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Epitaxial graphene perfection vs. SiC substrate quality

Research Article

Dominika Teklinska[1,2]*, Kinga Kosciewicz[1,2], Kacper Grodecki[1,3], Mateusz Tokarczyk[3], Grzegorz Kowalski[3], Wlodzimierz Strupinski[1], Andrzej Olszyna[2], Jacek Baranowski[1,3]

1 *Institute of Electronic Materials Technology, 133 Wolczynska Street, 01-919 Warsaw, Poland*

2 *Warsaw University of Technology, Faculty of Materials Science, 141 Woloska Street, 02-507 Warsaw, Poland*

3 *Institute of Experimental Physics, Faculty of Physics, University of Warsaw, 69 Hoza Street, 00-681 Warsaw, Poland*

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Abstract: Polytype instability of SiC epitaxial films was the main focus of attention in the experiment performed since this factor has a decisive influence on graphene growth, which was the second stage of the experiment. Layers deposited in various initial C/Si ratios were analyzed.
Our observations indicate that the initial C/Si ratio in epitaxial growth is a crucial parameter determining which polytype will be grown, in particular for cubic (3C) or hexagonal (4H) polytypes. If the initial C/Si ratio was close to its final value, the dominant polytype was 4H. On the other hand, when the initial C/Si ratio was close to zero, 3C became the major polytype in spite of a non favourable growth temperature.
The results for graphene growth on an epi-SiC layer and a bulk substrate, in which case the dominant polytype was 4H, are also presented. These results indicate that layers on epitaxial 4H-SiC are thicker, more relaxed and have better quality in comparison with samples on 4H-SiC substrates.
Morphology and defects in SiC epilayers were analyzed using Nomarsky optical microscopy, scanning electron microscopy (SEM) and high resolution X-ray diffraction (XRD). Graphene quality was characterized by Raman spectroscopy.

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1. Introduction

Epitaxial graphene is a new material composed of one or more two-dimensional sheets of carbon atoms in which each carbon atom is covalently bound to its 3 neighbors (sp^2 bonds) to form a honeycomb structure. Epitaxial graphene is grown on a silicon carbide substrate. The true scientific and technological potential of graphene may not be known until a very high quality material is created. This can only be achieved by resolving the issues of SiC substrate quality and the graphitization process at one atomic layer resolution. Preparation of highly-perfect graphene layers depends on the quality of the SiC substrate. Due to the high density of structural and surface

*E-mail: dominika.teklinska@itme.edu.pl

defects that result from bulk growth and polishing of SiC wafers, epitaxial growth of SiC undoped layers has been applied prior to the graphitization procedure. SiC epitaxy requires substrates with misorientation of 4 to 8^0 in order to stabilize polytype growth ("step-flow epitaxy"). However, SiC on-axis substrates are preferable for graphene to avoid atomic step edges on the surface.

It is already known that defects in epitaxial layers propagate from the substrates [1–3]. Low epi-defect concentration is necessary for the fabrication of graphene transistors such as field-effect transistors (FET) or single-electron transistors (SET). SiC epitaxial layer growth before final epitaxial graphene growth is required to lower the density of defects in the final SiC substrate. However, SiC layer growth on on-axis substrates is coupled with polytype instability and coexistence of the 4H and 3C polytypes is usually observed in epitaxial layers. Polytypism can be defined as the feature of a material enabling its crystallization into a number of different crystallographic configurations, which correspond to lattices having the same periodicity (unit cell extension) in two directions of the growth plane, while the third unit cell dimension, parallel to the growth axis, is an integral multiple of the same basic unit c_0 (2.518 Å in the case of SiC) which represents layer spacing [4, 5]. One configuration has cubic symmetry, i.e. face-centered cubic (f.c.c.) (cubic close-packed) structure. The second one, i.e. the hexagonal close-packed structure, has hexagonal symmetry (h.c.p.). For both configurations, the fraction of the total volume filled is 0.74. Commonly grown and studied polytypes have:

- the zinc blende structure (3C-SiC): This is formed out of two f.c.c. lattices, composed of Si or C atoms and displaced from each other one quarter of the body diagonal. The SiC zinc blende structure does not have inversion symmetry, i.e. the lattice is not invariant under inversion about any point. The 3C-SiC polytype consists of the cubic stacking of Si-C double layers in the (111) direction.

