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Characterization of epitaxial and CVD graphene with double metal-graphene contacts for gas sensing

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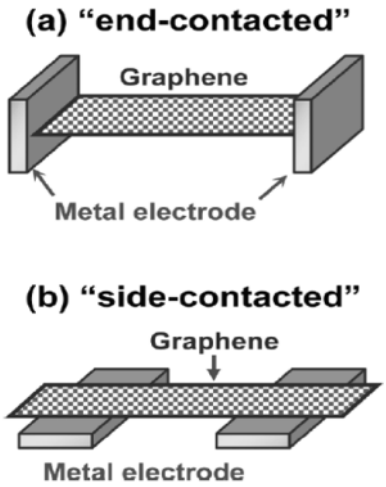
Abstract. Graphene is the promising material for the gas sensing application. High sensitivity to the nitrogen dioxide and ozone allows application of the simple graphene based devices for the environmental monitoring. The aims of the work were the fabrication of reliable graphene devices and the comparison of epitaxial and CVD-based graphene sensors for their sensing abilities. In order to increase sensitivity and reliability of graphene sensors the optimization of fabrication technology as well as operation parameters was done. Results demonstrated ultra high sensitivity of the fabricated epitaxial sensors upon exposure to NO_2 and ozone gases.

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 unique two-dimensional structure.[1,2] Adsorption ability and wide surface area of graphene make it attractive as a gas sensing material. In late years, interest for the air pollutants and their monitoring has been growing in our life. Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are typical air pollutants that cause environmental problems. There are demands for a small and cheap gas sensor for NO detection in medical field and its basic research area. From this point of view, it is necessary to develop high sensitive and inexpensive NO_x gas sensors to detect low concentration NO and NO_2 gases. Currently, gas sensing experiments have demonstrated epitaxial graphene to be an excellent material for developing NO_2 sensors. Graphene layers grown on SiC have demonstrated sensitivities down to parts per billion (ppb) levels, and shown high selectivity for NO_2 detection with respect to typical interfering gases [3].

However, the low adhesion of the graphene to the buffer layer on the SiC surface leads to their detachment along with the underlying graphene layers upon processing [3]. Instability of the contact resistance between metal and graphene layer limits the precision of the gas concentration measurement. A critical property for graphene based devices is the contact resistance at the metal-graphene interface. In [4] there were reported calculated contact resistances for the "end contacted" (Figure 1a) and "side-contacted" metal electrode (Figure 1b). For side-contacted interfaces it was found a decrease in contact resistance by factors ranging from 6751 for Au to 8.8 for Ti.

Figure.1. (a) Metal-graphene "end-contacted" interface. (b) "Side-contacted" interface.



This suggests a strong advantage for developing technology to achieve "end-contacted" interface. In this work we have studied devices with high fraction of "side-type" interface. We also have developed the contact fabrication technology with the good adhesion to the substrate and graphene layer.

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2. Experimental methods

Gas sensors were made from the epitaxial graphene films, which were grown by annealing single crystal 4H-SiC substrates in Ar ambient at temperature near 1600ºC. The size of chip with 6 devices was 5x5 mm. Depending on annealing time, temperature and quality of the wafer, the graphene films can contain 1-3 layers as was confirmed by Auger spectroscopy measurements. Raman spectroscopy measurement showed the presence of defects in multilayer graphene structures while single layer samples exhibit spectra typical for perfect graphene layers. CVD graphene films on oxidized silicon substrate were purchased from Graphene Supermarket (Graphene Laboratories Inc.) [https://graphene-supermarket.com] The size of chip was 10x10mm. 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. Ti/Au (5/50 nm) contacts were made by e-beam evaporation and lift-off photolithography using a laser writer over AZ5214 resist. Chip was assembled on TO-8 holder together with heater. For measurement 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 ϕ=0,02%) air by utilizing two step dilution system based on mass flow controllers (Aera FC-D980). The dilution ratio could be varied in the range 1:1–1:10^5, providing an output concentration in the range of 0.01 ppb to 10 ppm. For measurement of a sensor response to ozone, the calibrated source of ozone (Thermo Scientific Model 49i-PS), ozone meters, (Enviromix Gas system Calibrator 6100, and gas analyser (Thermoscientific Model 49i) were used for the gas generating and the measurement of the output concentration. Response of all 6 devices was measured simultaneously, using multichannel data acquisition system. Response, r, was expressed as a percentage, %, and defined as the relative change of the sample's resistance under exposure to the gas, $r = (R - R_o) / R_o$, where R is the resistance when the gas is applied, and R_o is the resistance of the graphene film under the initial conditions defined by the flow of the incoming air.

