Research Article

Ultrasensitive NO₂ Gas Sensor Based on Epitaxial Graphene

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We report about technology of fabrication and optimization of a gas sensor based on epitaxial graphene. Optimized graphene/metal contact configuration exhibited low contact resistance. Complementary annealing of graphene sensor after each gas exposure led to significant improvement in the sensing performance. The response of the annealed sensor to the nitrogen dioxide (NO₂) was tenfold higher than that of an as-fabricated graphene sensor. NO₂ concentration as low as 0.2 parts per billion (ppb) was easily detectable. Devices have high signal-to-noise ratio. The detection limit of the graphene sensor was estimated to be 0.6 ppt (parts per trillion). The present technology with additional annealing improves the performance of the graphene based sensor and makes it suitable for the environmental nitrogen dioxide gas monitoring.

1. Introduction

Graphene is a promising material that has unique properties like high surface-to-volume ratio, low electrical noise, and exceptional transport properties associated with its two-dimensional structure [1, 2]. Adsorption ability and high surface-to-volume ratio of graphene make it attractive as a gas sensing material. In the late years interest for the air pollutants and their monitoring has been growing in our life. Nitrogen monoxide (NO) and nitrogen dioxide (NO₂) are typical air pollutants that cause environmental problems. According to the European Commission air quality standards the NO₂ concentration should not exceed the limit of 40 µg/m³ at averaging period of one year [3]. There are demands for a small and cheap gas sensor for NO_x detection in medical field and in its basic research area. From this point of view, it is necessary to develop highly sensitive and inexpensive NO_x gas sensor, able to detect low concentrations of NO and NO₂ gases. Currently, gas sensing experiments have demonstrated epitaxial graphene to be an excellent material for future NO₂ sensors. Graphene layers grown on SiC have demonstrated sensitivities down to parts per billion (ppb) levels and shown high selectivity for NO₂ detection with respect to typical interfering gases [4]. Selectivity can be further improved by

gating technique [5] or by analyzing the low-frequency noise spectra [6, 7].

In the present study we report on fabrication of graphene based sensor which is extremely sensitive to NO₂ exposure. We propose a simple method to improve the sensing performance by means of additional annealing of the sensor at 120°C in the carrier gas flow. This annealing procedure has turned out to be a very effective way to enhance sensing properties of graphene by activating the high energy adsorption centres on graphene surface. Those centres are believed to give the major response at the low gas concentration.

Compared to pristine epitaxial graphene the response of annealed graphene was about tenfold higher. The detection limit of graphene based sensor was estimated as low as 0.6 ppt.

2. Experiment

2.1. Graphene Synthesis. A semi-insulating 4H silicon carbide 3" wafer was purchased from Cree Inc. and cut into 5 × 5 mm pieces. Before processing chips were cleaned in acetone, RCA1 solution and dipped for 5 sec in HF/H₂O (1:10). Epitaxial graphene film was grown on Si side of chip by annealing in Ar ambient at temperature near 1750°C during

5 min. Before growth the substrate was etched at 1600°C in 1-atm of 5% H_2 /95% Ar gas mixture in order to remove scratches from the surface.

2.2. Fabrication of Sensors. The sensor chip (size 5×5 mm) has six sensing devices, connected in series. Patterns for the sensor devices were made on the graphene surface of the substrate using laser photolithography over AZ5214 resist. Reactive ion etching in the argon oxygen plasma was used to remove the graphene layer from uncoated areas. Essential property for graphene based devices is contact resistance at the metal-graphene interface. In order to fabricate stable and low resistance contacts two-step metallization process has been used; see Figure 1. Double layer metal-graphene contacts were made by e-beam evaporation and lift-off photolithography. In both steps the Ti/Au (5/50 nm) were used. Our improved layout has several advantages: (1) in the first metallization contact pads are deposited directly on the SiC surface and thus have much better adhesion, (2) in the second metallization short metal ledges on top of graphene are less inclined to exfoliation and those have more stable contact to graphene, (3) the stripe-like metal contacts shape has more fraction of end-type of contact between metal and graphene [8] as compared to the conventional rectangular geometry and was expected to have low contact resistance, and (4) bonding wires are attached to the first metallization layer of the contact pads and do not damage the graphene film. More information concerning contact fabrication was presented in [9].

