Effect of residual gas composition on epitaxial graphene growth on SiC

J. Kunc, M. Rejchon, E. Belas, V. Dedić, P. Moravec, and J. Franc

Institute of Physics, Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 5, Prague 2, CZ-121 16, Czech Republic

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In recent years, graphene growth optimization has been one of the key routes towards large-scale, high-quality graphene production. We have measured in-situ residual gas content during epitaxial graphene growth on silicon carbide (SiC) to find detrimental factors of epitaxial graphene growth. The growth conditions in high vacuum and purified argon are compared. The grown epitaxial graphene is studied by Raman scattering mapping and mechanical strain, charge density, number of graphene layers and graphene grain size are evaluated. Charge density and carrier mobility has been studied by Hall effect measurements in van der Pauw configuration. We have identified a major role of chemical reaction of carbon and residual water. The rate of the reaction is lowered when purified argon is used. We also show, that according to time varying gas content, it is preferable to grow graphene at higher temperatures and shorter times. Other sources of growth environment contamination are also discussed. The reaction of water and carbon is discussed to be one of the factors increasing number of defects in graphene. The importance of purified argon and its sufficient flow rate is concluded to be important for high-quality graphene growth as it reduces the rate of undesired chemical reactions and provides more stable and defined growth ambient.

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I. INTRODUCTION

Epitaxial graphene growth on SiC is a scalable fabrication method of high quality graphene for post-silicon electronics and opto-electronics. Among novel devices, the growth technique, together with SiC wafer preparation, stands at the beginning of whole manufacturing process. It is therefore a key to understand conditions under which reproducible high quality graphene can be reached. The growth mechanisms has been studied both theoretically and experimentally. First-principles calculations has been done to study graphene buffer layer formation on SiC(0001), diffusion of carbon on SiC, stability and reactivity of atomic steps of SiC in the initial graphene growth stage. Experimental studies have been done to understand mechanisms of epitaxial graphene growth on SiC(0001), SiC(0001), non-polar SiC surfaces and to elucidate role of carbon diffusion and silicon sublimation. It has been shown that graphene with reduced pit density can be grown on nominally flat SiC substrates and graphene quality can be further improved when grown in high argon pressure. On the other hand, the carrier mobility has been observed to decrease with increasing argon pressure when time and temperature are kept constant. Other strategies to improve graphene quality involve thermal decomposition of deposited polymer adsorbate which acts as a carbon source. The SiC step bunching, as another issue reducing graphene mobility on SiC, has been solved by amorphous carbon step pinning. The thermodynamics of stable phases that governs the onset of graphene formation, oxidation and other chemical reactions has been discussed, too. However, there is a little or no experimental evidence of graphene growth conditions and composition of a residual gas inside a graphene furnace. These studies are restricted to gas phase dynamics during Chemical Vapour Deposition (CVD) graphene growth and to carbon nanotubes growth.

Here, we determine experimentally the residual gas content in a furnace for epitaxial graphene growth on SiC. The measurements are performed in-situ by residual gas analyzer during whole graphene growth. We show that the initial graphene growth is accompanied by chemical reaction of residual water and carbon. The results of Norimatsu indicate that control of the number of graphene layers require precise control of the first stage of SiC decomposition. We discuss that hydrogen, one of the products of the reaction of residual water and carbon, might be one reason for SiC step bunching during initial graphene growth stage. We compare the chemistry of graphene growth in high vacuum and in low argon pressure. The comparison of both growth techniques demonstrates that argon reduces the rate of water and carbon reaction. Therefore amount of hydrogen is smaller and graphene quality is higher. We discuss also the role of argon in terms of growth temperature, time and gas purity. The graphene quality is analyzed by Raman spectroscopy mapping and by Hall effect measurements. We compare growth in vacuum and high pressure argon in terms of charge density, strain, graphene grain size and their spatial variation.

