Interface Analysis at Atomic Level and Properties of Advanced Materials) employing TEM, I investigated epitaxial nitride layers (GaN, AlGaN, InGaN, AlN). During the stage, I participated in two scientific conferences [IIB12] and co-authored one scientific publication [IIC18].

After the stage, I was employed by the High Pressure Research Centre PAS "Unipress" (presently the Institute of High Pressure Physics PAS), in the Crystallization Laboratory directed by dr. hab. Izabella Grzegory, Prof. PAN. My research area was TEM investigations of high-pressure grown GaN crystals (doped and undoped) and also nitride epitaxial layers obtained by MOCVD and MBE. In this period, 20 scientific papers with my co-authorship were published [IIA47 - IIA61, IIC13, IIC15 – IIC17]. I participated in the research within the Strategic Government Program "Development of blue optoelectronic" under the grant "Start-up of fabrication of semiconductor laser emitting blue light of 50 mW power (GaN-InGaN) on bulk GaN crystal substrates" implemented in the High Pressure Research Centre PAS.

In 2006, I was employed by the Institute of Electronic Materials Technology (ITME) in the Semiconductor Epitaxy Group directed by dr. Włodzimierz Strupiński. In this period, 19 papers was published with my co-authorship [IIA22 - IIA35, IIC5 - IIC9] and also 5 poster presentations at scientific conferences were shown [IIIB7 - IIIB11]. I was also a manager of MNiSW grant "Growth and characterization of SiC layers on Si substrates".

Since 2008, I have been employed by the Faculty of Physics of University of Warsaw in the Solid State Physics Laboratory in the group directed by Professor Jacek Baranowski, and since 2010, by Professor Roman Stępniewski. In this period, the papers dealing with structural properties of GaN layers [IIA17, IIA38, IIA44, IIC10] and also graphene on Si surfaces, partially being subject of my habilitation [IIA5, IIA7, IIA18, IIA20] were published. I have participated in the research financed by the MNiSW ordered grant "Structural investigations of monocrystalline silicon carbide and epitaxial layers with particular emphasis on quantitative characterization of structural defects" and in the FlowGraf project of National Centre for Research and Development (NCBiR) "Graphene, generative flow sensors". I am a custodian of the High Resolution Ion Etching Laboratory in the Centre of New Technologies (CENT1) of the University of Warsaw. In the laboratory, we have a state-of-the-art electron microscope FIB/SEM with the apparatus for preparation of samples to TEM and SEM investigations.

Since 2010, I have also been employed by the Institute of Physics PAS in the MBE Growth of Nitride Nanostructures group of Professor Zbigniew Żytkiewicz. My research is devoted to TEM characterization of epitaxial structures. The results from that period are published in 10 papers [IIA1, IIA4, IIA6 - IIA8, IIA10, IIA11, IIA13, IIA15, IIC3] and shown in 6 poster presentations on scientific conferences [IIB1 - IIIB6]. I am also a manager of the National

Science Centre project "Molecular Beam Epitaxial growth and segregation phenomena analysis and their influence on the physical properties of (Al,Ga,In)N Layers".
The publications and presentations from this period are listed in Appendix 4 "List of scientific publications and originative professional achievements"

5.3 Research done after obtaining the PhD degree: works on other topics

In my scientific work, I have also participated in the following research projects by the Solid State Physics Division in the Faculty of Physics of the University of Warsaw:
- characterization of InAs/GaAs quantum dots, dr. hab. Adam Babinski, Prof. UW group, the results are published in 6 papers [IIA14, IIA19, IIA27, IIA30, IIA37, IIC4],
- characterization of GaMnAs/GaAs layers containing magnetic extrusions, Prof. Dariusz Wasik group, the results are published in 5 scientific papers [IIA24, IIA33, IIA36, IIA43, IIA45],
- characterization of II-VI photonic epitaxial layers (CdTe, ZnTe), dr. Wojciech Pacuski group, the results are published in 2 papers [IIA2, IIA3].

I have collaborated with the research groups from Faculty of Chemistry of University of Warsaw, investigating the following materials:
- iron nanocapsules surrounded by graphite (Fe/C), single and multiple walls carbon nanotubes, Prof. Hubert Lange group, the results are published in 4 papers [IIA23, IIA34, IIA35, IIA42] and in the book chapter [RK2],
- gold nanoparticles (Au); Prof. Ewa Górecka group, the results are published in the single paper [IIA29],
- silver nanoparticles (Ag); Prof. Magdalena Skompska group, the results are published in the single paper [IIA16].