- the wurtzite 4H-SiC structure: This is built up with the hexagonal stacking (h.c.p.) in the (0001) direction. By hexagonal or rhombohedral combinations of stacking sequences made of primitive cells with 4 Si-C bilayers, one can, respectively, built up other hexagonal (H) and rhombohedral (R) polytypes.

Presence of a 3C polytype in a predominantly 4H epitaxial layer causes generation of defects near the interface of 4H/3C polytypes, which should be avoided in graphene epitaxial layer growth. To obtain low epi-defect concentration in SiC layers, that is, to reduce the presence of the 3C polytype, a wide range of available initial C/Si ratio was applied.

2. Experiments

Epitaxial SiC layers were grown on Si-face (0001) 4H-SiC on-axis substrates in a horizontal hot-wall Chemical Vapor Deposition (CVD) reactor. Commercially available substrates were used in the experiment. Substrates were not analyzed in this experiment. 4H-SiC substrates are polytypically homogeneous. For n-type doping with nitrogen, the free carrier concentration saturates at 10^{18} cm^{-3} in these substrates. The precursors were SiH_4 or C_3H_8 and the carrier gas used in this experiment was hydrogen. *In situ* etching was applied before growth to remove scratches on 4H-SiC on-axis commercial substrates. This *in situ* etching was performed prior to the epitaxial growth in the 1400-1620°C temperature range at 75 mbar pressure [6]. The epilayers were grown at the temperature of 1620°C and the reactor pressure was 75 mbar. In order to compare ratios between the 3C and 4H polytypes in SiC epitaxial layers, the initial C/Si ratio was varied from 0.075 to 1.5. The final C/Si ratio was identical in all experiments and its value was 1.8. The thickness of the epilayers of SiC was 5 μm.

The growth of graphene was performed with a commercially available horizontal chemical vapor deposition (CVD) hot-wall reactor (Epigress V508), inductively heated by an RF generator [7]. Epitaxial carbon films were grown on semi-insulating 4H-SiC on-axis substrates with different polarities (0001)/(000-1). The graphene growth rate was controlled by changing the argon atmosphere conditions. Vaporizing Si atoms were reflected back to the sample due to collisions with Ar atoms. All of the samples were grown at the Institute of Electronics Materials Technology.

Epitaxial layers were characterized by defect selective etching (DSE) in molten KOH. The samples were etched at 450°C for 18 minutes and investigated by a Nomarsky optical microscope.

The etch pits were interpreted according to the literature [8, 9]:

- BPD etch pits are typically oval shaped and show a random orientation on the substrates.

- Threading Edge Dislocations (TED) have the form of hexagonal or triangular etch pits [9].

- Threading Screw Dislocations (TSD) develop as larger hexagonal or triangular etch pits than TEDs.

The surface morphology of the epilayers grown was observed using a Nomarsky optical microscope and a scanning electron microscope (SEM). In the case of the latter (SEM), the contrast of the polytypes (4H and 3C-SiC) was different because of differences in the lattice constant from their elementary cells. SEM studies of SiC polytypism were confirmed by measurements from an electron backscatter diffraction (EBSD) detector mounted inside the commercial scanning electron microscope (SEM) [10]. EBSD is an excellent experimental tool for the identification of unknown crystalline phases, which can be used to control polytypism using a scanning electron microscope [10]. The results described in this work show how to, in a simple way, analyze different SiC polytypes, especially the 4H polytype obtained from the 3C polytype, just using SEM. The structural defects were revealed by selective etching in molten KOH. The experiment was performed on a scanning electron microscope Hitachi SU-70.

