Raman scattering and low-frequency noise in epitaxial graphene chips

I A Eliseyev, A S Usikov, S P Lebedev, A D Roenkov, M V Puzyk, A V Zubov, Yu N Makarov, A A Lebedev, E I Shabunina, P A Dementev, A N Smirnov and N M Schmidt

1 Ioffe Institute, 26 Politekhnicheskaya, 194021 St. Petersburg, Russia
2 Nitride Crystals Inc., 9702 Gayton Road, Suite 320, Richmond, VA 23238, USA
3 ITMO University, 49 Kronverkskiy pr., 197101 St. Petersburg, Russia
4 Herzen University, 48 Moika emb., 191186 St. Petersburg, Russia

E-mail: zoid95@yandex.ru

Abstract. Graphene is considered as a promising candidate for manufacturing of sensors due to its extreme sensitivity to molecule absorption. In this work, we show the connection between the electrical and optical properties of epitaxial graphene chips grown on 4H-SiC and intended for the production of protein-based sensors. Using a complex of techniques, including Raman spectroscopy, atomic force microscopy, Kelvin probe microscopy, study of I-V characteristics and low-frequency noise, it is shown that the character of frequency dependence of the spectral density of voltage fluctuations and its value at a frequency of 1 Hz can be used for classification and selection of graphene chips for their application as sensors. Classification of the graphene chips will allow more efficient development of graphene-based biosensors.

1. Introduction

The unique properties of graphene make it possible to develop novel types of electronic devices, in particular, bio- and gas sensors [1-4]. Interaction of biomolecules on the graphene surface changes electronic state (resistance) of the graphene channel between two contacts in a chip. This effect is used in biosensors to register extremely low concentrations of markers of various socially significant diseases (hepatitis, oncology, HIV) at an early stage. Controllable technology of the graphene growth in a connection with deep understanding of both the properties of the graphene itself and the processes of its interaction with protein structures are necessary to get high-sensitive biosensors. Thermal destruction of the semi-insulating silicon carbide (SiC) substrate is a technology providing epitaxial graphene film of decent quality to be used for biosensor applications. However, the set of parameters of epitaxial graphene films important for sensor applications has not been fully understood to date.

The low-frequency noise measurement technique is a characterization tool for degradation phenomena in solid-state devices. [5, 6]. There are only several works focusing on low-frequency noise in the graphene films on SiC [7, 8]. However, the connections of the noise parameters with the crystal quality, thickness, strain and electron concentration of graphene are not fully understood yet.

The goal of this work was to study the properties of chips based on monolayer graphene films grown by thermal decomposition of semi-insulating 4H-SiC substrates. Together with low-frequency
noise, atomic force microscopy (AFM), Kelvin probe microscopy (KPFM), Raman spectroscopy, as well as the study of current-voltage (I-V) characteristics were used for the graphene chips characterization.

2. Experimental

In this work, graphene films were obtained by thermal decomposition of semi-insulating substrates (0001) ± 0.25° 4H-SiC with a size of 11 × 11 mm². The growth process was carried out in a graphite crucible with induction heating in an argon atmosphere (720–750 Torr) at a temperature of 1700–1800°C [9]. Rectangular chips were formed on the surface of graphene/SiC plates by laser photolithography in combination with ion-reactive etching in argon and etching in oxygen plasma. Ti/Au contacts (5 nm/50 nm) were fabricated using the methods of vacuum deposition and lift-off photolithography. After processing, the graphene / SiC plate was cut into individual 1.5 × 2 mm² chips and mounted on a PCB holder (figure 1a). Current-carrying parts of the holder, contact pads of the graphene/SiC die and the connection Au wires, which can be in contact with electrolyte liquid solutions and biological media, were covered with a chemical resistant lacquer to protect them from electrochemical corrosion and to avoid shunt currents. The contact pad (dark area on figure 1b) had a scallop-like interface with graphene. Surface terraces (steps) are an inherent property of graphene grown on SiC substrates. In the chips under study, the steps are inclined at approximately 20 degrees relative to the contact pads.