*Electronic address: kunc@karlov.mff.cuni.cz
II. SAMPLES AND EXPERIMENTAL SETUP

The wafers of 6H-SiC were purchased from II-VI Inc. and diced into $3.5 \times 3.5 \text{ mm}^2$ rectangles. The samples are $(500 \pm 25) \text{ µm}$ thick, semi-insulating high resistivity $(10^{10} \Omega \text{cm})$ vanadium doped SiC. Graphene is grown on the silicon face SiC(0001) with a wafer miss-cut $\pm 0.6^\circ$. The wafers were chemically-mechanically polished and the surface roughness is about 0.5 nm. Diced samples were rinsed and sonicated in both acetone and isopropylalcohol for 10 minutes. The semi-insulating samples were heated in a graphite crucible by radio-frequency (RF) induction heating at 250-270 kHz. The graphite used for fabrication of the crucible is iso-statically pressed (ISP) graphite and glassy (vitreous) graphite. The ISP used for fabrication of the crucible is iso-statically pressed (RF) induction heating at 250-270 kHz. The graphite used for fabrication of the crucible is iso-statically pressed (ISP) graphite and glassy (vitreous) graphite. The ISP graphite has density $1850 \text{ kg/m}^3$ and electrical resistivity $11 \times 10^{-4} \Omega \text{cm}$. The glassy graphite, purchased from Final Advanced Materials, has been used as a reference to study effect of crucible pre-baking. The high epitaxial graphene quality has been reached by Confinement Controlled Sublimation (CCS) technique [21]. The processing environment is either high vacuum $5 \times 10^{-6} \text{ mbar}$ or high purity argon (6N purity gas vessel). The argon is further purified to the level of 9N purity by gas purifiers to remove residual oxygen and water. The stainless steel gas tubes have been outgassed at temperature about 200°C for 2 hours prior to graphene growth to avoid contamination by residual water and impurities from the stainless steel surface. The temperature is monitored by either type C thermocouple or by two-color pyrometer working at 0.95 and 1.05 µm wavelengths. The pyrometer allows to measure temperature with spatial resolution of about 0.2 mm. The thermocouple type C is electrically isolated by alumina shielding. The graphite crucible is placed inside a hot wall reactor made of 4 mm thick and 250 mm long quartz tube. The quartz tube is opened from both sides to allow effective gas circulation. The growth environment has been studied by residual gas analyzer (Prisma Plus QMG 220). The CF-40 flanges are used for all connections except of the adapter between the furnace and the turbo-molecular pump and quartz tube feedthrough. The quartz feedthrough is made of two o-rings on both sides to allow leak-tight connection up to high vacuum $1.5 \times 10^{-6} \text{ mbar}$ and yet allowing easy access to the reaction chamber.

III. TEMPERATURE MEASUREMENTS

The standard furnace design for epitaxial graphene growth uses either thermocouple or pyrometer to monitor growth temperature. We have used both methods and compared them. The thermocouple is a cheaper method and it measures temperature inside the graphite crucible. It requires electrical isolation (made of alumina for high temperature purposes up to 2000°C) complicating furnace design and introducing other elements beside carbon and silicon (SiC sample and C based crucible).

We have found that the electrical shield made of alumina (polycrystalic Al$_2$O$_3$) is sputtered and deposited on a relatively colder quartz tube during cool down process. Energy-dispersive X-ray spectroscopy (EDS) has been performed to determine chemical composition of the sputtered material, as shown in Fig. 1 for three different positions along the inner part of quartz tube. We have found presence of aluminium and Al$_2$O$_3$ mixture. Their relative ratio changes along the quartz tube. As we have used thermocouple type C, which is composed of rhenium and tungsten, we have looked carefully for the traces of these metals as well. The negative result of our search has led us to conclusion that the sputtered alumina from the thermocouple electrical shield is a source of furnace contamination, very often seen in high temperature graphene furnaces. We expect alumina traces can also contaminate SiC wafer and graphene. Hence, in order to keep high graphene quality, we propose to use only remote temperature sensing by pyrometer. We also note it is essential to use two-color ratio pyrometer for the reason of possible contamination of furnace quartz windows. The contamination leads to decreased light intensity and to the lower effective temperature determined by one-color pyrometer.