Surface characterization methods (Nomarsky optical microscope, SEM) were supplemented by high resolution X-ray diffraction methods and X-ray topography. Standard multi-reflection high resolution set-up (Hart-Bartels X-ray optics) was chosen to investigate the samples both in diffractometric and rocking curve mode, as well as for high resolution reflection topography. In this way, insight into the volume characteristic of the SiC layer which is subsequently used for graphene layer construction was gained.

Raman scattering has proved to be a powerful method for characterizing carbon-based structures [11]. The Raman spectra of graphene-like structures consist of several bands. The most interesting are the so-called D, G and 2D bands [11, 12]. The actual number of graphene layers in the samples, its homogeneity, and both type of stacking and strain state can be estimated from analysis of Raman spectra [12–14]. The thickness uniformity of the graphene layer was also measured by Raman spectroscopy [14]. Micro-Raman scattering experiments were performed at room temperature, in back-scattering geometry, using the 532 nm line from Nd-YAG as a source of continuous wave excitation. Laser spot size on the sample surface was around 2 μm.

3. Results and discussion

Epitaxial SiC layers were grown with different initial C/Si ratio, which varied from 0.075 to 1.5. The final C/Si ratio was constant in each experiment and its value was 1.8. One can easily differentiate between 4H and 3C polytypes using SEM, since the contrast for the two polytypes is different. Light fields in Figure 1 exhibit the 3C-SiC polytype and the dark fields show the 4H-SiC polytype.

In Figure 1a, one can observe the dominance of the 3C polytype in comparison with the 4H polytype. At this stage of the experiment, the C/Si ratio was rising from 0.075 to 1.8. The analysis of the 4H to 3C ratio was performed by means of surface investigation of many samples crystallized in identical conditions. The next picture (Fig. 1b) shows an increase of 4H to 3C ratio, in the case of initial C/Si ratio equal to 1. The last picture (Fig. 1c) in this series of processes presents the dominant polytype 4H-SiC; here, the initial C/Si ratio was increased to 1.5. The pictures shown are only exemplary since there were many SEM topographs taken on the surfaces of the samples investigated. The analysis shows that the intentional ramping of the initial C/Si ratio during the first stage of growth influenced the formation of 4H or 3C polytype.

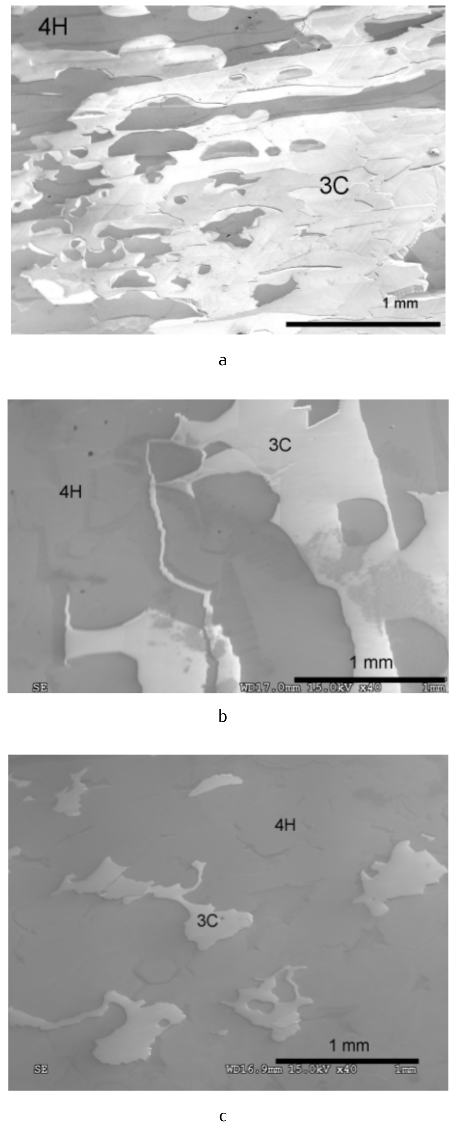


Figure 1. SEM images of surface epilayers grown with different initial C/Si ratio. (a) C/Si = 0.075, (b) C/Si = 1, (c) C/Si = 1.5.

