Proceedings of the 42th "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła 2013

CVD Growth of Graphene Stacks on 4H-SiC (0001) Surface — X-ray Diffraction and Raman Spectroscopy Study

M. Tokarczyk[a], G. Kowalski[a], K. Grodecki[a,b], J. Urban[a] and W. Strupiński[b]

[a]Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

[b]Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland

Features associated with short and prolonged growth time in the chemical vapor deposition process of growth of graphene stacks on SiC (0001) substrate are reported. In particular general bimodal (as far as d_{002} interlayer spacing is concerned) distribution of graphene species across the surface of the samples is observed. It consists of thin few layer graphene coverage of most of the sample surface accompanied by thick graphite-like island distribution. It points to the two independent channels of graphene stacks growth with two characteristic growth rates.

DOI: 10.12693/APhysPolA.124.768

PACS: 61.48.Gh, 61.72.Dd, 63.22.Rc

1. Introduction

The structural characterization of the various graphite and graphene structures with different lateral and thickness sizes requires specific approaches and dedicated experimental procedures. X-ray diffraction experiments have been only employed for the graphene studies mainly via grazing incidence X-ray diffraction (GXRD, SXRD) at synchrotron sources [1, 2]. Standard laboratory X-ray equipment was only employed for graphene-like structures of powder type only. Our measurements of graphene structures are based on standard laboratory X-ray source equipped with parallel beam Bragg reflection mirror and standard diffractometer as developed already in [3].

2. Samples

Our samples were grown by hot–wall horizontal chemical vapor deposition (CVD) reactor (Aixtron). We have evaluated four samples grown in different time schedules (increased growth time of the graphene stacks — 1, 2, 5, 8 min). Graphene growth was preceded by H_2 etching of the SiC substrate. Hydrogen etching at high temperature of SiC substrate prior to graphene growth removes all the mechanical surface damage but additionally creates stepped surface of the SiC face. Obtained surface was atomically stepped in our samples, but nominally the SiC substrate was on-axis (001) oriented. Details of the growth procedure can be found in [4].

X-ray analysis of the various samples including the ones chosen for this study show some regularity as far as crystallographic orientation of the surface steps is concerned. Usually the surface steps are on average oriented in such manner that step flats are well developed hexagonal (001) surfaces of SiC substrate with the vertical step planes being parallel to the (100) surfaces. The steps are usually arranged in the long parallel systems across the whole sample. Surface morphology of the similar samples was already assessed by atomic force microscopy (AFM) showing details of the step system [4]. Optical evaluation by the Nomarski technique of the sample surfaces in this study also shows the presence of the large screw dislocation based growth steps. In this case surface step morphology surrounding the dislocation steps is circular which disrupts locally the average step surface system as described above.

X-ray diffractometry employed in this study allows the assessment of the general substrate offset between the mechanically prepared substrate surface and nominal crystallographic (001) surface. It was found that the offsets are on average between 0.01 to 0.1 of the degree. The maximum offset for each sample (as measured by X-ray reflectometry) is always along the direction perpendicular to the surface steps edges. Optical examination also allowed to observe that the samples with long growth time (5 and 8 min) developed some additional surface structure approximately along the edges of the surface steps (Fig. 1).

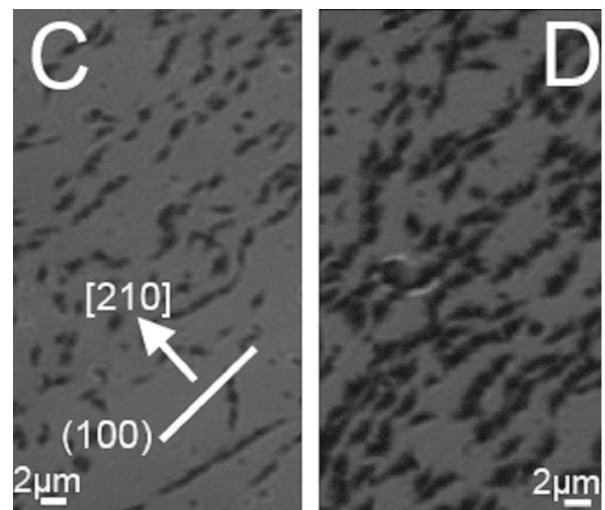

Fig. 1. Optical micrograph showing surface coverage of the two samples with longer growth time (5 min and 8 min). Black spots covering the samples surface (C — 20% surface coverage and D — 40% surface coverage) are ascribed to the graphite like thick structures.

