Raman and AFM studies of epitaxial graphene intended for manufacturing of transistors

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Abstract. Graphene is considered as a promising material for electronic applications. In this work, micro-Raman spectroscopy, atomic force microscopy and Kelvin-probe force microscopy are used to study three epitaxial graphene samples: two commercially-available ones and one grown using a home-made setup. The obtained data indicates significant differences in homogeneity of strain and doping level, concentration of bilayer inclusions, surface topography and surface potential. Analysis of the measurements data allows us to establish connections between the topography of the samples and their structural properties. The results of these studies will help to understand the characteristics of transistors that are to be made on the basis of the studied samples.

1. Introduction
Carbon atoms assembled in a two-dimensional hexagonal lattice, known as graphene, are a subject of extensive research. It was first obtained and characterized in depth by Nobel Prize winners A. Geim and K. Novoselov in 2004 [1]. One of the main proposed fields of graphene commercial use, designated in the mentioned pioneering work, is the field of electronics and namely the transistors [2]. Thermal decomposition of the Si (0001) face of semi-insulating SiC substrates is currently one of the most promising technologies of commercial graphene growth. The most important advantage of this method for electronic applications is the lack of the need to transfer the grown film onto a dielectric substrate. In this work, structural and electronic properties of three different epitaxial graphene samples intended for use as a basis of transistors are studied: two commercially available ones together with the sample grown by us using a home-made setup.

2. Experimental
Three epitaxial graphene samples grown on the Si-face of the 4H-SiC substrates were studied in this work: Sample 1 and sample 2 were the commercially available obtained from different manufacturers. Sample 3 was grown in a home-made setup using the method of SiC thermal destruction [3]. The growth process was carried out in a graphite crucible with induction heating at a temperature of 1750°C in an argon atmosphere (730±10 Torr). The duration of growth was 5 min, and the sample heating rate was 250°C/min.
Raman spectroscopy is a powerful tool for rapid and non-destructive investigation of the structural and electronic properties of graphene [4]. Micro-Raman spectra of graphene were measured at room temperature in the backscattering geometry using a Horiba Jobin-Yvon T64000 spectrometer. For the excitation of the Raman spectra, a Nd:YAG 532 nm laser was used. The laser power was limited to 4 mW in a spot with 1 μm diameter. Apart from local measurements, Raman mapping of the sample areas of ~10 × 10 and 12 × 12 μm² was carried out.

In addition to Raman spectroscopy, a combination of surface investigation methods was used to study the same areas of the samples. Atomic force microscopy (AFM) and Kelvin-probe force microscopy (KPFM) within the two-pass technique were employed in order to obtain information on surface topography, roughness and surface potential distribution. For these measurements, an Ntegra AURA setup (NT-MDT, Russia) was used.

3. Results and discussion

Figure 1 demonstrates the arrays of Raman spectra obtained after scanning the areas in the center of the studied samples. The spectra obtained after scanning the 10 × 10 and 12 × 12 μm² areas of the samples demonstrate characteristic Raman features of graphene: G (~1600 cm⁻¹) and 2D (~2700 cm⁻¹) lines originating from the vibrations in the graphene lattice and the broad spectral profile with two maxima in the 1200-1600 cm⁻¹ range corresponding to the buffer layer [5]. The high quality of the samples is indicated by the absence of the defect-related D line (~1350 cm⁻¹) in the Raman spectra. In case of Sample 2, the 2D line in all the spectra has a Lorentzian shape and a full width at half maximum (FWHM) of ~40 cm⁻¹, which is a fingerprint of single-layer graphene. In the spectral arrays obtained from samples 1 and 3, the 2D line in some of the spectra has an asymmetric shape well-described by a set of four Lorentzians. This indicates that a certain share of bilayer graphene (~5 and ~15%, respectively) is present on the surface of these samples [6]. According to the Raman analysis, the rest of the studied areas of samples 1 and 3 are covered by single-layer graphene.