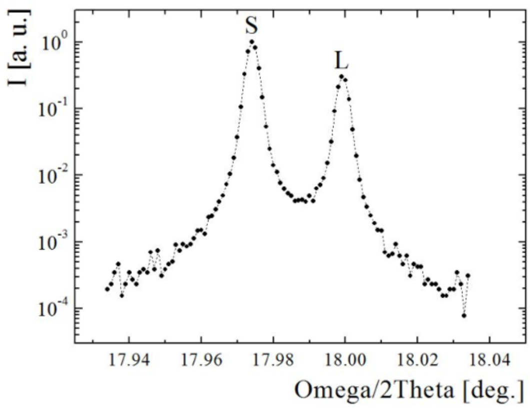
If the initial C/Si ratio was increased and its value was close to the final C/Si ratio, the major polytype was 4H-SiC. On the other hand, when the initial C/Si ratio was close to zero, 3C was the dominant polytype in spite of an unfavourable growing temperature. Dominance of 4H polytype in epitaxial layers was the main goal in this experiment since it is a precondition for performing the final stage of the experiment, namely growth of epitaxial graphene.

In our X-ray experiments, larger volumes and bigger surfaces of the samples than those shown in Figure 1 were investigated. The typical size of the sample was approximately 15×15 mm. The X-ray beam for the diffractometric scans and rocking curves had a size of 2×1 mm when impinging on the surface of the crystal in the rocking curve mode. That allowed recording of the status of the crystal lattice in a relatively small volume.

The most interesting parameter was the actual difference in lattice parameter between the basic SiC substrate and the SiC epi layer. It looks like that there was a 0.14% difference in lattice parameter between the substrate and the epi layer. That could be ascribed in the first approximation to the substrate containing the nitrogen dopant at the level of 10^{18} cm^{-3} and possibly some non intentional dopants as well. The lattice parameter value for the epi layer was closer to the perfect crystal value which could be expected for this growth process. Since the hexagonal lattice of the 4H polytype was dominant in the samples, one can expect relatively high signal to noise ratio for 4H X-ray measurements. That was not the case for the 3C polytype, at least for the sample which was measured in this experiment. But due to high resolution of X-ray optics, it was possible to measure the separate rocking curve signal from the 3C polytype as well (Fig. 2b). If the 3C signal had been higher (which means that the relative volume of the 3C polytype would have been higher), the 3C X-ray peak would have been recorded together with both peaks of the 4H lattice as seen in Figure 2a, since the lattice geometry was coordinated in a way that the (0001) hexagonal plane is almost parallel to the (111) cubic.

Having established the basic diffraction geometry for our samples, it was possible to record on a bigger scale (roughly 10 × 10 mm) the reflection topography, where we reflect only from the 3C polytype. That gave a bigger map of the 3C polytype in almost the whole of the crystal. Figure 3b and 3d were visual proof of the 3C polytype being uniformly distributed with every 60° turn about the (111) cubic or (0001) hexagonal directions of the sample lattice. One can conclude that the 3C polytype does not have one preferential direction for growth and all possible directions are covered.

The SEM method looks at the surface morphology, while



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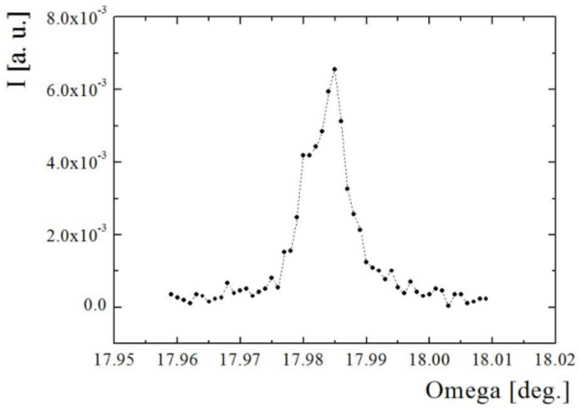

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Figure 2. X-ray measurements taken for sample from Fig. 1. (0.075 initial Si/C ratio). (a) Diffractometric scan (omega/2theta) taken around angular position for symmetrical reflection from the basal crystallographic plane (0004) of the hexagonal SiC 4H polytype lattice. S - substrate peak position, L - epi layer peak position. (b) Rocking curve for symmetrical reflection from (111) type plane of the SiC 3C polytype. That peak should be visible also for the previous scan but, due to low intensity, it is hidden in the wings of the reflection from the 4H polytype.