3. Experimental and modeling

X-ray laboratory setup was based on a Phillips X-pert diffractometer which was equipped with a Cu sealed tube X-ray source. The system was outfitted with a Phillips parallel beam Bragg X-ray mirror in front of the X-ray tube. We have used this setup to measure the graphene structures grown on SiC (001) substrate by CVD method. Our experiment was configured to achieve the measurable intensity levels in spite of the relatively low diffracting volume of the graphene stack. That was accomplished by large X-ray beam footprint on the sample surface as well as significantly long counting time.

Since our graphene containing samples were all oriented along the c axis of the hexagonal SiC lattice, it implies that our scan was "symmetric", with respect to SiC bulk (001) planes as well as to all graphene structures parallel to this plane. The Bragg diffraction from graphene stacks will occur when there are graphene planes parallel to the main sample surface. So we were probing in our experiments the d_{002} type interplanar spacing of the graphene stacks structure. Measurements were all centered on the angular position for nominal (002) reflection of graphite. We assume that graphene stack is growing as thin film parallel to the local SiC substrate planes and follows local morphology of the SiC surface. That was convincingly shown in transmission electron microscopy (TEM) experiments [5–8]. Since each sample represents the system comprising the thin graphene film and bulk substrate we should expect diffraction pattern build by SiC scattering (mainly bulk like) and graphene stack scattering but with intensity many orders smaller than for SiC X-ray reflections.

When the graphene stacks are more than 5 layers thick, one can use standard Bragg formula for the calculations of the apparent d spacing.

In the case of very thin graphene stacks (1–5 layers) we have used the Debye type formula of scattered X-ray intensity developed by Yang et al. [9, 10] for estimation of the number of layers and d spacing of the graphene. That is necessary since the position of the Bragg peak resulting from the diffraction from ultrathin graphene layer no longer follows standard Bragg formula for the diffracted peak position [9, 11]. The Yang calculations were directed originally for the turbostratic graphite structures but since we cannot exclude this type of graphene stack structure it appears that it can be used as most general case within the approximation used by Yang et al. [9]. That approximation in general will cover the AB, ABC, AA and turbostratic stacking sequences in graphene stacks. The Yang approximation averages carbon density within the single graphene plane and is independent of the specific atom positions. That does not concern intensity modeling scattered by single graphene-like plane.

To calculate the intensity scattered by single graphene plane we have used model of 500 atom graphene plane of rectangular shape and used appropriate formula of intraplane scattering from Yang et al. [9]. Our model was built around this approach taking into account scattering from multilayer graphene species and single layer scattering. Since the model has to take into account non uniform surface coverage by graphene both in number of layers and proportion of the surface coverage we have introduced weighted summation over p_M parameter describing fractional surface area covered by all graphene stacks that are M layers thick. We have used for our modeling two different d_{002} interplanar spacing since the graphene structures showed bimodal distribution. One value coming from thin graphene covered the step flats and second attributed to graphite type structures developed along the step edges. To simplify the modeling procedure we have used general background constant B and scaling constants $A_{1,2,3}$ together with d_{002} graphene layer spacing, p_M fraction parameter and number of planes M as fitting parameters for our calculations. B and A constants take care of such parameters as absorption and polarization factors etc. But since they are slowly varying functions of scattering angle θ, they can be accommodated in scaling and background factors. Any buckling and roughness of the graphene planes was not taken into consideration since large X-ray beam footprint averages over all small local disturbances of this kind. Our modeled scattered intensity $I(s)$ may be summarized as follows:

$$I(s) = A_1 \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} f^2 \frac{\sin(2\pi s r_{ij})}{2\pi s r_{ij}} + A_2 \sum_{M=2}^{M_x} \left(p_M \frac{1}{M\pi s^2} \sum_{n=1}^{M-1} (M-n) \times f^2 \cos\left(2\pi s n d_{K1}^{002}\right) \right) + A_3 p_L \frac{1}{L\pi s^2} \sum_{n=1}^{L-1} (L-n) f^2 \cos\left(2\pi s n d_{K2}^{002}\right) + B,$$

where p_M and p_L are surface coverage fractions ($\sum p_M + p_L = 1$), $s = \frac{2\sin\theta}{\lambda}$, $\lambda = 0.1541874$ nm is weighted average of the $K_{\alpha 1}$ and $K_{\alpha 2}$ wavelengths, r_{ij} is the distance between i-th and j-th atoms for single layer scattering, f is the atomic scattering factor of carbon, d_{K1}^{002}, d_{K2}^{002} are average values of graphene layers d spacing, M and L are number of layers for thin and thick fractions respectively, M_x — maximum number of layers for thin graphene, N — number of atoms taken into account for single layer modeling (500 in our case).