IV. GRAPHITE CRUCIBLE

We study here the effect of graphite crucible gas adsorption. The commonly used ISP graphite and glassy graphite crucibles are compared. The major issue of ISP graphite is its high porosity and permeability to gases. The high permeability leads to undesired contamination by air when samples are exchanged or graphite crucible is stored at ambient conditions for longer time (order of hours and longer). A glassy graphite is impermeable to gases hence it is more convenient to keep the furnace environment clean of air residual gasses. The residual gas stored in ISP graphite is removed within the first two pre-
bake graphene growth stages. The pressure usually grows from $1.5 \times 10^{-6}$ mbar to $10^{-3}$ mbar or more if crucible is not well baked. The well baked crucible exhibits small rise of the residual gas pressure by less than one order of magnitude, typically $1.5 \times 10^{-6}$ mbar to $10^{-5}$ mbar. Contrary to ISP graphite, glassy graphite is impermeable to gasses and the pre-baking removes surface absorbants only. The glassy carbon crucible is less susceptible to long exposure to air, however, its pre-baking at temperature much higher than the growth temperature is also necessary, as is shown in Fig. 2. The well-baked graphite crucible exhibits comparable strength of peaks at M/z=12 (carbon) and 14 (nitrogen), which is also signature of leak-tight vacuum chamber. The unbaked glassy graphite exhibits more than 2× stronger nitrogen peak which is supposed to come from glassy graphite surface. We use peak at M/z=14 instead of M/z=28 because the latter one overlaps with carbon monoxide.

V. GROWTH ATMOSPHERE

The general growth process consist of three stages. The pre-baking stage (I.), depicted in Fig. 2, is used for crucible outgassing at 800°C for 10 minutes. The second pre-baking stage (II.) at 1000-1100°C for 10 minutes is used to decompose native oxide layer on SiC wafer. The graphene growth stage (III.) is performed at temperatures 1400-2000°C at times in the range of minutes to hours. Fig. 3 depicts relative content of growth ambient in all three growth stages for the case of growth in high vacuum (a) under continuous vacuum pumping by a turbo-molecular pump, low pressure argon (b) under continuous pumping and small argon leak and growth in high vacuum using glassy graphite crucible (c). The graphene growth stage (III.) has been kept at 30 minutes to show long-time evolution of the growth ambient. A change of relative content is caused by different pump-rate (e.g. slow hydrogen pumping), outgassing from vacuum chamber walls (mainly water) and chemical reactions. We have identified that oxidizing reactions appear at every temperature rise (from step (I.) to (II.) and from step (II.) to (III.)) resulting in reduced both relative and absolute amount of oxygen. These reactions are however negligible for very small content of oxygen in the chamber. The major identified reaction is a reaction of two major components in the furnace, carbon and water. We discuss this process in detail here. The epitaxial graphene can be grown fast (2-5 minutes) at higher temperatures or slowly (20-90 minutes) at lower temperatures. We have found that 1430°C for 20 minutes is equivalent to 1500°C for 5 minutes by amount of
grown graphene. It is however not equivalent in growth conditions concerning the growth environment. We show difference between the two regimes. The main issue is a content of water and carbon monoxide, as shown in Fig. 4 at the beginning of graphene growth. A water content is about 10-15% for times shorter than 5 minutes, but it grows then steadily and it completely dominates the growth atmosphere at times longer than 30 minutes. A detail of growth ambient in high vacuum in Fig. 4(a,d,f) shows sharp pressure rise accompanied by sharp rise of ion current at M/z=28 by 8×10^{-9} A. Similarly, the ion current increases at masses M/z=44 by 0.6×10^{-9} A and M/z=12 by 0.25×10^{-9} A. A significant rise of hydrogen is also present by amount of 6×10^{-9} A. The water ion current is unchanged within first 60 s of growth stage (III.). The step rise of ion current is expected instead due to the step rise of temperature and consequent step rise of mean velocity of ions. The lack of such ion step rise of water can be attributed to the reduction of total amount of water in the chamber. The rise of M/z=28 by 8×10^{-9} A is attributed to CO. The rise of CO is confirmed by rise of ion current at M/z=12 by 0.25×10^{-9} A, which is 3% (expected CO contribution is 5%) of the major ion current rise at M/z=28. The minor ion current peak at M/z=14 by 0.05×10^{-9} A (0.6% of M/z=28, expected CO contribution is 1%) is also attributed to CO.