Devices also have additional contacts in Hall bar configuration enabling measurements of carrier concentration and mobility. The chip was assembled on TO-8 holder together with a heater and Pt100 temperature sensor. View of the chip with devices is presented in Figure 2(b). Current channels of the sensor devices were oriented along the atomic terraces on the graphene surface according to AFM image (Figure 2(a)). Terrace-oriented devices demonstrate superior performance as compared to randomly oriented devices [9].

2.3. Experimental Setup. For measurements of a sensor response to NO_2 , the custom made gas system was used. NO_2 gas (originally diluted to 10 parts per million (ppm) with air) was mixed with dry (relative humidity RH = 0.02%) air by utilizing two-stage dilution system based on mass flow controllers (Aera FC-D980). The dilution ratio could be varied in the range $1:1-1:10^6$, providing an output concentration in the range of 0.01 ppb to 10 ppm. Response was measured, using multichannel data acquisition system and LabView software. Response, r , was expressed as a percentage, %, and defined as the relative change of the sample's resistance under exposure to the gas, $r = (R - R_0)/R_0$, where R is the resistance when the gas is applied and R_0 is the resistance of the graphene film under the initial conditions defined by the flow of the incoming air. To avoid the influence of nonlinearity in the response, time difference (slope) of the response was also used to estimate the gas concentration. Time differential values are obtained by the derivative of a polynomial fitted to the temporal response.

FIGURE 1: Cross-section (a) and top (b) view of the two-step metallization process of the metal-graphene contact fabrication.

2.4. Characterization. AFM was performed using Ntegra instrument (NT-MDT, Russia). Raman scattering was measured using Micro-Raman Alpha 30RA spectrometer (WITec, Germany) with 532 nm excitation. Auger spectra were collected using CMA128 spectrometer (VG, UK) and 4.5 keV excitation e-beam.

3. Results and Discussion

3.1. Graphene Characterization. Raman spectrum of the grown film is shown in Figure 3. Paper [10] claimed that “only unambiguous fingerprint in Raman spectroscopy to identify the number of layers for graphene on SiC(0001) is the line width of the 2D peak.” FWHM of 2D Raman peak for our sample is 40 cm^{-1} . According to [10], FWHM of 40 cm^{-1} indicates the existence of single-layer graphene on SiC. Intensity of D peak is relatively high which indicates the presence of disorder, such as finite size domains [11], atomic scale defects, and armchair-type edge defects [12]. Additionally graphene film can have large stress due to very fast cooling rate during growth. The stress may be responsible for unusual ratio between intensities 2D and G peaks. Auger spectrum of the grown film is shown in Figure 4. The number of graphene layers on top of SiC was evaluated using the method described in [13] and was also found to be about one layer. Observation of half-integer Quantum Hall effect in the epitaxial graphene fabricated by the same technology and conditions and with the similar Raman spectra confirms the presence of single-layer graphene [14].

3.2. Gas Sensing Performance. In Figure 5 the response of an as-prepared graphene sensor on exposure to NO_2 gas

FIGURE 2: AFM image of $13 \times 13 \mu\text{m}$ graphene surface area (a) and sensor chip with 6 devices mounted on TO-8 holder (b).

FIGURE 3: Raman spectrum of epitaxial graphene. SiC background is subtracted.

FIGURE 4: Auger spectrum of epitaxial graphene.

(exposure periods are marked as grey bands, in 0.2 ppb–2 ppb concentration range) at the room temperature is presented. It is known [3] that epitaxial monolayer graphene is originally *n*-doped. NO_2 is a strong oxidizer, withdrawing electrons from the surface on which it adsorbs. Therefore its adsorption on graphene surface is expected to reduce the density of electrons in the case of *n*-type material, thus leading to the increase in resistivity. Response has integrator-like behavior. Under NO_2 exposure resistivity is increasing linearly with time, slope of the curve being proportional to the NO_2 concentration. When gas exposure is interrupted the resistivity remains practically constant without significant recovery. Such behavior indicates relatively strong bonding of NO_2 molecules to the graphene surface.

The resistivity of the devices had drastically changed from about 30 k Ω to 15 k Ω after annealing of the sensor chip at 120°C in the carrier gas flow. Possible reason for such behavior can be thermal desorption of the contaminations that remained on the sensor surface after fabrication process. In Figures 6 and 7 the response of the annealed graphene sensor on the exposure to NO_2 at the room temperature is presented for the low and the high concentration accordingly. Response of the annealed sample has become about tenfold stronger as compared to that of the as-prepared sensor.