![Figure 1. (a) Optical image of the typical graphene/SiC chip studied in this work. The chip is assembled on a holder of foiled textolite (PCB holder). The holder size is 5 × 20 mm². (b) Magnified optical image of the graphene chip mounted on a holder demonstrating the configuration of contacts.](image)

The graphene sensing surface area in the chip was 1 × 1.5 mm². The chips under study were obtained from three different graphene/SiC plates: EG319, EG313, and EG335. In total, 6 chips (2 chips per plate) were examined.

Atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) measurements were carried out within a two-pass technique on Ntegra AURA setup (NT-MDT, Russia). Raman spectra were measured at room temperature in the backscattering geometry using a T64000 spectrometer (Horiba Jobin-Yvon, France) equipped with a confocal microscope, which allowed obtaining information from the region of a graphene film 1 μm in diameter. Along with local measurements, the measurements of sample areas of 10 × 10 μm² with subsequent plotting of Raman maps of spectral lines parameters were performed. To excite the Raman spectra, a YAG: Nd solid-state laser with a wavelength of 532 nm was used. The laser power on the sample was 4.0 mW in a spot with a diameter of 1 μm.

The I-V measurements were measured using the KEITHLEY 6487 power source. The power spectral density of voltage fluctuations was measured in the frequency range of 1 Hz - 50 kHz. For
noise measurements, the studied samples were connected in series with a low-noise load resistor $R_L$ whose resistance varied from 100 Ohm to 13 kOhm depending on the current through the chip. The voltage fluctuations $S_v$ at the resistors $R_L$ were amplified by a low-noise preamplifier SR560 (Stanford Research Systems, USA) and subsequently measured by SR 770 FET NETWORK Analyzer (Stanford Research Systems, USA). The background noise of the preamplifier does not exceed 4 nV/$\sqrt{\text{Hz}}$ at 1 kHz, which is approximately equivalent to Johnson–Nyquist noise of a 1000 Ohm resistance.

3. Results and discussion

Low-frequency noise is a sensitive tool to study the overall quality of the material or device. The spectral density of voltage ($S_V$) or current ($S_I$) fluctuations at 1 Hz allows one to integrally characterize the material quality. Commonly, the quality of bulk compounds is quantitatively evaluated by the Hooge parameter $\alpha_H$ based on the empirical formula [7]:

$$\frac{S_I}{f^2} = \frac{S_V}{V^2} = \frac{\alpha_H}{fN}$$

where $N$ is the total number of charge carriers and $f$ is the frequency.

The application of this parameter, which was initially introduced for characterization of the volume noise, to diagnostics of a 2D system such as graphene monolayers displays conceptual difficulties as shown in [7]. However, several works present experimental data on the correlation of $S_V$ or $S_I$ at 1 Hz with the quality of graphene layers [7, 8]. The shape of the noise spectra provides integral information about peculiarities of the defect systems in a material. The appearance of generation-recombination noise in the frequency independent region on the noise spectrum indicates the presence of a specific trapping state and enables one to evaluate its parameters. A change in the $\gamma$ index in $1/f^\gamma$ from 1 to 2.5 accompanied by a simultaneous increase in $S_V$ or $S_I$ can be caused by the presence of a gradient of mechanical stress [6].

The resistance measurements were carried out on all chips processed from graphene/SiC plates. The resistance spread for the chips processed from the first plate (EG319) was 4% with an average value of 8.3 kOhm. The chips processed from the second plate (EG331) showed a 6% of the resistance spread with an average value of 12.5 kOhm. The chips of the third plate (EG335) demonstrated the lowest average resistance values ~ 4.9 kOhm and their spread was near 2%. The I-V characteristics of all the chips were linear, as shown on figure 2a.

![Figure 2](image-url)

**Figure 2.** (a) I-V characteristics of the chips under study. (b) Frequency dependence of the spectral density of low-frequency noise ($S_V$). Solid lines are the experimental data, dashed and dotted lines denote the $1/f$ and $1/f^2$ frequency dependences, respectively.
The $S_V$ spectrum (figure 2b) revealed a typical for graphene $1/f$ tendency [7, 8] for all the chips except one (EG331-9), which demonstrated maximum noise amplitude at 1 Hz. The noise spectrum of this chip contains a region with frequency dependence close to $1/f^2$. For the chips under study, there is a large scatter (more than four orders of magnitude) in the maximum $S_V$ values at 1.22 Hz. However, no relation between the noise and the values of chip resistance was observed. Moreover, maximum $S_V$ (1.22 Hz) in the chips from the plate EG-331, which have close values of resistance, differs by almost three orders of magnitude. The chips from the plate EG319 that have the lowest $S_V$ (1.22 Hz) among all the chips under the study demonstrate the $S_V(f)$ values close to each other. The $S_V$ values at 1.22 Hz are given in figure 2b for all the chips. To clarify the reason of the $S_V$ values spread, several characterization methods were applied.