We conclude that there is no absolute change of nitrogen (M/z=28, 14) and all content changes can be explained by increasing amount of CO and similar amount of hydrogen. The shift of hydrogen peak towards longer times is caused by slower pumping of hydrogen than pumping of CO, water and other heavier ions. The ion current rise at mass M/z=44 by 0.6×10^{-9} A is due to the carbon dioxide (CO2). Therefore the dynamics of growth ambient is dominated by chemical reaction

\[
C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) + 7.5\%(CO_2(g) + CH_4).
\]

The major chemical reaction given by equation (1) is observed mainly on the short time scale below 30 s after each temperature step rise. The time scale between 30-100 s is dominated by pumping the products of Eq. (1) out of the furnace. The long time scale above 2 minutes is dominated by both pumping of the residual gas and water outgassing from the stainless steel furnace walls. This behavior has been observed both in high vacuum and low pressure argon and also in the case of glassy graphite crucible in high vacuum, as is shown in Fig. 4. The content changes only slowly for longer times (>60 s), however, water becomes slowly dominant gas. The water source is at the surface of stainless steel furnace walls.
The main issue is that it can promote reaction with carbon even further, hence creating defects in a graphene layer. Therefore it is more preferential to grow graphene at higher temperatures for shorter times.

As the residual gas analysis has shown preferable shorter growth times and higher temperatures, we grow single layer graphene between 1500-1550°C for 5 minutes in high vacuum. Buffer grows at about 1500°C, shifted towards higher temperatures with respect to growth in high vacuum. Buffer grows at about 1410-1430°C in high vacuum and at about 1450°C at 800-1050 mbar argon pressure. The growth has been always done in the same graphite crucible with a hole 1 mm in diameter and 10 mm long. Argon acting on graphene growth is twofold. First, it is equivalent to CCG method, where the lowered silicon sublimation is due to the small volume in nearly closed graphite crucible. Second, argon pressure acts as an inhibitor for water outgassing, as has been discussed in previous paragraphs as the major source of residual gas and potential cause of defects formation in epitaxial graphene. We note, that high purity argon is necessary in order to obtain overall purity of growth conditions comparable to those in high vacuum at 1 × 10⁻⁵ mbar. An equivalent purity of argon gas for graphene growth at 1000 mbar is 8N (=1000 mbar/10⁻⁵ mbar). A lower argon purity results in higher relative content of residual gas, which leads to higher total amount of mainly water at 1000 mbar argon pressure growth (the total amount of water is discussed with respect to the total amount of water at high vacuum (10⁻⁵ mbar) growth). Beside the gas purity, also the background outgassing in the furnace has to be taken into account. A typical water background pressure in unbaked furnace is 10⁻⁶ mbar-10⁻⁵ mbar. If the background water pressure is higher, the overall argon purity in the furnace will be lower even with gas purifiers, as is described in Fig. 4. Fig. 5 demonstrates overall gas purity as a function of total argon pressure for inlet of 9N (6N) pure argon. The total gas purity cannot be higher than the value at 10⁻⁵ mbar high vacuum. An equivalent purity of growth conditions comparable to those in 800 mbar 9N pure argon atmosphere. We have analyzed the positions, Full Width at Half Maximum (FWHM) and integrated intensities of D, G and 2D peaks, respectively.