3. Experimental results

Sensor optimization was performed in three ways:

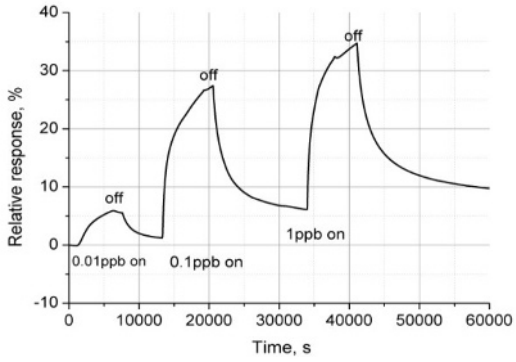
1. Annealing parameters were optimized in order to obtain graphene layer with the maximum sensitivity to NO_2.
2. Contact configuration and composition were optimized in order to obtain lowest and stable contact resistance in long time period and wide temperature range
3. Operation parameters like temperature, additional UV irradiation and post-exposure annealing were adjusted for the best performance.

In our previous study it was found [5], that the most sensitive devices were based on double layer graphene. We have associated such behavior with large amount of defects in such layer which can act as adsorption centers. Later we have utilized chips with the high quality single layer graphene devices which were oriented along atomic steps, using data, obtained by AFM.

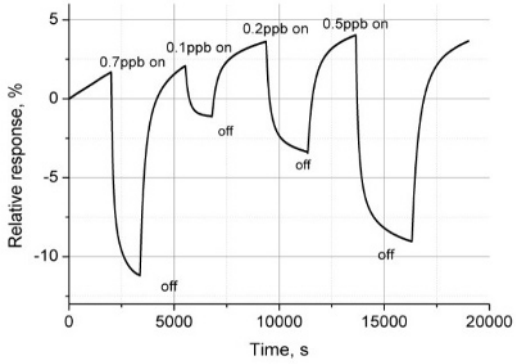
In Figure.2 the gas response of prepared single (a) and double layer (b) graphene sensors at the temperature 100°C is shown.

Figure 2. Response on exposure of gas mixture containing NO_2 gas at 100°C for monolayer (a) and double layer (b) graphene based devices.

a)



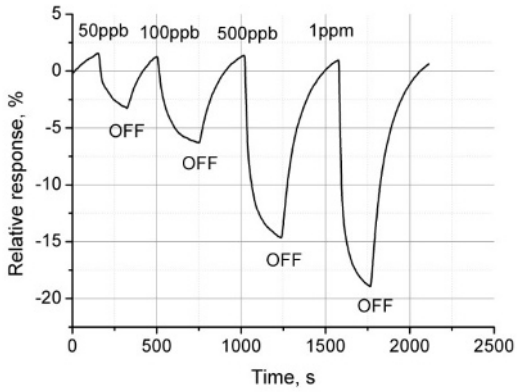
b)