X-ray topography was recorded from at least 16-20 microns, which probably covered most of the epi layer volume. Observable black contrast on the X-ray topographs represent the 3C polytype and its extent on the picture follows the change attributed to the C/Si ratio which influences the growth of this polytype. One can recognize some of the features from Figure 1 SEM in Figure 3 X-ray topography, most easily seen in Figure 1a and Figure 3b. We can conclude from the X-ray topography that the second sample investigated (Figure 3c, 3d) includes less 3C polytype than the first one roughly by a factor of two. The third sample was not measured.

Different values of initial C/Si ratio have impact on the formation of 4H and 3C polytypes. Presence of 3C polytype in epitaxial layers also causes generation of defects near the interface between those two polytypes, which should be prevented in the final step of the experiment, namely in the growth of epitaxial graphene.

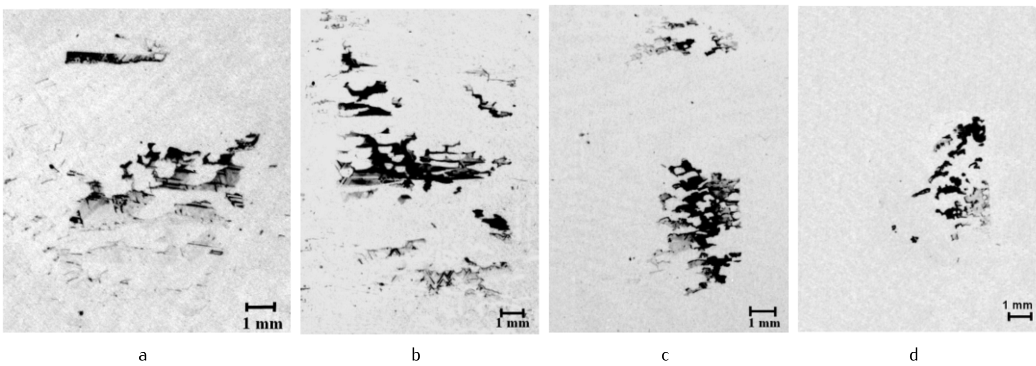


Figure 3. X-ray reflection topography, highly asymmetrical case (311) reflection for the 3C polytype only; exit beam almost perpendicular to the surface of the sample. (a), (c) Basic angular setup. (b), (d) Same diffraction conditions but the crystal turned by 60° with respect to surface normal. Same area of the crystal, most of the 10×15 mm of the sample covered by the X-ray beam. (a), (b) Sample as in Figure 1a. (c), (d) Sample as in Figure 1b.