First part of the formula is a single layer scattering intensity, second part is a scattering intensity from thin stack of multiple graphene layers and third part calculates the intensity of the thick graphite like structure. Any buffer layers structure between graphene stack and substrate as in [12] is not taken into account. That could be easily added to our model but buffer structure influence on the calculated intensity will be insignificant in the angular range of our experiment [12]. All fitted intensity curves were added to the standard intensity registered for

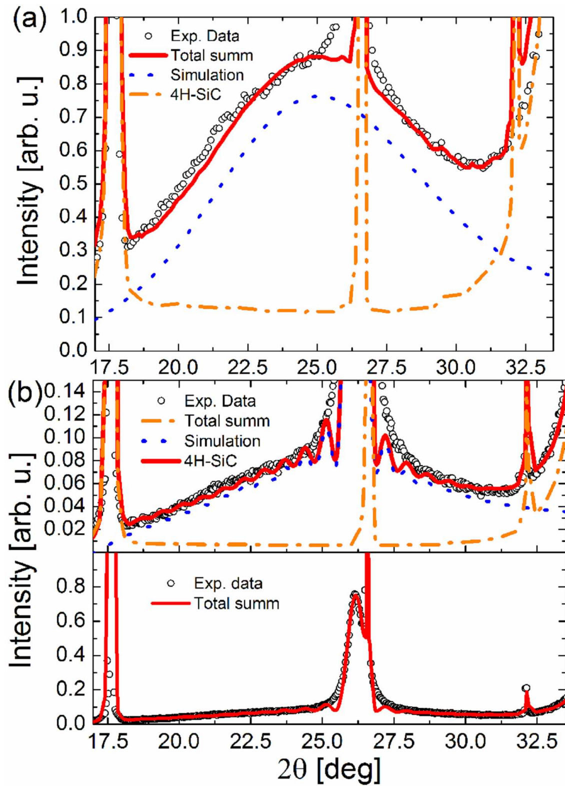

Fig. 2. Experimental and fitted intensity for the CVD grown graphene stacks. Sample (a) with 2 min growth time, (b) 5 min growth time.

the bare substrate of the SiC sample. SiC intensity distribution shows usual reflections attributed to the bulk SiC (004) reflection as well as quasiforbidden reflection (002) and fully forbidden (003) reflection. (002) and (003) reflections are activated due to the stacking faults present in the SiC substrate. That serves as angular markers for all intensities registered for our samples. We present only results for 2 and 5 min samples (Fig. 2a,b).

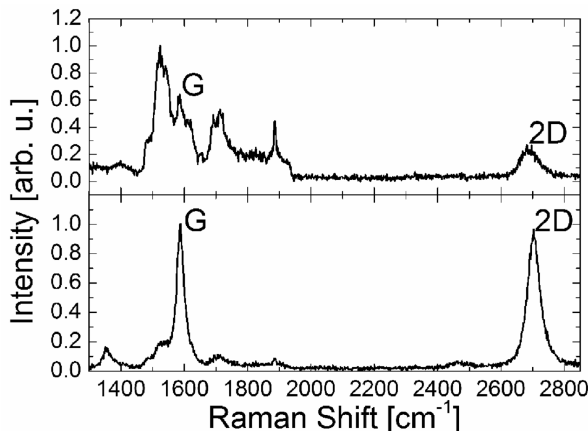

Fig. 3. Example of the Raman spectra for sample C — 5 min growth time (upper part — thin layer, lower part — thick layer).

Our X-ray measurements, for all four samples were compared with confocal micro-Raman spectroscopy measurements performed in backscattering geometry employing the 532 nm line of Nd-YAG laser. The laser beam spot size on the sample surface was in the range of about 300 nm in diameter. The Raman measurements were performed in series of steps across the sample to allow assessment of the range of graphene stacks thickness. The graphene thickness was assessed using relative intensity of the 2D band.

Collected Raman spectra were used to cross-reference the number of graphene layer estimates as already suggested in [13], as well as to confirm the overall presence of the graphene on the substrate surface. We present only results for 5 min sample (Fig. 3).

4. Discussion

The d spacing obtained from X-ray experiment and Raman estimates of number of layers are shown in Table together with the fitted number of layers (M, L) estimated from calculations.