![Figure 1](image.png)

**Figure 1.** (a), (b), (c) – Arrays of Raman spectra of the samples 1, 2 and 3, respectively. The spectra are obtained upon subtracting the second-order spectrum of the 4H-SiC substrate.

Correlation between the G and 2D lines positions obtained from the analysis of the spectral arrays is shown on figure 2. The positions of the G and 2D Raman lines of graphene are simultaneously influenced by two main factors: electron concentration (n_e) and the value of strain (ε) [7]. Using the analysis first introduced by Lee et al [7] and taking into the value of Fermi velocity in graphene grown on SiC [8], we determined the average values of strain and doping level for each sample. Variation of points along the dependence denoted by the solid line on figure 1(d) should be associated with local inhomogeneity in the magnitude of strain, and variation along the X axis - with local inhomogeneity in the electron concentration. It should be noted that the points corresponding to bilayer graphene were excluded from the consideration since at the moment there is no established procedure for determining the strain and doping level for multilayer epitaxial graphene using Raman spectroscopy. Since we did not observe any significant splitting or broadening of the G line in the Raman spectra, which may indicate presence of uniaxial strain [9] we will further assume that graphene is biaxially strained and will use the ε_|| designation to denote biaxial strain.
For sample 1, we obtain $\varepsilon_i = (-0.26 \pm 0.03)\%$ and $n_e = (6.0 \pm 0.8) \times 10^{12} \text{ cm}^{-2}$. Hereinafter the "-" sign denotes the compressive biaxial strain. In case of sample 2, the values of strain and electron concentration, as well as their variation across the studied area are significantly higher compared to the values obtained for the sample 1 ($\varepsilon_i = (-0.38 \pm 0.05)\%$, $n_e = (7.5 \pm 1.5) \times 10^{12} \text{ cm}^{-2}$). Sample 3 demonstrates the lowest values of strain and electron concentration: $\varepsilon_i = (-0.18 \pm 0.04)$ and $n_e = (5.0 \pm 1.0) \times 10^{12} \text{ cm}^{-2}$, respectively. As one can see from figure 2, for this sample the electron concentration, as well as the $\varepsilon_i$ value vary rather strongly in the studied area.

Figure 2. Correlation dependence between the positions of the $G$ and $2D$ lines for three samples under study. Data obtained from Raman mapping of the samples are denoted by symbols. Solid line shows dependence obtained for biaxially strained electrically neutral graphene [10] and open blue squares show dependence of the electron concentration for unstrained graphene [11]. Both dependences corrected taking into account the value of Fermi velocity in graphene grown on SiC [8].

The results of the AFM and KPFM studies of the samples together with the Raman maps of strain distribution, which are presented on figure 3, allow us to establish the connections between the topography of the samples and their properties. Essential differences between the topography of the samples can be observed. The surface of the sample 1 is formed by relatively small and irregular steps with average width of ~600-700 nm and height of ~2-3 μm (figure 3 (a)). Topography of the sample 2 is completely different, showing wide (~10 μm) and high (~5-7 μm) steps. In addition, steps of smaller (~1-2 μm) width but similar height (figure 3 (b)) are observed between them. Sample 3 demonstrates a topography picture with narrow (500-800 nm) elongated steps (figure 3 (c)). The average height of these steps (~1.5 nm) is significantly lower than that of samples 1 and 2. KPFM maps shown on figure 3 (d-f) allow us to determine the presence and distribution of bilayer inclusions by analyzing the surface potential distribution. Surface potential of bilayer graphene is known to be ~100-150 mV higher than that of single-layer graphene [12]. In case of samples 1 and 3, we can see regions of increased potential ($\Delta U \sim 100$ mV), which correspond to bilayer graphene. These areas coincide with the areas of bilayer graphene on Raman maps (figure 3 (g, i)) that were determined by analyzing the $2D$ Raman line shape. The maximum surface potential difference in case of sample 2 is very small (~15 mV) compared to the typical difference between single-layer and bilayer graphene. In combination with the fact that no fingerprints of bilayer graphene were found in the Raman spectra obtained in the same area, this allows us to conclude that this sample is covered by single-layer graphene only.
Figure 3. Surface topography maps (a, b, c), surface potential maps (d, e, f) and Raman maps of biaxial strain $\varepsilon_{||}$ (g, h, i) maps obtained in the same areas of the studied samples. The hatched areas on the Raman maps correspond to bilayer graphene.