![AFM and KPFM images](image-url)

**Figure 3.** AFM topography (a, c, e) and KPFM surface potential (b, d, f) maps of the as-grown graphene/SiC wafers. Light color areas in KPFM maps denote bi-layer graphene areas. The wafer number is indicated for every pair of AFM and KPFM images.

The joint application of AFM and KPFM measurements provided simultaneous control of surface roughness and an assessment of thickness distribution of the graphene layer for the as-grown graphene/SiC plates. The information on the presence and proportion of bilayer inclusions in the samples under study is important for sensor applications: for example, the sensitivity of NO$_2$ sensors is
known to depend on the number of graphene layers [10]. The AFM topography maps measured on the as-grown plates (figure 3a, c, e) demonstrate elongated terraces with a width of 0.5-3 μm and a height of 1-3 nm located on the sample’s surface. Bilayer graphene is observed mainly at the edge of the wider terrace. The bilayer graphene, which can be seen as brighter areas on the surface potential maps (figure 3b, d, f), usually forms discontinuous areas on the terraces, and its fraction turned to be no more than 20%. Surface RMS roughness and bilayer fraction of the graphene/SiC plates are accumulated in table 1.

Raman spectroscopy is a recognized tool for graphene diagnostics and quality assessment [1]. The use of this technique allowed us to determine many important properties of graphene in the studied chips, such as number of graphene layers, presence of defects, charge carrier concentration and strain. Figure 4 shows typical Raman spectra of the investigated chips. The spectra of all the chips are composed of two main spectral lines of graphene: G (1600 cm⁻¹) and 2D (~2700 cm⁻¹), as well as the bands in the 1200-1600 cm⁻¹ spectral region corresponding to the buffer layer [11]. The defect-related D line of graphene was absent in all the spectra, which is a confirmation of high quality of the graphene films. In most of the spectra obtained during mapping measurements for all of the studied samples, the 2D line had a symmetric Lorentzian shape and a full width at half maximum (FWHM) of about 35 cm⁻¹, which is inherent in monolayer graphene [12].

Figure 4. Typical Raman spectra of the chips under study. The spectra are given after subtraction of the second-order spectrum of the 4H-SiC substrate.

The carrier concentration and strain in graphene/SiC chips were estimated considering monolayer graphene by the method of separating the contributions of strain and doping to the Raman spectra in graphene [13], taking into account the effect of the silicon carbide substrate on the position of the spectral lines of graphene [14].

The FWHM distribution map of the 2D Raman line of graphene was analyzed to determine the fraction of bilayer graphene (σ_{2L}) [12]. The σ_{2L} values obtained by using Raman spectroscopy and KPFM methods are in qualitative agreement, but differ from each other by 5-10 % due to different spatial resolutions of the two methods. Figure 5 shows maps of spatial distribution of the biaxial strain (ε) and the concentration of free charge carriers (n_e) constructed for selected chips based on Raman spectroscopy data.

The parameters of all graphene/SiC chips in this work estimated by AFM (root mean square (RMS) surface roughness of the graphene film), KPFM (bilayer graphene fraction σ_{2L}), Raman spectroscopy (n_e, ε, and σ_{2L}) and low-frequency noise (S_v) measurements are presented in table 1.
The lowest $S_v$ values as well as the minimum spread of these values are typical for chips manufactured from the plate EG319. This fact may point to better quality of this graphene film, in comparison to that of plates EG331 and EG335. Moreover, the obtained $S_v$ values are comparable to the best results mentioned in [8].

