Growth kinetics of epitaxial graphene on SiC substrates

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Optical absorption and Raman scattering studies of epitaxial graphene structures obtained by annealing of carbon terminated face of 4*H*-SiC(000-1) on-axis substrates using standard chemical-vapor deposition reactor are presented. Two series of samples grown at different argon pressures in the reactor and different annealing times were studied. Optical absorption and Raman scattering were used to determine the number of graphene layers formed on the substrate surface. The observed dependence of the number of graphene layers formed on annealing time and argon pressure strongly indicates that the growth kinetics of graphene is limited by Si evaporation and two-dimensional Si diffusion.

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I. INTRODUCTION

Since the first demonstration that an isolated graphene sheet can be prepared by micromechanical exfoliation from graphite,[1] graphene and multilayered graphene structures attracted a lot of interest. Excellent thermal conductivity and high room-temperature electron mobility[2] make this material very promising for electronic applications. However, due to the small sizes of flakes (tens square microns) the application of exfoliated graphene is very limited. More promising method of producing large area flakes of graphene is epitaxial growth on SiC substrates.[3,4] In this method graphene layers are produced by a sublimation of Si atoms from SiC substrates at high temperatures. Large area of single graphene layer and/or multilayer graphene structures received in a controllable way is a big challenge and the growth still requires a lot of research. In spite of a lot of studies devoted to the mechanism of initial graphitization and formation of the first graphene layer,[5–7] the growth mechanism and the kinetics of a formation of subsequent layers has been rarely investigated up to now. However, recently Tanaka *et al.*[8] reported the dependence of the growth rate on graphitization time of the Si-terminated SiC substrates. This process can depend on various growth parameters including gas pressure in the reactor, temperature, and annealing time. Also the choice of substrate's polytype, orientation and polarity, as well as the pretreatment before annealing (decomposition) seems to be very important. In this paper we investigate graphene layers grown on C face of 4*H*-SiC (000-1) oriented on-axis substrates in standard chemical-vapor deposition (CVD) reactor used for SiC epitaxy in argon atmosphere. This method is promising for the integration of well developed SiC technology with the growth and processing of graphene. In order to learn more about growth mechanism of graphene structures in this method several samples grown at different argon pressures and different annealing times were studied. The obtained structures were examined using atomic force microscopy (AFM), optical absorption, and micro-Raman spectroscopy.

It was shown that in the case of micromechanical cleavage of graphite the number of graphene layers transferred can be estimated using the analysis of the shape of the two-dimensional (2D) band.[9,10] For graphene grown on Si-face of SiC and then transferred to the Si substrate covered by SiO_2, close correlation between full width at half maximum (FWHM) of 2D band and number of graphene layers was observed, whereas no correlation between number of layers and FWHM of the 2D band was observed for the graphene layers transferred from the C-face SiC.[11] The situation is much more complicated in the case of the graphene structures on the SiC substrates for which due to interaction with the substrate substantial changes of the shape and the 2D band energy position are observed.[12–14] Systematic studies of the properties of graphene layers fabricated under different technological conditions (argon pressure and annealing time) would provide new information about optimal condition for the growth of graphene structures.

In parallel to Raman spectroscopy, optical absorption is a supplementary method that can be used for graphene characterization. Despite being only one atom thick, graphene flake was found to absorb a significant fraction (2.3%) of incident white light.[15] Theoretical calculations showed that in the visible spectral range the optical absorption is frequency independent,[16] what is observed experimentally.[15] We have noticed that in the case of on-axis growth on carbon polarity SiC graphene is loosely bound with the SiC surface, and it can be easily removed from a fraction of SiC sample. In order to establish the net absorption of the graphene layers, the measured signals have been normalized to the transmission of SiC substrate. Our recent results show transmission of graphene to be constant for wavelengths in the range 500–1100 nm,[17] which makes such optical transmission an efficient tool to characterize single-layer and multilayer graphene. The optical transmission in visible spectral range through N graphene layers on SiC (normalized to the transmission through a plain SiC wafer) can be expressed as[18]

$$T = \left(1 + \frac{N\sigma_0}{1 + n_{\mathrm{SiC}}}\sqrt{\frac{\mu_0}{\varepsilon_0}}\right)^{-2}, \tag{1}$$

where $\sigma_0 = e^2/(4\hbar)$ is interband conductivity and $n_{\mathrm{SiC}} = 2.55$ is refractive index of SiC. Since normalized reflection is two

order of magnitude smaller than absorption,[16] for $N\sigma_0\sqrt{\mu_0/\varepsilon_0} \ll 1+n_{\mathrm{SiC}}$, which is valid for $N \ll 150$, Eq. (1) can be rewritten to describe normalized absorption as

$$A = 1 - T = \frac{2N\sigma_0}{1+n_{\mathrm{SiC}}}\sqrt{\frac{\mu_0}{\varepsilon_0}} = 0.0129N. \quad (2)$$

Therefore optical absorption is a good method of determining the number of graphene layers.