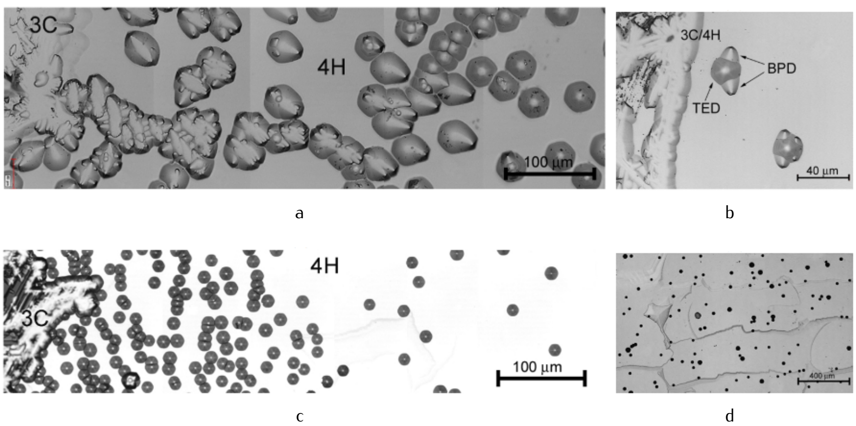
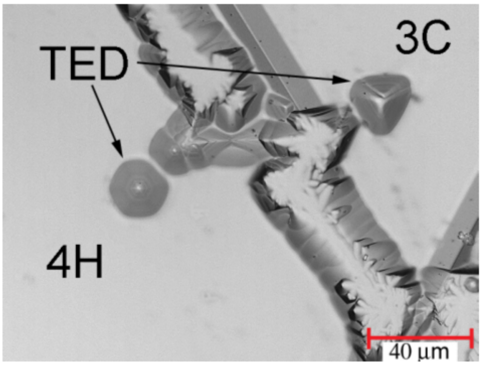


Figure 4. Nomarsky optical microscope images of the surface near the interface between polytypes 4H and 3C after selective etching in molten KOH after epitaxial growth with different initial C/Si ratio (a), (b) C/Si $= 0.075$; (c), (d) C/Si $= 1.5$.

Observation near the interface of 4H and 3C polytypes indicates the different character of dislocation with different initial C/Si ratio (Figure 4). In Figure 4a, 4b, when the initial C/Si ratio was close to zero, near the 4H/3C interface there were mixed threading edge dislocations (TEDs) and basal plane dislocations (BPDs). On the other hand, when the initial C/Si ratio was 1.5 near the 4H/3C interface, there were TEDs, but there were no BPDs – Figure 4c, 4d.

It is well known that BPDs act as a source of expanding stacking faults (SF) formation in the basal plane during bipolar injection [15]. In the case of epitaxial layers grown on on-axis substrates, usually BPD generation is avoided. However, growth on on-axis oriented substrates is connected with polytype instability and the coexistence of 3C and 4H polytypes is usually observed in the epitaxial layers.



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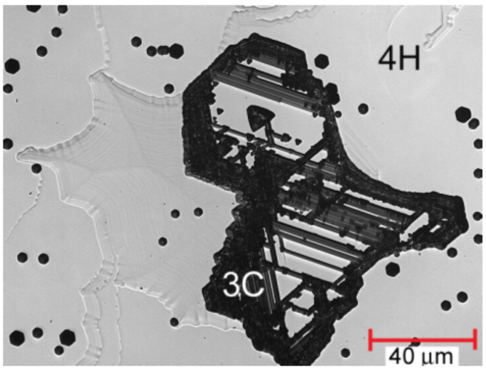

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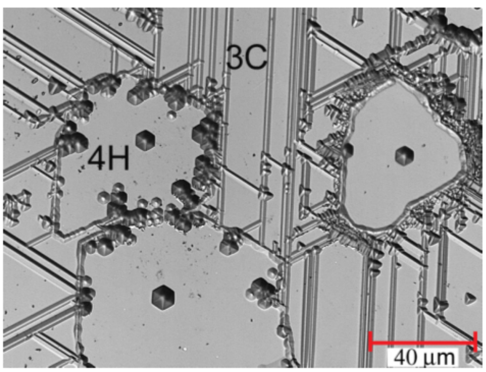

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Figure 5. Nomarsky optical microscope images after selective etching in molten KOH (a) different characters of dislocation due to differences in elementary cell in polytypes 4H and 3C; (b), (c) exact boundary between those two different crystallographic polytypes as revealed by characters of etch pits.