In the ppb concentration range, due to short exposure time and relatively low NO_2 concentration, there are no visible signs of saturation on the response curve; in the same way as for the as-prepared sensor the linear increase in resistivity was observed during exposure. The slope of

FIGURE 5: Response on exposure to the gas mixture containing NO_2 (exposure periods are marked as light grey bands) at room temperature for as-fabricated graphene based sensor.

FIGURE 6: Response on exposure to the gas mixture containing NO_2 in the low concentration range (exposure periods are marked as light grey bands, annealing periods as dark grey, and recovery periods as hatched bands) at room temperature for the annealed graphene based sensor in the low concentration range. Knee on response curve is highlighted by two additional lines.

the response curve being proportional to the NO_2 gas concentration is presented in Figure 8. In order to recover the initial sensor condition annealing at 120°C was applied after each exposition period.

Starting from 2 ppb of NO_2 concentration the small knee appears on the response curve (see Figure 6), which may indicate the existence of two different types of adsorption centers: low-energy adsorption centres of graphene (sp^2 -bonded carbon) and high-energy adsorption centres like oxygen group and defects [15, 16]. The concentration of structural defects and therefore possible presence of high energy centres can be relatively high according to the Raman spectrum (Figure 3).

When the graphene sensor is exposed to the lower concentrations of NO_2 (see Figure 6), the adsorption centers

FIGURE 7: Response on exposure to the gas mixture containing NO_2 in the high concentration range (exposure periods are marked as light grey bands, annealing periods as dark grey, and recovery periods as hatched bands) at room temperature in the high concentration range.

FIGURE 8: Dependence of the response curve slope on NO_2 concentration. The values were calculated for the first 10 minutes of exposure by the gas mixture containing NO_2 .

with high binding energy are occupied first. As soon as they are filled, the centres of adsorption with low binding energy start to play major role in gas response. This hypothesis is supported by the recovery behavior of the sensor after exposure to different concentrations of the NO_2 gas: after exposure to low concentrations the response curve is nearly horizontal (Figure 6, hatched bands after exposure periods with 0.2, 0.5, and 1 ppb concentrations), which indicates no desorption due to the strong binding of NO_2 molecules, while at higher gas concentration the desorption becomes significant, which indicates weaker binding energy (Figures 6 and 7 hatched bands after exposure periods with 2 ppb, 0.1, 0.2, and 0.5 ppm concentrations).

Changes in carrier concentration and mobility of the graphene film were measured by means of Hall effect during

FIGURE 9: Changes in the carrier mobility (solid line) and concentration (dashed line) during the exposure to the gas mixture containing 10 ppb of NO_2 . Sample was annealed at 120°C before measurements.

exposure to the gas mixture containing 10 ppb of NO_2 and the results are presented in Figure 9. The measurements were done at room temperature and the sample was annealed at 120°C before measurements. The dependencies of charge carrier density and mobility on the time of exposure exhibit two different regions: in the beginning of exposure to NO_2 gas the carrier density decreases and mobility increases, while further exposure leads to gradual reversing of both parameters. It can be supposed that there are two types of scattering centers, with high and low energy, and in the beginning of the adsorption process NO_2 molecules passivate the defects (with high adsorption energy) on the graphene surface and thus reduce scattering of the carriers that in turn leads to initial increase in mobility. During further exposure the NO_2 molecules adsorb on pristine surface of graphene (low-energy centers). In this case, according to [17] the acceptor states are almost entirely localized at the adsorbed NO_2 molecule and the associated carriers have a considerably lower mobility than those in the graphene bands. It should make the carrier mobility in the graphene device decrease with time of NO_2 exposure. Indeed we have observed almost linear decrease in mobility with exposure time in the region of the higher exposure time (Figure 9).