I have also collaborated with dr. inż. Ryszard Sitek from the Faculty of Materials Science and Engineering of Warsaw University of Technology in structural investigations of TiAl/Ti$_6$Al$_4$V layers, the results are published in the single paper [IIA9].

The publications and presentations described above are listed in Appendix 4 "List of scientific publications and originative professional achievements"

6. References

[1] P. Delhaes (ed.), World of Carbon: Graphite and Precursors, Gordon and Breach, Amsterdam (2001).
[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
[3] A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).
[4] A. K. Geim, Nobel lecture. Random walk to graphene. Rev. Mod. Phys. **83**, 851 (2011).
[5] K. S. Novoselov, Nobel lecture. Graphene: materials in the flatland. Rev. Mod. Phys. **83**, 837 (2011).
[6] M. I. Katsnelson and K. S. Novoselov, Solid State Commun. **143**, 3 (2007).
[7] K. S. Novoselov, A roadmap for graphene, Nature **490**, 192 (2012).
[8] R. J. Young, I. A. Kinloch, L. Gong, and K. S. Novoselov, Compos. Sci. Technol. **72**, 1459 (2012).
[9] X. Wang, L. J. Zhi, and K. Müllen, Nano Lett. **8**, 323 (2008).

[10] M. D. Stoller, S. J. Park, Y. W. Zhu, J. H. An, and R. S. Ruoff, Nano Lett. **8**, 3498 (2008).

[11] F. Rana, IEEE Trans. NanoTechnol. **7**, 91 (2008).

[12] T. Kuila, S. Bose, P. Khanra, A. K. Mishra, N. H. Kim, J. H. Lee, Biosens. Bioelectron. **26**, 4637 (2011).

[13] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[14] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

[15] M. Wang, C. Yan and L. Ma, Graphene Nanocomposites, Composites and Their Properties, http://www.intechopen.com (2012).

[16] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).

[17] Z. Klusek, P. Dabrowski, P. Kowalczyk, W. Kozlowski, W. Olejniczak, P. Blake, M. Szybowicz, T. Runka, Appl. Phys. Lett. **95**, 113114 (2009).

[18] W. Liu, Ch-H. Chung, C.-Q. Miao, Y.-J. Wang, B. −Y. Li, L. −Y. Ruan, K. Patel, Y. −J. Park, J. Woo, Y. −H. Xie, Thin Solid Films **518**, S128 (2010).

[19] A. J. Pollard, R. R. Nair, S. N. Sabki, C. R. Staddon, L. M. A. Perdigao, C. H. Hsu, J. M. Garfitt, S. Gangopadhyay, H. F. Gleeson, A. K. Geim, A. Gorling, J. Phys. Chem A **113**, 11565 (2009).

[20] W. A. de Heer, C. Berger, X. Wu, P. N. First, E. H. Conrad, X. Li, T. Li, M. Sprinkle, J. Hass, M. L. Sadowski, M. Potemski, G. Martinez, Solid State Comm. **143**, 92 (2007).

[21] K. S. Novoselov, E. McCann, S. V. Morozov, V. I. Falco, M. I. Katsnelson, U. Zeiter, D. Jiang, F. Schedin, and A. K. Geim, Nat. Phys. **2**, 177 (2005).

[22] M. I. Katsnelson, K. S. Novoselov, and A. K. Geim, Nat. Phys. **2**, 620 (2006).

[23] J. Hass, W. A. de Heer and E. H. Conrad. J. Phys. Condens. Matter **20**, 323202 (2008).

[24] J. Hass, J. E. Millán-Otoya, P. N. First, and E. H. Conrad, Phys. Rev. B **78**, 205424 (2008).

[25] C. Berger, S. Zhimin, L. Xuebin, W. Xiaosong, N. Brown, C. Naud, D. Mavou, L. Tianbo, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).

[26] P. Mallet, F. Varchon, C. Naud, L. Magaud, C. Berger and J.-Y. Veuillen, Phys. Rev. B **76**, 041403 (2007).

[27] R. M. Tromp and J. B. Hannon, Phys. Rev. Lett. **102**, 106104 (2009).

[28] M. Orlita, C. Faugeras, P. Plochocka, P. Neugebauer, G. Martinez, D. K. Maude, A.-L. Barra, M. Sprinkle, C. Berger, W. A. de Heer, and M. Potemski, Phys. Rev. Lett. **101**, 267601 (2008).