The presence of 3C polytype in epitaxial layers causes the formation of the full range of defects near the interface of the 4H and 3C polytypes, which highly increases density of defects in epitaxial layers. Especially when the initial C/Si ratio was low, the dominant polytype was 3C and the density of defects was one order higher because of the large area of interface between 4H and 3C polytypes. Polytype 3C crystallizes in a cubic lattice. As far as TEDs are concerned in this polytype, it looks like they have (111) cubic direction, which means that their etch pits have a triangular crystallographic form. On the other hand, 4H-SiC is a hexagonal lattice polytype. Etch pits for dislocations recorded in this polytype have hexagonal crystallographic form in line with the hexagonal plane (0001). This is fully in accordance with the measurements from X-ray rocking curves which reveal the mutual geometry of both lattices, hexagonal and cubic.

After selective etching in molten KOH, dislocation in the two polytypes (4H and 3C) has different character due to differences in elementary cell (Figure 5a). Based on this view, we can easily differentiate hexagonal polytypes from cubic ones. This method also shows where the exact boundary between these two different crystallographic polytypes is placed (Figure 5b, 5c). Near the boundary of the 3C polytype one can see a lot of TEDs. This exhibits where near the interface there is a sharp crystallographic transition between 4H polytype and 3C polytype.

Epitaxial graphene was grown on (0001) and (000-1) polarity SiC epitaxial layers and also on SiC substrates, in both cases with 4H as the dominant polytype.

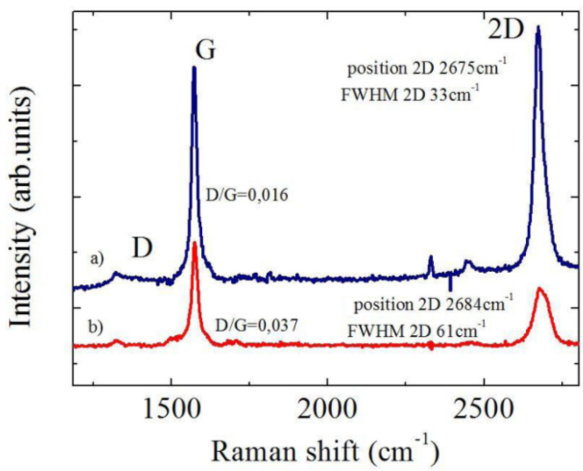

Figure 6. Raman spectra of epitaxial graphene grown on (a) epitaxial 4H-SiC (000-1) and (b) 4H-SiC (0001) substrate. The 2D band has lower FWHM and is red-shifted for graphene grown on epitaxial 4H-SiC with respect to graphene grown on 4H-SiC substrate.

For the Raman spectra obtained for the graphene samples grown on epitaxial 4H-SiC (000-1), the position of the 2D band was red-shifted in comparison to graphene obtained on the same polarity of 4H-SiC bulk substrates annealed in the same conditions. The intensities of the 2D and G bands were higher and the FWHM of the 2D band lower. The intensity of the D band was almost the same for both samples, but the D/G ratio for graphene grown on epitaxial 4H-SiC substrate was lower. This suggests that the multi-graphene layers on epitaxial 4H-SiC were thicker, more relaxed and of slightly better quality in comparison with samples on 4H-SiC substrate.

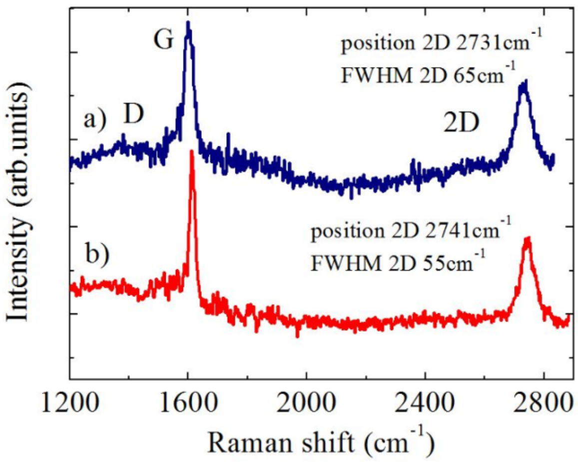

Figure 7. Raman spectra of epitaxial graphene grown on (a) epitaxial 4H-SiC (0001) and (b) 4H-SiC (0001) substrate. The 2D band has higher FWHM and is red-shifted for graphene grown on epitaxial 4H-SiC in comparison with graphene grown on 4H-SiC substrate.