As it is seen from Figure 7, at higher (more than 0.1 ppm) NO_2 concentrations, when adsorption centers are rapidly occupied, the response starts to follow the Langmuir adsorption law with saturation at higher exposures. At the concentration of 1 ppm the inversion of the carrier type from n to p was observed with the simultaneous change of the response direction. Similar effect was reported in [3]. Change in the polarity of Hall voltage during the exposure confirms the inversion of the majority carrier type. We should emphasize here that the “high” concentration in our experiments which is in range 0.1 ppm–1 ppm corresponds to “low” or even “ultralow” NO_2 concentration reported in most of publications [3, 18]. It means that our sensor is 2–3 orders more sensitive. One of the reasons for such an excellent performance is that we have used annealing at 120°C after each exposure. In [3, 18] the authors observed initial large

FIGURE 10: Slope of the response curve versus NO_2 concentration in three different measurement cycles (shown by different symbols). The values were calculated for the first 10 minutes of exposure by the gas mixture containing NO_2 .

resistivity change after first contact with the gas containing NO_2 . Then next exposures showed significantly smaller changes. As reported in [18] adsorption centers with high binding energy were responsible for a first resistivity jump. In next stages of exposure those centers are completely filled and do not participate in gas response because the recovery time is quite long. On the contrary, the annealing at 120°C returns the initial condition of the sensor surface as shown in Figure 6. In Figure 9, the most significant change of mobility and carrier concentration is in the beginning of exposure, when high-energy centers participate in the adsorption process. Another reason for the outstanding performance of our sensor is the high concentration of high-energy centers in our samples. It is possible that these two factors make our sensor extremely sensitive to NO_2 . The similar sensitivity was reported in [19] where authors have used additional UV irradiation for NO_2 desorption. UV irradiation may be capable of efficiently removing strongly bonded NO_2 molecules.

3.3. Reproducibility. The reliability of the sensor was measured by monitoring its response over a period of several days. In Figure 10 slope of the response curve versus NO_2 concentration is plotted for 3 measurement cycles. It was observed that the response was very stable and reproducibly repeated in several measurement cycles supporting potential application of graphene based device as a gas sensor.

3.4. Interference with Humidity Change. In order to investigate influence of humidity on the sensor's response on exposure to NO_2 , the humidity level was changed from 0.01% to 50% RH during the NO_2 exposure period (Figure 11). Increasing of humidity mediated the simultaneous increase in the response by about 1%; however slope of the response

FIGURE 11: Response on exposure to the gas mixture containing NO_2 (exposure periods are marked as light grey bands) at different humidity levels, high humidity pulse marked as hatched band at room temperature. Slope of response curve is highlighted by additional lines.

curve returned to the same value of 0.03%/min after about 15 min. Decreasing the humidity back to initial value did not recover the initial slope of the response curve, but it decreased to the value 0.021%/min, probably due to slow desorption of the water vapor at room temperature. These results mean that change of humidity from 0.01% to 50% (from 2.3 ppm to 12000 ppm) mediates change in the response of only 30%. Thus the selectivity to the water vapor could be estimated as 83000.

3.5. Detection Limit. The improved contacts layout with double layer metallization in our sensors shows significantly better stability as compared with conventional single-layer contacts. Devices with single-layer metallization usually exhibit noticeable level of ripple and step-like resistivity change due to poor metal adhesion to graphene layer, while modified devices show very stable and flat response curve. In order to find the noise-limited sensitivity of the sensors, variations in conductance due to the random system noise and drift were measured. The RMS noise fluctuations were found to be in the range $\pm 0.0004\%$. The instrument detection limit IDL (according to IUPAC) is the smallest concentration or absolute amount of analyte that has a signal significantly larger than the signal arising from a reagent blank. It can be given by expression: $S_{IDL} = S_{Blank} + 3 * \sigma_{Blank}$, where S_{blank} is signal for reagent blank and σ_{Blank} is deviation for reagent blank signal. Since 0.5 ppb NO_2 gives a response of 1%, the noise limited resolution of the sensor was estimated as 0.6 ppt (parts per trillion). This is more than sufficient for application in sensing of environmental pollution by nitrogen dioxide.

4. Conclusions

In summary, we have fabricated the ultrasensitive sensors for NO_2 , based on epitaxial graphene. The contact shape has

been optimized in order to obtain low level of ripples during thermal cycling, typical for the gas sensing application. The as-fabricated devices demonstrate inferior sensitivity as compared with annealed samples, which may be due to surface contamination after fabrication steps. Devices annealed at 120°C are extremely sensitive to NO_2 exposure down to sub-ppt level. The extreme sensitivity is thought to be due to activation of the adsorption centers with the high binding energy. Those centers are believed to give the major contribution to the response in the low concentration range. Sensor annealing after exposure seems to be a simple and reproducible method to improve the sensing performance of a graphene based gas sensor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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