We compare here two epitaxial graphene samples grown in high vacuum (HV-graphene) at 10⁻⁵ mbar and in 9N pure argon at 800 mbar (Ar-graphene). First, Raman spectroscopy has been performed in order to determine strain, charge density distribution and graphene grain size. We have used confocal microscope with 100× magnification microscope objective and numerical aperture NA = 0.9. The excitation laser wavelength was 532 nm and the laser power at the sample was 5 mW. The characteristic Raman spectra of HV-graphene and Ar-graphene are shown in Fig. 6. Nearly absent D-peak shows on better graphene quality grown in ultra pure argon atmosphere. We have analyzed the positions, Full Width at Half Maximum (FWHM) and integrated intensities of D, G and 2D peaks, respectively. We have constructed spatial maps of G and 2D peak positions, G and 2D peak FWHM and spatial maps of I_G/I_D and I_2D/I_G, as shown in Fig. 7 and Fig. 8 for HV-graphene and Ar-graphene, respectively. The positions of G and 2D peak has been calculated as Center of Mass (COM) of each peak after subtracting SiC background signal. The larger grain size of Ar-graphene can be seen from the fine structure of all spatial maps. We have used these spatial maps further to determine mechanical strain ε

$$\epsilon = \frac{\omega_{2D} - \omega_{2D,0}}{2\omega_{2D,0}}. $$

![Graph showing Raman spectra comparison](image-url)

**VI. RAMAN SPECTROSCOPY**

![Spatial maps of G and 2D peak](image-url)
FIG. 7: Maps of Raman spectra parameters shown for a characteristic graphene sample grown in high vacuum at $5 \times 10^{-6} - 10^{-5}$ mbar at 1550°C for 5 minutes. The analyzed Raman spectra parameters are G peak position (a), G peak FWHM (b), 2D peak position (c), 2D peak FWHM (d), ratio of integrated G peak and D peak intensities (e) and ratio of integrated 2D peak and G peak intensities. The scale bar 1 µm is shown in the left bottom corner in each map. The statistical analysis is depicted in a form of histogram for each analyzed parameter including units and the range of values used in color scales.

The effects of charge density on the position of 2D peak are negligible [23]. The charge density $n_{2D}$ is determined from G peak position $\omega_G$ and strain $\epsilon$,

$$n_{2D} = \alpha [ (\omega_G - 2 \gamma_G \omega_{G,0} \epsilon) - \omega_{G,0} ] ,$$

(3)

where $\gamma_G$ is Grüneisen parameter for G peak, $\omega_{G,0} = 1582 \text{ cm}^{-1}$ is G peak position for unstrained ($\epsilon = 0$) and neutral ($n_{2D}=0$) graphene. Parameter $\alpha=10^{12} \text{ cm}^{-2}/1 \text{ cm}^{-1}$ is approximately a proportionality factor between G peak position and graphene charge density, as determined theoretically [24] and confirmed experimentally [23, 25]. Graphene grain size $L_a$ can be determined from the ratio $I_G/I_D$ [26–29] of integrated G peak intensity ($I_G$) and D peak intensity ($I_D$),

$$L_a(\text{nm}) = 2.4 \times 10^{-10} \lambda^4(\text{nm}) \frac{I_G}{I_D},$$

(4)

giving $L_a = 19 \text{ nm} \times \frac{I_G}{I_D}$ for excitation wavelength 532 nm.

FIG. 8: Maps of Raman spectra parameters shown for a characteristic graphene sample grown in ultra-pure argon (9N purity) at 800 mbar at 1600°C for 5 minutes. The analyzed Raman spectra parameters are G peak position (a), G peak FWHM (b), 2D peak position (c), 2D peak FWHM (d), ratio of integrated G peak and D peak intensities (e) and ratio of integrated 2D peak and G peak intensities. The scale bar 1 µm is shown in the left bottom corner in each map. The statistical analysis is depicted in a form of histogram for each analyzed parameter including units and the range of values used in color scales.
Figure 7 (f) and Figure 8 (f) show spatial and this method can be used to determine the number of SiC, therefore we are in the limit of 1 to 2 layers. The expected strain \( \varepsilon_{\text{theory}} = \frac{13a_0 - 6\sqrt{3}a_0_\text{SiC}}{13a_0} = 0.19\% \) is determined from graphene \((a_0_\text{G} = 2.462 \text{Å})\) and SiC \((a_0_\text{SiC} = 3.073 \text{Å})\) lattice constants at 300 K assuming \(6\sqrt{3} \times 6\sqrt{3}R30^\circ\) SiC-graphene super-cell containing 13 graphene unit cells and mutual rotation of graphene and SiC lattices by 30°. Both samples show low doping level in the range \(0.2 - 4 \times 10^{12} \text{cm}^{-2}\) and the statistically significant amount of low density areas show on electron-hole puddles \(53\). A small doping is also evidenced by G peak FWHM in the range of 14-18 cm\(^{-1}\) \(50\).