II. EXPERIMENTAL DETAILS

The investigated samples were fabricated in hot-wall CVD reactor Epigress VP508. Prior to the growth *in situ* etching process of the SiC substrates was carried out in hydrogen and propane atmosphere. After etching, samples were annealed at temperature of 1600 °C in argon atmosphere. This enabled to control the growth rate of carbon films, as will be shown later. Two series of samples have been studied. For the first one, the same annealing (graphitization) times (10 min) have been used, whereas different argon pressures between 5 mbar and 800 mbar in the reactor have been kept during the growth process. The second series of samples have been obtained at fixed argon pressure of 100 mbar, using different graphitization times from 10 to 40 min.

Micro-Raman scattering experiments were performed at room temperature, in backscattering geometry, using 532 nm line from Nd-YAG laser as a source of continuous wave excitation. Laser spot diameter on the sample surface was about 2 μm. Since in the case of epitaxial graphene the characteristic excitations (except so-called 2D band) overlap with strong background related to the second order of SiC spectrum,[12,14,19–22] we focused our analysis on discussion of the 2D band.

Optical absorption measurements have been performed in the spectral range between 500 and 1100 nm using single grating monochromator. This enabled us to ensure that transmission is indeed constant in the whole spectral range and can be used to obtain the number of layers using Eq. (2). The incident beam from halogen lamp was chopped with 328 Hz and focused on the sample surface with the light spot size about 500 μm. Transmitted beam was focused on the Si detector and measured by the lock-in amplifier.

III. EXPERIMENTAL RESULTS

As verified by atomic force microscopy, changing annealing time and the argon pressure during growth allows us to study different stages of the graphene formation, starting from isolated graphene flakes at highest pressures and shortest annealing times to continuous substrate coverage with different number of carbon layers for lowest pressures and longest annealing times.[23]

In the case of full coverage of the substrate the optical absorption measurements enabled us to establish the number of graphene layers on the SiC substrate.

A. Dependence of number of graphene layers on argon pressure

Investigations of the first series of samples showed that changing the argon pressure in reactor from 5 to 800 mbar during annealing resulted in decreasing of optical absorption from 0.23 to 0.015 (Fig. 1). This corresponds to the decreasing number of graphene layers from 18 to one layer. Similar trend is observed in the Raman scattering measurements. Typical Raman spectra obtained for different argon pressures in the reactor are presented in Fig. 2. The observed FWHM of 2D band varies between 40 and 60 cm^{-1} and seems to be not correlated with the argon pressure value, and thus with the number of graphene layers formed on the SiC substrate. This result is very similar to those obtained for the few layers graphene grown on the C-face of 4*H*-SiC and 6*H*-SiC crystals,[11] where the observed broadening was attributed the morphology changes that develop in the course of the graphitization procedure. Surprisingly the dependence of the integrated intensity of 2D peak on pressure is consistent with optical absorption (Fig. 1), and decreases more than six times when changing argon pressure from 5 to 400 mbar. In spite of the fact that the mechanism responsible for the observed correspondence between 2D peak intensity and optical absorption needs to be verified. it could be used as an alternative method of the estimation of number of grown graphene layers. The information about the dependence of the average number of graphene layers grown on the argon pressure al-

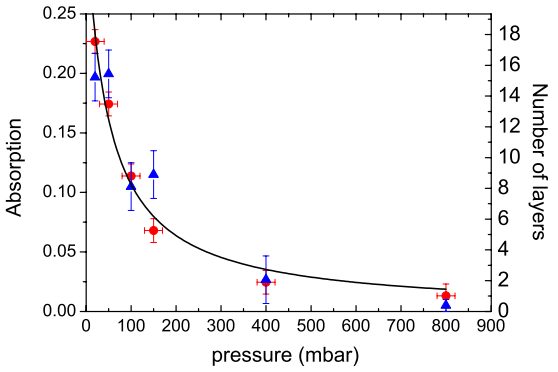

FIG. 1. (Color online) Circles: the optical absorption dependence on argon pressure during growth process at temperature $T = 1600$ °C and annealing time $t = 10$ min. Right axis corresponds to the number of graphene layers, calculated according to Eq. (2). Triangles: integrated intensity (in arbitrary units) of 2D band Raman signal.