It is shown (optical observations, X-ray experiment) that longer growth time creates thick graphite like structures alongside the thin graphene coverage of the rest of the sample surface. Similar features were already reported in [4] and they were observed as "puckers" structures on AFM images. It is well known that such structures (puckers) are common in thick graphene stacks. Our X-ray experiment and intensity modeling shows that CVD growth process consists of two independent channels. Short growth time (1 min) results in surface coverage by thin graphene stacks with d_{002} spacing slightly above nominal value for graphite (3.40 Å — sample A) and surface probably not fully covered, although fitted fractional coverage parameters indicate 2 layer and 3 layer structures for this sample. B sample shows development of the thin part with some addition of 4 layer structure and the d_{002} spacing being smaller and closer to 3.35 Å nominal value for graphite (see Table). Samples C and D show the presence of the thick part (37–39 layers) together with thin part already showing d spacing with nominal value of AB stacking (3.35 Å). Thick part shows consistently larger value of the d spacing (3.403–3.405 Å). That indicates that the growth process of the thick part is different than for thin part and produces the graphene stacks of the type usually attributed to turbostratic phase containing graphite [14]. Our modeling also shows that the thin part develops as uneven coverage of the surface (2, 3, and 4 layer structures) progressively developing thicker graphene stacks with smaller d spacing (Table). That correlates well with AFM observations [4]. There are some indications that the onset of growth of thick part already starts also with the short growth time — 2 min. Let us note the asymmetry of the intensity distribution on the left hand side of the (003) forbidden reflection of the SiC substrate, Fig. 2a. One can conclude that growth rate of the thick part is significantly larger than for the thin part of the graphene stacks.

TABLE

Main fitting parameters: d^{002}_{K1}, d^{002}_{K2} — graphene layer spacings, p_M and p_L — surface coverage fractions indexed by number of layers, of the calculated intensity distributions with Raman estimates of number of layers.

Sample	d_{002} spacings [Å]	Thin part			Thick part		Raman estimate of number of layers
		p_2	p_3	p_4	p_{37}	p_{39}	
A — 1 min	3.40 ± 0.025	0.7	0.3	–	–	–	from 1 to 2
B — 2 min	3.37 ± 0.025	0.4	0.5	0.1	–	–	from1 to 5
C — 5 min	thin 3.35 ± 0.025 thick 3.405 ± 0.002	0.64	–	0.16	0.2	–	from 1 to 30
D — 8 min	thin 3.35 ± 0.025 thick 3.403 ± 0.002	0.18	0.3	0.12	–	0.4	from 1 to 35

5. Conclusions

It is shown that CVD method of growth of graphene layer stacks on 4H-SiC (0001) surface is strongly influenced by the stepped surface morphology. Prolonged growth time (> 2 min) results in bimodal surface coverage with thin few layer graphene covering the surface step flats and thick multilayer graphene along the edges of the steps. Both stack systems differ as far as interlayer spacing is concerned. Thin part is showing d spacing characteristic for AB stacking order with thick part with larger spacing as for turbostratic arrangement.

Acknowledgments

This work was supported by GRAF-TECH/NCBR/02/19/2012 "FLOWGRAF" grant.

References

[1] J. Hass, R. Feng, J.E. Millán-Otoya, X. Li, M. Sprinkle, P.N. First, W.A. de Heer, E.H. Conrad, C. Berger, *Phys. Rev. B* **75**, 214109 (2007).

[2] A. Coati, M. Sauvage-Simkin, Y. Garreau, R. Pinchaux, T. Argunova, K. Aid, *Phys. Rev. B* **59**, 12224 (1999).

[3] M. Tokarczyk, H. Kępa, G. Kowalski, 2010, unpublished results.

[4] K. Grodecki, R. Bożek, W. Strupinski, A. Wysmołek, R. Stępniewski, J.M. Baranowski, *Appl. Phys. Lett.* **100**, 261604 (2012).

[5] J. Borysiuk, R. Bożek, W. Strupiński, A. Wysmołek, K. Grodecki, R. Stępniewski, J.M. Baranowski, *J. Appl Phys.* **105**, 023503 (2009).

[6] J. Borysiuk, R. Bożek, W. Strupiński, J.M. Baronowski, *Mater. Sci. Forum* **645-648**, 577 (2010).

[7] J. Borysiuk, R. Bożek, K. Grodecki, A. Wysmołek, W. Strupiński, R. Stępniewski, J.M. Baranowski, *J. Appl. Phys.* **108**, 013518 (2010).

[8] J. Borysiuk, J. Sołtys, R. Bożek, J. Piechota, S. Krukowski, W. Strupiński, J.M. Baranowski, R. Stępniewski, *Phys. Rev. B* **85**, 045426 (2012).

[9] D. Yang, R.F. Frindt, *J. Mater. Res.* **11**, 1733 (1996).

[10] D. Yang, S. Jiménez Sandoval, W.M.R. Divigalpitiya, J.C. Irwin, R.F. Frindt, *Phys. Rev. B* **43**, 12053 (1991).

[11] H. Fujimoto, *Carbon* **41**, 1585 (2003).

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

[13] M. Tokarczyk, G. Kowalski, H. Kępa, K. Grodecki, A. Drabińska, W. Strupiński, in: *XTOP 2012: 11th Biennial Conf. on High Resolution X-ray Diffraction and Imaging*, 2012, Abstracts, p. 408.

[14] W. Ruland, *Chemistry and Physics of Carbon*, Vol. 4, Eds. P.L. Walker, P.A. Thrower, Dekker, New York 1968.