Sensors have opposite sign of response, which is related to the different type of conductivity: n-type for single layer graphene and p-type for double layer. NO_2 is a well known strong oxidizer with electron withdrawing capability, and thus takes away electrons from the surface on which it adsorbs. Therefore its adsorption on graphene layers is expected to reduce the density of electrons for n-type of material, this causes increasing of resistivity. On the other hand for the p-type material resistivity decreases due to NO_2 adsorption. Both sensors are very sensitive to NO_2 gas exposure, especially based on oriented single layer graphene. It shows the response 5% at NO_2 concentration as low as 0.01 ppb. Response of the sensor based on double layer graphene about 10 times less than one based on single layer. Probably orientation along the

atomic steps is the critical issue for the sensor performance. In any case the sensitivity of investigated sensor to NO_2 gas is much higher than was previously reported in [3,6]. In Figure 3 the gas response of double layer graphene sensors to ozone exposure at the temperature 120°C is shown. Due to high chemical activity of ozone, it is difficult in the current setup to control reproducibly the gas concentration in sub-ppb range. That is why the minimal ozone concentration was set to 50 ppb. Sensitivity to ozone seems not as high as to NO_2, but still enough for the environmental monitoring. In EU, the current target value for ozone concentrations is 60 ppb [7].

Figure 3. Response on exposure of gas mixture containing ozone at 120°C for double layer graphene based device.

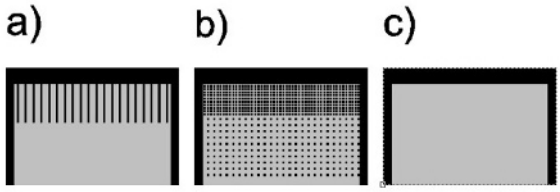


Value of response is proportional to the gas concentration in the wide (50ppb-1ppm) range.

Response of CVD graphene based devices on NO_2 exposure is significantly smaller, as compared to response of epitaxial graphene based devices and typically is a few percents for NO_2 concentration in ppm range.

In order to evaluate the optimal contact configuration three different contact types in first metallization (shown as black color) which is directly bonded to the substrate were used: narrow metal fingers, metal dots inside metal-graphene contact area and simple flat contact configuration. Second metallization always covered the area shown in Figure 5 as grey color overlapping the first metallization.

Figure 5. Finger (a), dot (b) and flat (c) contact configurations

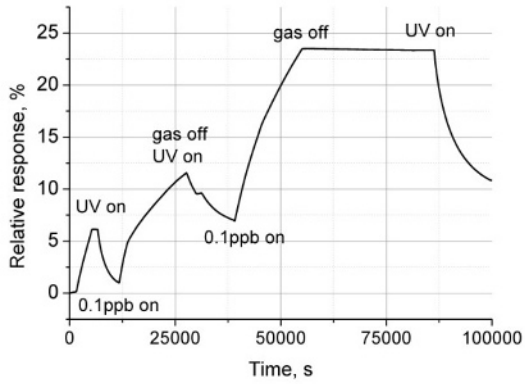


We expected larger fraction of "end type" contact fraction and therefore lower contact resistance for configurations with fingers and dots. Additionally, metallization on top of graphene (shown as grey color) has much shorter bridges between strong bonded to substrate areas of first metallization (shown as black lines or dots). It makes less probable exfoliation of metal from graphene during thermo-circling. Also, 3 devices have carbon layer between metal and graphene. Sensor resistivity measurement showed that devices with improved contact shape have less resistivity than those with the simple shape. Device with dot-like contact shape showed lowest resistivity, which is in agreement with the larger fraction of the end-type interface. However the level of gas response was about the same for all types of contact. Devices with carbon underlayer exhibited higher resistivity compare devices without carbon.

We have reported in [5] that the full recovery of the graphene based sensor is slow at the room temperatures. For single layer graphene based sensor the recovery time is several days. Increasing the operation temperature from 25ºC to 100ºC reduces recovery time to about one-two hours (Fig.2). Another promising method for fast recovery is the UV irradiation of the sensor surface with the help of AlGaN LED or short annealing at elevated temperature. In Figure 6 response of the single layer based sensor to exposure 0.1 ppb of NO_2 gas is shown.