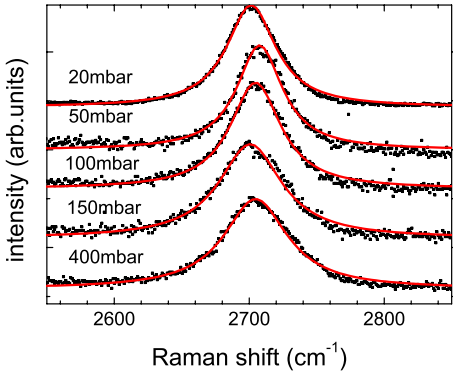

FIG. 2. (Color online) Representative normalized Raman spectra obtained for samples fabricated at different argon pressure in the CVD reactor and the same annealing time of 10 min at 1600 °C.

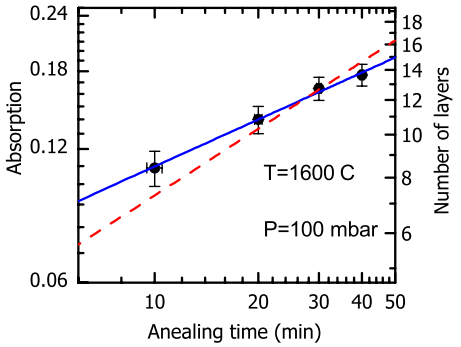

FIG. 3. (Color online) The optical absorption dependence on annealing time in growth process at temperature $T=1600$ °C and argon pressure $p=100$ mbar in the log-log scale. Right axis corresponds to the number of graphene layers, calculated according to Eq. (2). Dashed line and solid line: power-law dependence with the exponents 0.5 and 0.35, respectively.

lows us to discuss the mechanisms that govern the growth kinetics of graphene on SiC.

Creation of subsequent graphene layers can be related to three processes: releasing of Si from the SiC crystal lattice, Si out-diffusion, and its evaporationlike desorption into the ambient atmosphere. For the viscous flow regime, what is the case of our experimental conditions, one can expect that evaporation rate of Si from the sample surface should be inversely proportional to the argon pressure.[24] We observe a slightly different behavior. Solid curve shown in Fig. 1 was fitted using the relation:

$$N = \frac{C}{p + p_0}, \tag{3}$$

with $p_0=48\pm9$ mbar. We assign this value to "effective pressure" of Si vapor interacting with graphene layers and/or graphene-SiC interface. It could be understand that Si atoms have to overcome some effective barrier to be released out. It has to be noticed that the growth rate of graphene layer is time dependent (what is discussed below) and the layer thickness dependence shown in Fig. 1 reflect its mean value. The better understanding of details responsible for the growth kinetics is required for more precise analysis of the pressure dependence of the growth rate.

B. Dependence of number of graphene layers on annealing time

Investigations of the second series of samples showed that changing the annealing time from 10 to 40 min caused nonlinear increase in the optical absorption from 0.10 to 0.18 (Fig. 3). According to Eq. (2) this corresponds to an increase in number of layers from 8 to 14. The observed behavior can be approximated using power-law dependence with the exponent equal to 0.35.

It can be discussed in terms of out diffusion of Si atoms to the surface. For the similar processes such as iron[25,26] or Si (Ref. 27) oxidation at high temperature the square-root relationship $d\sim t^{0.5}$ was observed. Such behavior is typical for the chemical reactions that are governed by one dimensional diffusion of reagents directly through the layer of the oxide (D1 process in Ref. 28). However, in a case of SiC decomposition Silicon atoms cannot escape directly through already grown subsequent graphene layers and the process of Si out diffusion could be more complex in comparison to mentioned above classical examples. Our data are limited, and we cannot perform a detailed analysis of the factors that determine the growth process. However, assuming a crude description with a power law, we observe the exponent value which is lower than 0.5 (see Fig. 3). This could be a manifestation of the importance of two dimensional interlayer (or in-plane) diffusion (D2 process in Ref. 28). Thus, the role of substrate steps which create natural channel for Si desorption seems to be crucial in this process. This is already known that nucleation of new graphene layers starts in their vicinity.[29,30] Similar analysis, as performed above, can be done in the case of layers grown on Si terminated surface using data recently published by Tanaka *et al.*[8] The results presented in Fig. 4 of Ref. 8 can be well approximated with the power-law dependence with the exponent value in the range 0.1–0.2. This value is significantly smaller than obtained in our case for C terminated SiC. This can be understood as manifestation of different conditions of diffusion process for Si and C terminated surface, respectively. This could be connected with the fact that the first graphene layer on the Si terminated surface strongly interacts with substrate and subsequent layers[12,31] what can effectively block interlayer Si diffusion. This is probably not a case of loosely bonded graphene layers on C terminated surface.