The Raman spectra for graphene grown on epitaxial 4H-SiC (0001) showed similar results as on the opposite polarity, namely the positions of the G and 2D bands were red-shifted and the FWHM of the 2D band was higher than in the case of graphene grown on bulk 4H-SiC. The D band for both spectra was too small to estimate the quality of graphene layers. These results imply that graphene layers grown on epitaxial 4H-SiC (0001) are thicker [16] and more relaxed than graphene layers grown on bulk 4H-SiC (0001).

4. Summary

Three different initial C/Si ratios were investigated in order to find the impact of this parameter on the quality of SiC epilayers grown from these substrates. The first conclusion concerns the effect of the C/Si ratio on polytype instability, especially of cubic (3C) and hexagonal (4H) polytypes. Intentional ramping of the C/Si ratio during the first stage of growth influenced formation of 4H or 3C polytypes.

Recently, the most important goal in SiC epitaxial layer growth has been to avoid all types of defects which have impact on the quality of epitaxial graphene. An initial C/Si ratio close to its final value provides an opportunity for decreasing the fraction of 3C polytype. This procedure helps to reduce dislocation density and avoids BPDs near the 4H/3C interface in epitaxial layers on 4H-SiC on-axis substrates. Therefore, epilayers with low dislocation density are strongly recommended for the growth of epitaxial graphene.

Observation of graphene layers on bulk substrates and on SiC epitaxial layers on both polarities indicates that graphene grown on epitaxial layers has slightly better quality than graphene grown on substrates only, due to lower density of defects in epitaxial SiC layers. This can be easily seen from the Raman measurements where the quality of the graphene layers obtained is slightly better for the SiC epi layers.

Additionally, based on considerable differences between the character of KOH etched dislocations in the two polytypes, namely 3C and 4H, we have presented a simple way of differentiating between polytype 4H and 3C after KOH etching.

5. Acknowledgements

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References

[1] H. Tsuchida, I. Kamata, M. Nagano, J. Cryst. Growth 306, 254 (2007)
[2] T. Hori, K. Danno, T. Kimoto, J. Cryst. Growth 306, 297 (2007)
[3] S. Ha, H.J. Chung, N.T. Nuhfer, M. Skowroński, J. Cryst. Growth 262, 130 (2004)
[4] A.R. Verma, P. Krishna, Polymorphism and polytypism in crystals, Monographs in Crystallography (Wiley, New York, 1966)
[5] C.D. Lee, R.M. Feenstra, O. Shigiltchoff, R.P. Devaty, W.J. Choyke, Mater. Res. Soc. Symp. P. 693, I3.40.1 (2002)
[6] W. Strupinski, K. Kosciewicz, J. Weyher, A. Olszyna, Mater. Sci. Forum 600-603, 155 (2009)

[7] W. Strupinski et al., Mater. Sci. Forum 615-617, 109 (2009)

[8] S.A. Sakwe, R. Muller, P.J. Wellmann, J. Cryst. Growth 289, 520 (2006)

[9] D. Zhuang, J.H. Edgar, Mat. Sci. Eng. R 48, 1 (2005)

[10] K. Kosciewicz, W. Strupinski, W. Wierzchowski, K. Wieteska, A. Olszyna, Mater. Sci. Forum 645-648, 251 (2010)

[11] C. Faugeras et al., Appl. Phys. Lett. 92, 011914 (2008)

[12] N. Camara et al., Phys. Rev. B 80, 125410 (2009)

[13] T. Yu et al., J. Phys. Chem. C 112, 12602 (2008)

[14] A. Drabińska et al., Phys. Rev B 81, 245410 (2010)

[15] J.P. Bergman, H. Lendenmann, P.A. Nilsson, U. Lindefelt, P. Skytt, Mater. Sci. Forum 299, 353 (2001)

[16] D. Su Lee et al., Nano Lett. 8, 4320 (2008)