[29] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, Ph. Avouris, Science **327**, 662 (2010).

[30] J. M. Cai, P. Ruffieux, R. Jaafar, M. Bieri, Th. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. L. Feng, K. Müllen, R. Fasel, Nature **466**, 470 (2010).

[31] M. Y. Han, B. Ozyilmaz, Y. B. Zhang, and P. Kim, Phys. Rev. Lett. **98**, 206805 (2007).

[32] W. Jaskólski, A. Ayuela, M. Pelc, H. Santos, and L. Chico, Phys. Rev. B **83**, 235424 (2011).

[33] H. Santos, A. Ayuela, W. Jaskólski, M. Pelc, and L. Chico, Phys. Rev. B **80**, 035436 (2009).

[34] L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, A. K. Geim, Science **320**, 356 (2008).

[35] C. Stampfer, E. Schurtenberger, F. Molitor, J. Güttinger, T. Ihn, K. Ensslin, Nano Lett. **8**, 2378 (2008).

[36] T. Ohta, A. Bostwick, T. Seyller, K. Horn and E. Rotenberg, Science **313**, 951 (2006).

[37] J. B. Oostinga, H. B. Heersche, X. L. Liu, A. F. Morpurgo, and L. M. K. Vandersypen, Nature Mater. **7**, 151 (2008).

[38] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, Science **323**, 610 (2009).

[39] R. R. Nair, W. C. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H. M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov, A. K. Geim, Small **6**, 2877 (2010).

[40] H. C. Schniepp, J-L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, and I. A. Aksay, J. Phys. Chem. B **110**, 8535 (2006).

[41] K. Kim, J. Y. Choi, T. Kim, S. H. Cho, and H. J. Chung, Nature **479**, 338 (2011).

[42] K. P. Loh, Q. L. Bao, P. K. Ang, and J. X. Yang, J. Mater. Chem. **20**, 2277 (2010).

[43] K. Z. Milowska, J. A. Majewski, J. Phys. Chem. C **118**, 17395 (2014).

[44] J. Slawinska, P. Dabrowski, I. Wlasny, Z. Klusek, I. Zasada, Phys. Rev. B **85**, 235430 (2012).

[45] K. Z. Milowska, M. Woińska, M. Wierzbowska, J. Phys. Chem. C **117**, 20229 (2013).

[46] Jakub Sołtys, rozprawa doktorska 2014 rok
Tytuł: Modelowanie własności fizycznych i wzrostu jedno i wielowarstwowego grafenu, izolowanego oraz na powierzchniach SiC; Instytut Wysokich Ciśnień Polskiej Akademii Nauk.

[47] Y. Q. Wu, P. D. Ye, M. A. Capano, Y. Xuan, Y. Sui, M. Qi, J. A. Cooper, T. Shen, D. Pandey, G. Prakash, and R. Reifenberger, Appl. Phys. Lett. **92**, 092102 (2008).

[48] W. Strupiński, A. Drabińska, R. Bożek, J. Borysiuk, A. Wysmołek, R. Stępniewski, K. Kościewicz, P. Caban, K. Korona, K. Grodecki, P.A. Geslin and J. M. Baranowski, Mater. Sci. Forum **645-648**, 569 (2010).

[49] The International Centre for Diffraction Data: ICDD No. 04-007-8496, graphite.

[50] C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009).

[51] F. Speck, J. Jobst, F. Fromm, M. Ostler, D. Waldmann, M. Hundhausen, H. B. Weber, and Th. Seyller, Appl. Phys. Lett. **99**, 122106 (2011).

[52] S. Forti, K. V. Emtsev, C. Coletti, A.A. Zakharov, C. Riedla and U. Starke, Phys. Rev. B **84**, 125449 (2011).

[53] C. Virojandara, A. A. Zakharov, R. Yakimova, and L. I. Johansson, Surf. Sci. **604**, L4 (2010).

[54] W. Strupinski, K. Grodecki, A. Wysmolek, R. Stepniewski, T. Szkopek, P. E. Gaskell, A. Grüneis, D. Haberer, R. Bozek, J. Krupka, and J. M. Baranowski, Nano Lett. **11**, 1786 (2011).

[55] H. Hibino, S. Mizuno, H. Kageshima, M. Nagase, and H. Yamaguchi, Phys. Rev. B **80**, 085406 (2009).