IV. CONCLUSIONS

We have investigated the growth kinetics of graphene layers obtained by thermal decomposition of C terminated SiC substrates. The observed dependence of graphene layers number on argon pressure and annealing time allows to conclude that Si atom evaporation and two dimensional interlayer diffusion are responsible for the growth kinetics of multilayer graphene structures on SiC.

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[1] 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).
[2] A. K. Geim and K. S. Novoselov, Nature Mater. **6**, 183 (2007).
[3] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, J. Phys. Chem. B **108**, 19912 (2004).
[4] C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayo, T. B. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).
[5] A. J. Van Bommel, J. E. Crombeen, and A. Van Tooren, Surf. Sci. **48**, 463 (1975).
[6] I. Forbeaux, J.-M. Themlin, and J.-M. Debever, Phys. Rev. B **58**, 16396 (1998).
[7] R. M. Tromp and J. B. Hannon, Phys. Rev. Lett. **102**, 106104 (2009).
[8] S. Tanaka, K. Morita, and H. Hibino, Phys. Rev. B **81**, 041406(R) (2010).
[9] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, Phys. Rev. Lett. **97**, 187401 (2006).
[10] Y. Y. Wang, Z. H. Ni, T. Yu, Z. X. Shen, H. M. Wang, Y. H. Wu, W. Chen, and A. Thye Shen Wee, J. Phys. Chem. C **112**, 10637 (2008).
[11] D. S. Lee, C. Riedl, B. Krauss, K. von Klitzing, U. Starke, and J. H. Smet, Nano Lett. **8**, 4320 (2008).
[12] J. Borysiuk, R. Bożek, W. Strupiński, A. Wysmołek, K. Grodecki, R. Stępniewski, and J. M. Baranowski, J. Appl. Phys. **105**, 023503 (2009).
[13] N. Camara, J.-R. Huntzinger, G. Rius, A. Tiberj, N. Mestres, F. Pérez-Murano, P. Godignon, and J. Camassel, Phys. Rev. B **80**, 125410 (2009).
[14] N. Ferralis, R. Maboudian, and C. Carraro, Phys. Rev. Lett. **101**, 156801 (2008).
[15] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, Science **320**, 1308 (2008).
[16] T. Stauber, N. M. R. Peres, and A. K. Geim, Phys. Rev. B **78**, 085432 (2008).
[17] A. Drabińska, J. Borysiuk, W. Strupiński, and J. M. Baranowski, Mater. Sci. Forum **645-648**, 615 (2010).
[18] J. M. Dawlaty, S. Shivaraman, J. Strait, P. George, M. Chandrashekhar, F. Rana, M. G. Spencer, D. Veksler, and Y. Chen, Appl. Phys. Lett. **93**, 131905 (2008).
[19] C. Faugeras, A. Nerriere, M. Potemski, A. Mahmood, E. Dujardin, C. Berger, and W. A. de Heer, Appl. Phys. Lett. **92**, 011914 (2008).
[20] Z. H. Ni, W. Chen, X. F. Fan, J. L. Kuo, T. Yu, A. T. S. Wee, and Z. X. Shen, Phys. Rev. B **77**, 115416 (2008).
[21] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz, Nano Lett. **7**, 238 (2007).
[22] J. Röhrl, M. Hundhausen, K. V. Emtsev, Th. Seyller, R. Graupner, and L. Ley, Appl. Phys. Lett. **92**, 201918 (2008).
[23] K. Grodecki, A. Drabińska, R. Bożek, A. Wysmołek, K. P. Korona, W. Strupiński, J. Borysiuk, R. Stępniewski, and J. M. Baranowski, Acta Phys. Pol. A **116**, 835 (2009).
[24] G. R. Fonda, Phys. Rev. **31**, 260 (1928).
[25] M. H. Davies, M. T. Simnad, and C. E. Birchenall, J. Met. **3**, 889 (1951).
[26] J. C. Slattery, K.-Y. Peng, A. M. Gadalla, and N. Gadalla, Ind. Eng. Chem. Res. **34**, 3405 (1995).
[27] B. E. Deal and A. S. Grove, J. Appl. Phys. **36**, 3770 (1965).
[28] J. D. Hancock and J. H. Sharp, J. Am. Ceram. Soc. **55**, 74 (1972).
[29] K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, and T. Seyller, Nature Mater. **8**, 203 (2009).
[30] M. Hupalo, E. H. Conrad, and M. C. Tringides, Phys. Rev. B **80**, 041401(R) (2009).
[31] W. Norimatsu and M. Kusunoki, Chem. Phys. Lett. **468**, 52 (2009).