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Graphene based sensor for environmental monitoring of NO₂

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Abstract

Ultrasensitive gas sensor based on epitaxial graphene on SiC has been fabricated. The sensor exhibits strong and reproducible response to nitrogen dioxide (NO₂) in the concentration in air down to 1 part-per billion (ppb). Prototype of the transportable device for environmental monitoring allows fast and reproducible measurements of NO₂ concentration in the range typical for environmental pollution (5 ppb – 50 ppb).

Keywords: nitrogen dioxide; graphene

1. Experimental details and results

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]. High 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 dioxide (NO₂) is typical air pollutants that causes environmental and health problems. From this point of view, it is necessary to develop highly sensitive and inexpensive gas sensor, able to detect low concentrations of NO₂ gas. Currently, gas sensing experiments have demonstrated that epitaxial graphene can be an excellent material for future NO₂ sensors. Graphene layers grown on...
SiC have demonstrated sensitivities down to ppb level, and shown high selectivity for NO$_2$ detection with respect to typical interfering gases [2, 3].

Graphene films were grown on 6H SiC wafer, (obtained from Nitride Crystals Inc.) by annealing in Ar ambient at temperature 1700°C. 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. Raman and Auger spectroscopies confirm existence of single-layer graphene on the sample surface. Ti/Au contacts to graphene were made by E-beam evaporation and lift-off photolithography. Patterns for the sensor devices were made on graphene surface using RF-plasma etching. Sensor chip (size 1.5 mm x 1.0 mm) was assembled on a holder together with Pt100 resistor, which was used as a heater. Suspended construction of the sensor (Fig.1a) has low thermal inertia and allows fast thermal circling. Sensor together with sampling system and computer interface were assembled into the unit suitable for mobile monitoring of NO$_2$ concentration (Fig.1b).

In Fig.2 the block diagram of the measurement setup is presented. Procedure of the measurement of the gas concentration consist of 3 main stages: regeneration, stabilization and exposure to the sampling gas. Pump (1) provides the gas flow through the sensor (2). During regeneration and stabilization the three way valve (3) directs the ambient air flow through the charcoal filter (4) which eliminates nitrogen dioxide from the incoming gas. Pure air is necessary for successful regeneration of the graphene sensor surface. Desorption rate of nitrogen dioxide from graphene surface is very slow at room temperature. In order to recover the sensor to its initial condition an annealing at 110°C was applied after each exposition period. This method significantly increases sensitivity to low
nitrogen dioxide concentrations [3]. Since sensor mostly operated at room temperature, it has low power consumption. During the sampling time three way valve replaces purified air to sample gas (5).

Gas mixtures containing NO\textsubscript{2} were prepared by Sonimix 600A gas dilutor manufactured by LN-Industries. Verification has been performed with Apna 360 Horiba Scientific chemiluminescence analyzer. For other gases the custom made gas system was used. Sample gas was mixed with dry (relative humidity RH=0.02%) or humid air by utilizing two stage dilution system based on mass flow controllers (Aera FC-D980) and liquid injection system. The dilution ratio could be varied in the range 1:1–1:10\textsuperscript{6}, providing an output concentration in the range of 0.1 ppb to 100 ppm. 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.

In Fig.3a the response of graphene sensor on exposures to gas mixture containing NO\textsubscript{2} gas (exposure periods are marked as grey bands), in 20ppb and 50ppb concentration range at the room temperature is presented. Under low NO\textsubscript{2} exposure the resistivity was increasing approximately linearly with time. At higher exposures response curves became to deviate from linear law, indicating possible saturation [3]. In order to eliminate effect of saturation, in the typical measurement circle, the exposure was interrupted when the responses were changed by 1% from initial value. Since graphene sensor has very high signal to noise ratio [3] this limitation practically does not affect the sensitivity. The sample gas concentration was calculated from the slope of the response curve using linear fitting of the temporal response during sampling time. In Fig.3b the response of graphene sensor on short exposures to gas mixture containing NO\textsubscript{2} gas (exposure periods are marked as grey bands), in 10 ppb – 50 ppb concentration range at the room temperature is presented. Slope of curves is being proportional to the applied NO\textsubscript{2} concentration. In Fig.4a the verification of graphene based gas sensor is presented. In that figure the dependence of the measured by developed sensor NO\textsubscript{2} concentration and by Horiba Scientific gas analyzer for two measurements circles is presented. Device exhibits good linearity and reproducibility for NO\textsubscript{2} concentration range, typical for environmental monitoring.

![Fig.3. (a) Long measurements of NO\textsubscript{2} concentration in air. Exposure periods for 20 ppb (black line), and 50 ppb (green line) of NO\textsubscript{2} are shown as light and dark grey bands. Annealing period shown as hatched band. (b) Short measurements of NO\textsubcript{2} concentration in air. Exposure periods for 10 ppb (black line), 30 ppb (red line) and 50 ppb (green line) of NO\textsubscript{2} are shown as light, medium and dark grey bands. Annealing period shown as hatched band. Response curves for 30 ppb and 50 ppb are shifted on 0.5% and 1% respect to 10ppb curve in vertical direction.](image)

One of the main problem that hinder the development of commercial graphene-based sensors is a response to the variation of humidity levels present in the environment. Graphene based sensor may have poor selectivity like other non-functionalized sensors to water vapor or other gases. The response to humidity change from 0.01 to 10\textsuperscript{\%}RH (3-3000ppm) is shown in Fig4a. In Fig.4b the response on exposure to other important pollutant: ammonia (red line) is also presented. Sensor shows practically no response to humidity change and only minor response to 50ppm of NH\textsubscript{3}. Sensor also was tested on sensitivity to acetone, isopropanol and toluene at concentration range up to 100ppm and did not show any sign of response.

In summary the graphene based sensor for environmental monitoring has been developed. The device show...
excellent reproducibility and selectivity to NO$_2$. Sensor due to its low cost and low power consumption shows great potential for ultrasensitive detection of NO$_2$.

Fig. 4. (a) NO$_2$ concentration measured by graphene sensor versus true concentration measured by gas analyzer. Black triangle correspond result of the first measurement circle, white triangles second measurement circle, solid line linear approximation. (b) Response on exposure to water vapor (black line) and ammonia (red line). Exposure periods shown as light grey band, annealing as hatched band.

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