[56] T. Ohta, A. Botswick, J. L. McChesney, Th. Seyller, K. Horn, and E. Rotenberg, Phys. Rev. Lett. **98**, 206802 (2007).

[57] P. A. Stadelmann, Ultramicroscopy **21**, 131 (1987).

[58] W. Norimatsu and M. Kusunoki, Phys. Rev. B **81**, 161410(R) (2010).

[59] J. W. González, H. Santos, M. Pacheco, L. Chico, and L. Brey, Phys. Rev. B **81**, 195406 (2010)

[60] K. F. Mak, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **104**, 176404 (2010).

[61] J. C. Charlier, J. P. Michenaud, and X. Gonze, Phys. Rev. B **46**, 4531 (1992).

[62] J. L. Tedesco, G. G. Jernigan, J. C. Culbertson, J. K. Hite, Y. Yang, K. M. Daniels, R. L. Myers-Ward, C. R. Eddy Jr., J. A. Robinson, K. A. Trumbull, M. T. Wetherington, P. M. Campbell, and D. K. Gaskill, Appl. Phys. Lett. **96**, 222303 (2010).

[63] L. I. Johansson, S. Watcharinyanon, A. A. Zakharov, T. Iakimov, R. Yakimova, and C. Virojanadara, Phys. Rev. B **84**, 125405 (2011).

[64] J. Hass, F. Varchon, J. E. Millán-Otoya, M. Sprinkle, N. Sharma, W. A. de Heer, C. Berger, P. N. First, L. Magaud, and E. H. Conrad, Phys. Rev. Lett. **100**, 125504 (2008).

[65] A. Al-Temimy, C. Riedl, and U. Starke, Appl. Phys. Lett. **95**, 231907 (2009).

[66] I. Forbeaux, J.-M. Themlin, A. Charrier, F. Thibaudau, and J.-M. Debever, Appl. Surf. Sci. **162–163**, 406 (2000).

[67] S. Latil and L. Henrard, Phys. Rev. Lett. **97**, 036803 (2006).

[68] S. Latil, V. Meunier, and L. Henrard, Phys. Rev. B **76**, 201402(R) (2007).

[69] M. Aoki and H. Amawashi, Solid State Commun. **142**, 123 (2007).

[70] K. Mak, J. Shan, and T. Heinz, Phys. Rev. Lett. **104**, 176404 (2010).

[71] M. Orlita, C. Faugeras, J. Borysiuk, J. M. Baranowski, W. Strupinski, M. Sprinkle, C. Berger, W. A. de Heer, D. M. Basko, G. Martinez, and M. Potemski, Phys. Rev. B **83**, 125302 (2011).

[72] F. Varchon, P. Mallet, L. Magaud, and J.-Y. Veuillen, Phys. Rev. B **77**,165415 (2008).

[73] L. B. Biedermann, M. L. Bolen, M. A. Capano, D. Zemyanov, and R. G. Reifenberger, Phys. Rev. B **79**, 125411 (2009).

[74] P. Simonis, C. Goffaux, P. A. Thiry, L. P. Biro, Ph. Lambin, and V. Meunier, Surf. Sci. **511**, 319 (2002).

[75] J. M. Carlsson, L. M. Ghiringhelli, and A. Fasolino, Phys. Rev. B **84**,165423 (2011).

[76] K. Kim, Z. Lee, W. Regan, C. Kisielowski, M. F. Crommie, and A. Zett, ACS Nano **5**, 2142 (2011).

[77] F. Hiebel, P. Mallet, L. Magaud, and J.-Y. Veuillen, Phys. Rev. B **80**, 235429 (2009).

[78] O. V. Yazyev and S. G. Louie, Nature Mater. **9**, 806 (2010).

[79] M. Sprinkle, D. Siegel, Y. Hu, J. Hicks, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fe`vre, F. Bertran, S. Vizzini, H. Enriquez, S. Chiang, P. Soukiassian, C. Berger, W. A. de Heer, A. Lanzara, and E. H. Conrad, Phys. Rev. Lett. **103**, 226803 (2009).

[80] S. Krukowski, J. Sołtys, J. Borysiuk, and J. Piechota, J. Cryst. Growth **401**, 869 (2014).

[81] M. Aliofkhazraei, N. Ali, W. I. Milne, C. S. Ozkan, S. Mitura, J. L. Gervasoni (ed.), Graphene Science Handbook, vol. 6 Applications and Industrialization, chapter 21 (in press 2016)