FIG. 9: The spatial distribution of mechanical strain (a,c) and charge density (b,d) in epitaxial graphene grown in high vacuum \(5 \times 10^{-6} - 10^{-5} \text{mbar}\) (a,b) and 800 mbar 0N-argon atmosphere (c,d). The statistical distribution of strain and charge density in both types of graphene samples is shown in corresponding histograms for high vacuum grown graphene (blue histograms) and high pressure argon grown graphene (red histograms). The scale bars are shown in the left bottom corner of each map; 1 \(\mu\)m for high vacuum grown graphene and 0.5 \(\mu\)m for high pressure argon grown graphene.

Number of graphene layers has been determined by several authors \(30\) from the ratio of integrated 2D peak \(I_{2D}\) and integrated G peak intensity \(I_G\). This ratio \(N = I_{2D}/I_G = 2\) for single layer graphene, \(N = 1\) for bilayer and it is \(N < 1\) for more than two graphene layers. We note this relation is the most disputable and it is probably valid only in the limit of few graphene layers. It cannot be used e.g. for number of graphene layer determination of multilayer graphene on C-face of SiC. Our graphene samples have been grown about 50°C above the lowest graphitization temperature at 5 minutes and graphene has been always grown on Si-face of SiC, therefore we are in the limit of 1 to 2 layers and this method can be used to determine number of graphene layers. Fig. 7 (f) and Fig. 8 (f) show spatial map of the ratio \(I_{2D}/I_G\) including statistical analysis in a form of histogram. Both samples consist of mostly single layer. A 2D-peak FWHM is \((35±3)\ \text{cm}^{-1}\) in both samples. The narrow 2D peak is also a fingerprint of a single layer graphene \(31\) and FWHM values about 30 cm\(^{-1}\) has been correlated with charge mobility of about \(10\ 000\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) at Dirac point \(32\). The grain size in HV-graphene is \(L_{a,HV} = (400 ± 200)\ \text{nm}\) and it reaches \(L_{a,Ar} = (1.5 ± 0.5) \mu\text{m}\) in Ar-graphene. Strain is \(\varepsilon_{HV} = (0.24 ± 0.05)\%\) and \(\varepsilon_{Ar} = (0.21 ± 0.04)\%\) in HV and Ar grown graphene, respectively. The expected strain \(\varepsilon_{\text{theory}}\) is determined from graphene \((a_0_\text{G} = 2.462 \text{Å})\) and SiC \((a_0_\text{SiC} = 3.073 \text{Å})\) lattice constants at 300 K assuming \(6\sqrt{3} \times 6\sqrt{3}R30^\circ\) SiC-graphene super-cell \(54\) containing 13 graphene unit cells and mutual rotation of graphene and SiC lattices by 30°. Both samples show low doping level in the range \(0.2 - 4 \times 10^{12} \text{cm}^{-2}\) and the statistically significant amount of low density areas show on electron-hole puddles \(53\). A small doping is also evidenced by G peak FWHM in the range of 14-18 cm\(^{-1}\) \(50\).

FIG. 10: Charge transport properties of pristine graphene (solid lines) and for graphene in fluctuating electrostatic potential (dashed lines) as a function of mean Fermi level \(E_F\). The charge density of electrons (black lines) and holes (red lines) is shown in part (a). The Hall coefficient \(R_H\) (black lines) and \(\mu R_{\text{sq}}\) product (red lines) are shown in part (b). The standard deviation of the electrostatic potential is taken to be \(\delta V = 100 \text{ mV}\) (all dashed curves).