Figure 6. Response on exposure of gas mixture containing 0.1 ppb NO_2 gas at 20°C and recovery under UV irradiation (a) and annealing at 100°C (b) graphene based devices.

a)



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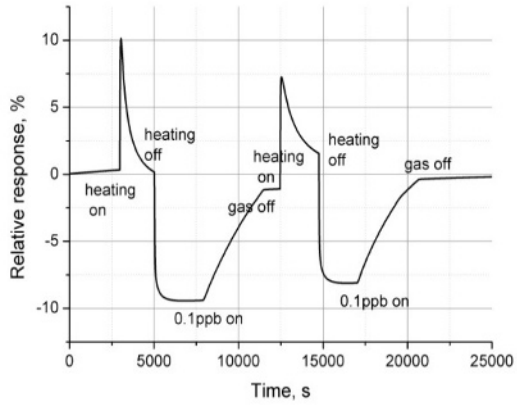


At the room temperature the value of response (resistivity) does not saturate in the reasonable period of time. When the exposure interrupted the resistivity of the sensor remains practically constant. Irradiation of the surface by (370 nm 0.75 mW) UV LED allows to recover

the sensor resistivity in relatively short period of time. However resistivity does not return to the value which was before the first exposure (Figure 6 (a)). Much better results shows flashing the sensor after exposure at the temperature 100°C. In Figure 6 (b) response on exposure of gas mixture containing 0.1 ppb NO_2 gas at 20°C and recovery after annealing at 100°C are shown. Recovery becomes much faster and the resistivity returns to similar value after each annealing circle.

The reliability of the sensor was measured by monitoring its response over a period of several days. In Figure 7 response to ozone in various concentrations in 4 measurement cycles is shown. 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.

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 results are shown in Figure 7. The peak-to-peak fluctuations were found in the range ± 0.0025% while the drift was 0.01%. Since 0.01 ppb NO_2 gives a response of 5% the noise limited resolution of the sensor can calculated as ~ 5 ppq (parts per quadrillion) and drift limited ~ 20 ppq. This is more than sufficient for application in environmental pollution sensing.

Figure 7. Response on exposure of gas mixture containing ozone at 120°C in 4 measurement circles (marked with different symbols)

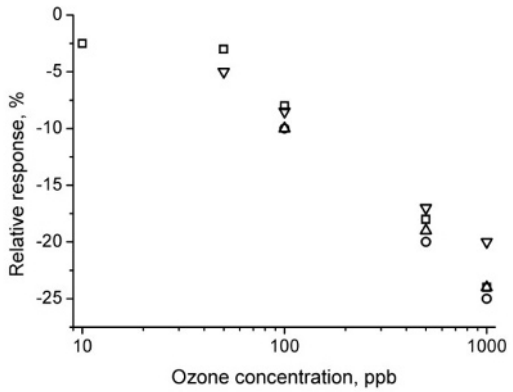
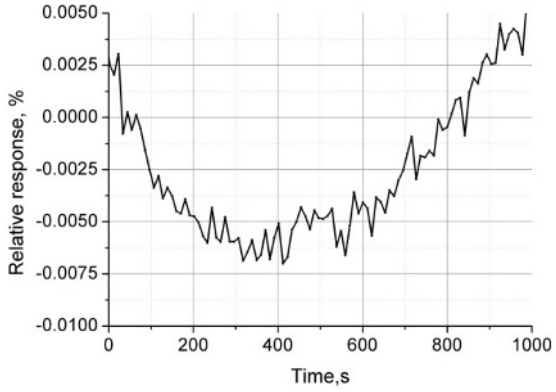


Figure 8. Noise and drift of a graphene based device.



Conclusions

In summary, simple resistive devices, based on epitaxially grown graphene were fabricated and tested on their sensitivity to NO_2 and O_3 gases. Graphene layers and the contact configuration were optimized in order to obtain the best performance. Devices are extremely sensitive to low concentrations of NO_2 down to ppq range. Response and recovery times are slow at the room temperature, but can be significantly reduced with operation at the elevated temperature or by additional irradiation by UV light.

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