A correlation between the surface topography and strain distribution can be found by analyzing the biaxial strain distribution maps (figure 3 (g-i)). For all the three samples, we can see that the areas of increased strain have the shape and direction similar to the steps on the topography maps. This may point to the fact that these areas are connected with the step edges. In case of sample 2, we can observe the area of increased strain in the bottom right corner (figure 3 (h)). This area coincides with the area of narrow and high steps on the topography map (figure 3 (i)).

4. Conclusion
Three epitaxial graphene samples were studied by a combination of AFM, KPFM and Raman mapping. Combined analysis of the data of these three techniques allowed us to conclude that the presence of high and wide regular steps on the surface of the sample results in absence of bilayer inclusions, however, leads to large strain and doping level inhomogeneity. In case of smaller steps of irregular shape, the average values of strain and doping level as well as inhomogeneity of these parameters decrease, but the percentage of bilayer graphene increases. The influence of strain inhomogeneity, doping level and surface topography of the graphene/SiC samples on their electronic properties will be investigated by studying the transport characteristics of the transistors manufactured on the basis of studied samples.

References
[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric Field Effect in Atomically Thin Carbon Films Science 306 666–9
[2] Lin Y M, Dimitrakopoulos C, Jenkins K A, Farmer D B, Chiu H Y, Grill A and Avouris P
2010 100-GHz transistors from wafer-scale epitaxial graphene *Science* **327** 662

[3] Lebedev S P, Amel’chuk D G, Eliseyev I A, Barash I S, Dementev P A, Zubov A V. and Lebedev A A 2020 Surface morphology control of the SiC (0001) substrate during the graphene growth *Fullerenes Nanotub. Carbon Nanostructures* **28** 281–5

[4] Ferrari A C and Basko D M 2013 Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* **8** 235–46

[5] Fromm F, Oliveira M H, Molina-Sánchez A, Hundhausen M, Lopes J M J, Riechert H, Wirtz L and Seyller T 2013 Contribution of the buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001) *New J. Phys.* **15** 1–12

[6] Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S and Geim A K 2006 Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **97** 187401

[7] Lee J E, Ahn G, Shim J, Lee Y S and Ryu S 2012 Optical separation of mechanical strain from charge doping in graphene. *Nat. Commun.* **3** 1024

[8] Eliseyev I A, DavydoV Y Y, Smirnov A N, Nestoklon M O, Dementev P A, Lebedev S P, Lebedev A A, Zubov A V, Mathew S, Pezoldt J, Bokai K A and Usachov D Y 2019 Optical estimation of the carrier concentration and the value of strain in monolayer graphene grown on 4H-SiC *Semiconductors* **53(14)** 1904-9

[9] Mohiuddin T M G, Lombardo A, Nair R R, Bonetti A, Savini G, Jail R, Bonini N, Basko D M, GalioS C, Marzari N, Novoselov K S, Geim A K and Ferrari A C 2009 Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grüneisen parameters, and sample orientation *Phys. Rev. B* **79** 205433

[10] Ding F, Ji H, Chen Y, Herklotz A, Dörr K, Mei Y, Rastelli A and Schmidt O G 2010 Stretchable graphene: A close look at fundamental parameters through biaxial straining *Nano Lett.* **10** 3453–8

[11] Froehlicher G and Berciaud S 2015 Raman spectroscopy of electrochemically gated graphene transistors: Geometrical capacitance, electron-phonon, electron-electron, and electron-defect scattering *Phys. Rev. B* **91** 205413

[12] Panchal V, Pearce R, Yakimova R, Tzelenchuk A and Kazakova O 2013 Standardization of surface potential measurements of graphene domains *Sci. Rep.* **3** 1–8