VII. HALL MEASUREMENTS

We have measured Hall effect to determine charge density and carrier mobility. The room temperature measurements have been performed in magnetic field up to \(±0.35\ \text{T}\) in van der Pauw configuration. A direct current (DC) source has been used (\(I = 1 \mu\text{A}\)) and all combinations of current directions and voltages have been
measured to determine specific resistance and Hall coefficient. Typical transport coefficients are shown in Tab. I. We have observed twice lower specific resistance and 1.8× higher apparent carrier mobility of argon grown graphene. We note that all samples show small negative Hall coefficient $R_H$ in the range from -50 to $-100 \ \Omega/T$, indicating n-type doping on the order of upper $10^{12} \ \text{cm}^{-2}$. Such charge densities are consistent with data in Ref. [37].

We assume normal potential fluctuations smear out the Fermi level and in the limit of $B \to 0 \ T$ by Eq. (9)

$$ R_H = \frac{1}{e(n_{2D} \mu_e + p_{2D} \mu_h)}. \quad (9) $$

The Hall coefficient is plotted in Fig. 10 (b) for pristine graphene (solid black curve) and for the case of electrostatic potential fluctuations $\delta V = 100 \ \text{mV}$ by dashed black curve. The Hall coefficient is largely reduced for all mean Fermi level positions. The value $\delta V = 100 \ \text{mV}$ is taken as an upper bound determined in other works [38, 40]. A small measured Hall coefficient $R_H$ in the range of 50 to $-100 \ \Omega/T$ suggests Fermi level in the range of 5-10 meV for $\delta V = 100 \ \text{mV}$, which corresponds to about $5 \times 10^{13} \ \text{cm}^{-2}$ electron and $4 \times 10^{11} \ \text{cm}^{-2}$ hole density. The analysis of transport properties reduces now to determine $n_{2D}$, $p_{2D}$, $\mu_e$, $\mu_h$. Because we have determined $R_C$ and $R_H$ and estimated $\delta V$, we cannot determine any transport properties prior to further assumptions. The electron and hole charge densities are coupled by two common parameters, mean Fermi level $E_F$ and electrostatic potential fluctuations $\delta V$. We assume equal electron and hole mobilities $\mu_e = \mu_h$, which reduces number of unknown parameters to three (being equal to three measured properties ($R_C$, $R_H$, $\delta V$). We use measured Hall coefficient $R_H$ to determine mean Fermi level from Fig. 10 (b). The mean Fermi level provides a value of $R_C \mu = 690 \ \Omega/T$, which leads immediately to carrier mobility provided the specific resistance $R_C$ is known. We get carrier mobilities 2900 and 6000 cm$^2$/V$\cdot$s$^{-1}$ for vacuum and argon grown graphene, respectively.