Table 1. Estimated parameters of the samples under study. The methodology of measurements, based on the data of which the given values were obtained, is indicated in parentheses. The minus sign of the $\varepsilon_\parallel$ value indicates the compressive strain. The numbers after ± indicate the scatter of the values of $n_e$ and $\varepsilon_\parallel$ in the studied area.

| Chip name | RMS, nm (AFM) | $n_e$, cm$^{-2}$ (Raman) | $\varepsilon_\parallel$, % (Raman) | $S_v$, V$^2$/Hz (LF-noise at 1.22 Hz) | $\sigma_{2\Delta}$, % (Raman) | $\sigma_{2\Delta}$, % (KPFM) |
|-----------|--------------|-------------------------|-----------------------------|-------------------------------------|------------------|------------------|
| EG319-3   | 0.25         | 3.1±0.3                 | -0.09±0.02                  | 2*10$^{13}$                         | 15               | 15               |
| EG319-4   | 3.1±0.4      |                         |                            | 4*10$^{14}$                         | 20               |                  |
| EG331-9   | 1.7          | 2.2±0.5                 | -0.20±0.03                  | 2*10$^9$                            | 18               |                  |
| EG331-10  | 2.9±0.5      |                         | -0.21±0.02                  | 7*10$^{13}$                         | 15               |                  |
| EG335-3   | 0.73         | 4.0±0.3                 | -0.18±0.02                  | 8*10$^{11}$                         | 15               |                  |
| EG335-5   | 4.0±0.3      |                         | -0.16±0.02                  | 2*10$^{13}$                         | 15               | 5                |

Figure 5. Raman maps of the estimated values of $n_e$ (a, c, e, g) and $\varepsilon_\parallel$ (b, d, f, h) for selected chips. The chip number is indicated for every pair of $n_e$ and $\varepsilon_\parallel$ maps. Regions of bilayer graphene are colored blue.

Comparative investigation of the chips processed from plate EG319 by other methods confirms the conclusion about better quality of this graphene film compared to others investigated in this work. As it is shown in table 1, chips EG319-3 and EG319-4 demonstrate minimum RMS roughness and compressive strain, moderate electron doping, and smaller fraction of the graphene bilayer.

The results obtained allow us to clarify the observed difference in the $S_v$ values by three orders of magnitude between the chips EG331-9 and EG331-10.

As one can see from the analysis of graphene thickness (table 1), the $\sigma_{2\Delta}$ values estimated for every chip correlate with the $S_v$ values in some cases: chip EG331-10 with higher uniformity and lower bilayer fraction demonstrated much lower $S_v$ compared with the chip EG331-9. However, when we
consider chips made on the basis of different plates, we see no correlation between the $\sigma_{2L}$ and $S_v$ parameters, since the chips made on the basis of the plate with the lowest $\sigma_{2L}$ did not demonstrate the lowest values of $S_v$. A possible explanation for the lack of correlation between $\sigma_{2L}$ and $S_v$ is that the bilayer regions in all three samples are scattered and do not form a continuous network.

On the other hand, we have found that the uniformity of distribution of the $v_0$ and $n_e$ parameters, which is a measure of uniformity and therefore quality of the graphene film itself, is connected to the $S_v$ values. The spatial distributions of the biaxial strain and electron concentration values of the chip EG-331-9 (figure 5a, b) are less uniform compared to those of the chip EG331-10 (figure 5c, d). It is clear that the $S_v$ difference between these two chips correlates with the magnitude of spread of the $v_0$ and $n_e$ parameters.

Similarly, lower uniformity of the spatial distribution of the $v_0$ and $n_e$ values in the chip EG335-3 (figure 5e, f) compared to the chip EG335-5 (figure 5g, h) results in increasing of the $S_v$ values by more than two orders of magnitude.

In general, a relation between the graphene film parameters estimated by Raman spectroscopy, AFM, and KPFM, and the results of low-frequency noise measurements was found. It has been established that the surface roughness, biaxial strain, and inhomogeneity of the biaxial strain distribution, which are specific of epitaxial graphene/SiC plates and chips, are connected to the $S_v$ values of the same chips. Hence, the $S_v$ values reflect the quality of graphene and they can be used for the graphene chips selection for their application as sensors.

4. Conclusion

It is shown that the set of techniques used in this work allows us to characterize properties of graphene/SiC chips on the integral and local level. The values of compressive strain, electron concentration, and inhomogeneity of their distribution across the ship surface, which might be caused by uneven topography of the substrate, are shown to be connected to the $S_v$ values. The spectral density of voltage fluctuations $S_v$ as well as its values at 1 Hz can be used for selection of graphene chips for their application as sensors.

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