VIII. DISCUSSION

The results of Raman scattering and Hall effect measurements lead us to conclusion that graphene grown in ultra-pure argon at 800 nbar is of higher quality than graphene grown in high vacuum. The growth in high vacuum leads to smaller graphene grain size below 1 μm even if the growth conditions are well optimized by high temperature bakeout of graphite crucible, gas inlet pipes.
to vent the furnace and the furnace itself. The key issue in graphene growth is a presence of water and water outgassing from stainless steel surfaces. We have observed chemical reaction of water and solid state carbon in all stages of graphene growth. This reaction is important within first one minute of each graphene growth step. It becomes important again when graphene is grown for longer times above 20-30 minutes. This is caused by gradual furnace warm up and consequent water outgassing from previously colder furnace parts. Even though it would be thermodynamically more preferable to grow graphene slowly, providing high crystal quality, the water outgassing acts against long growth times. As we do not know the origin of carbon, we assume that the main source is a graphite crucible for a time scale below 60 s at the beginning of each growth step. However, as graphene grows, the carbon source can be also graphene itself. This reaction of water and carbon from partially formed graphene will be a cause of higher defect density and smaller grain size, as we have observed in Raman spectra analysis. A disadvantage of short growth time is that there is no temporally stable growth atmosphere content. Moreover, it differs slightly from one sample to another. The hydrogen produced in a reaction of carbon and water can also cause SiC etching or it can react with carbon, increasing defect density in graphene even more. Hydrogen is therefore undesired gas during graphene growth. The growth in argon has been shown to lead to more stable growth atmosphere content with small rate of carbon and water reaction and also smaller amount of hydrogen. The high argon pressure reduces both water outgassing and also mean free path of water molecules. The shorter mean free path can be used to restrict water transport towards grown graphene when growth is performed in argon flow. We also point out that it is essential to use ultra-pure argon (8 or 9N) at the furnace inlet. A common 6N argon at 1000 mbar is in terms of total amount of residual gas equivalent to vacuum growth at 10^{-5} mbar (if background outgassing causes lower or equal pressure). Therefore, growth in 6N argon at 1000 mbar will lead to much worse graphene than the one grown in HV at 10^{-6}-10^{-5} mbar. The argon flow rate is not supposed to improve the overall amount of residual gas because this residual gas in homogeneously spread within the furnace volume. Contrary to that, the 9N argon at 1000 mbar is equivalent to HV at 10^{-6} mbar in terms of total amount of residual gas. These two growth conditions are initially equivalent. However, the growth conditions are more preferable for argon growth at the later stages of graphene growth for two reasons. First, water outgasses in HV and causes graphene degradation (pressure rises to 10^{-5} mbar). Water outgassing is strongly reduced in high pressure argon, therefore the total amount of impurities remains nearly constant. Second, any possible residual gas in ultra pure argon can be removed by growth in argon flow. The argon flow should be only higher than the outgassing rate. Air permeability of graphite brings constrictions on a crucible storage. The nitrogen and water is absorbed into the crucible after longer exposure to air. It is therefore suggested to store ISP graphite in vacuum or inert gas. Glassy graphite is impermeable to air components, however, the surface absorbants still lead to higher desorption when glassy graphite crucible is heated to growth temperatures. Raman spectroscopy has proven to be a versatile tool to determine most of basic graphene properties as mechanical strain, charge density, graphene grain size, number of graphene layers or even to estimate electrostatic potential fluctuations and carrier mobility. We have measured graphene Raman spectra using several microscope objectives with different magnification and numerical apertures. We point out that although relative strength of SiC Raman spectrum and intensity of graphene spectrum (particularly intensity of G peak) have been used to determine number of graphene layers by some authors [43], this method can be only calibrated (intensity ratio to the number of layers) to a given experimental set up and it is not transferable. The reason is mainly due to the different microscope objective numerical apertures (NA). The smaller the aperture is the longer the Rayleigh length. It causes that small NA objective probes signal deeper from bulk crystal, even if it is focused properly on a surface graphene layer. As a result, relative intensity of graphene to SiC bulk spectrum will be smaller than the ratio determined from Raman spectra measured with high-NA objective. A similar issue comes up in a grain size determination from the ratio of D to G peak intensity. If low-NA objective is used, graphene signal is weak relatively to SiC signal and the D peak can seem to be negligible with respect to SiC [44]. The small D peak is then mistakenly identified as a signature of high quality graphene. Hall effect measurements have been used to quantify graphene electronic quality. The apparent carrier mobilities are almost twice higher in argon grown graphene. The analysis of transport measurements has been done also within a model of electron hole puddles. This model is in agreement with our Raman scattering analysis which has indicated very low charge density below 1.5 \times 10^{12} \text{cm}^{-2}. The carrier mobility is twice higher for argon grown graphene within the model of electron hole puddles, too.

IX. CONCLUSION

We have analyzed experimentally graphene growth environment and its influence on graphene quality. Residual gas analysis has shown important role of water reaction with carbon in high vacuum growth ambient. We have shown reduced role of the residual gas in 9N pure argon and we have compared high vacuum and argon grown graphene. The gas purity is a detrimental factor for high quality graphene for electronic applications. The mechanical strain, charge density, graphene grain size and number of graphene layers has been determined from Raman spectroscopy mapping. Hall measurements
in van der Pauw configuration have provided information about charge density consistent with Raman spectroscopy. A carrier mobility has been modeled within electrostatic potential fluctuations model to provide realistic model of mean Fermi level dependence of Hall coefficient. The estimated lower bound of carrier mobility has been modeled within an analytical model of mean Fermi level dependence of Hall coefficient.

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