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journal homepage: www.elsevier.com/locate/snbHighly sensitive and selective detection of NO₂ using epitaxial graphene on 6H-SiCMd.W.K. Nomani^{a,*}, Razib Shishir^a, Muhammad Qazi^a, Devendra Diwan^a, V.B. Shields^b, M.G. Spencer^b, Gary S. Tompa^c, Nick M. Sbrokekey^c, Goutam Koley^a^a Department of Electrical Engineering, University of South Carolina, Columbia, SC 29208, USA^b Department of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14853, USA^c Structured Materials Industries, Inc., Piscataway, NJ 08854, USA

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ABSTRACT

Epitaxial graphene grown on SiC substrates is one of the most promising methods for achieving large-area uniform graphene films. Our experimental results demonstrate that graphene layers grown on both the Si and the C-faces of semi-insulating 6H-SiC can offer very high NO₂ detection sensitivity and selectivity, as well as fast response time. Exposure to only 500 ppb NO₂ reduced the conductivity by 2.25%, while 18 ppm caused a reduction of 10%. In contrast, high concentrations of commonly interfering gases, namely, CO₂ (20%), H₂O (saturated vapor), NH₃ (550 ppm), and pure O₂ increased the conductivity by a maximum of 2%. Graphene on the C-face of SiC resulted in somewhat lower sensitivity for the test gases, with the conductivity changing in an opposite direction compared to the Si-face for any particular gas. The conductance changes due to molecular adsorption were correlated with changes in the surface work function (SWF). Measurements conducted at higher temperature showed significantly higher changes in conductivity and shorter response times.

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1. Introduction

Recently, there has been an increased demand for cost effective, highly sensitive, and selective gas sensing devices that can be easily integrated in smart sensor networks. One very important application is the detection of environmental pollutants and toxic gases released from power plants, chemical industries, fertilizer plants, and automobiles. Traditionally, transition metal oxides such as In₂O₃, SnO₂, ZnO, and WO₃ have been used for sensing a large variety of these toxic gases, volatile organic compounds, and chemical warfare agents [1–4]. Such oxides, however, suffer a serious drawback, which is a strong dependence of their critical sensing parameters on growth methods and process conditions. In the past decade, carbon nanotubes (CNTs) have been used for sensing a wide range of analytes including atmospheric pollutants, chemical warfare agents, and volatile organic compounds, where the sensing mechanism is based on changes in conductance [5–7] or capacitance [8].

Since its first demonstration in 2004, graphene, a two-dimensional (2D) monolayer of sp²-bonded carbon atoms, has attracted huge interest among researchers, due to its distinctive mechanical, thermal, and electrical properties [9–12]. In partic-

ular, graphene exhibits remarkably high electron mobility as the charge carriers resemble Dirac fermions, and electron transport in graphene remains ballistic up to 0.3 μm through ambient condition [9]. Other significant properties include carrier-density-dependent conductivity, anomalous quantum Hall effect, and minimum quantum conductivity [13–16]. These unusual properties of carriers in graphene stem from its unique band structure, which exhibits conduction and valence bands with near-linear dispersion that touch at the Brillouin zone corners to make it a zero bandgap material.

For successful development of graphene-based nanoelectronic devices and sensors, availability of high quality and large-area graphene films is necessary. Several processes, both physical and chemical, have been proposed to obtain graphene. Mechanical cleavage of graphite was initially used to produce single-layer graphene sheets [13]. However, this approach offers no control over the number of graphene layers, and is an inefficient process that is not suitable for large-scale production. Graphene is also reportedly obtained by reducing from graphene oxide (GO) [17]. However, hydrazine, a toxic and unstable compound, used for the chemical reduction in this process, was found to introduce extra nitrogen functional groups on graphene surface, which can affect the sensing response [18,19]. Furthermore, chemical vapor deposition (CVD) has been described in the literature to produce large-area graphene films, but a purification process is needed to eliminate the catalyst particles and obtain clean graphene sheets [20]. Recently, growth of graphene layers with sizes up to 10 mm × 10 mm on copper foils

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at 1000 °C by CVD of carbon using a mixture of methane and hydrogen has been reported [21]. However, in this technique transfer of the synthesized graphene film to another substrate is necessary.

Recently, epitaxial graphene on SiC has been shown as a viable route for mass-production of uniform, wafer-size graphene layers particularly for technological applications although graphitization of SiC by Si sublimation was demonstrated as early as the 1960s [14,22–24]. At present, this technique results in very high quality graphene films, whose size is limited basically by the size of SiC substrate. This technique also offers the possibility of integrating graphene-based sensors with SiC-based high temperature integrated circuits. In this article, we demonstrate a high-performance gas sensor based on epitaxial graphene grown on both Si and C-faces of SiC, using both amperometric and potentiometric sensing techniques. Our experiments clearly demonstrate the superior capability of graphene-based sensors to operate in harsh environments at high temperatures.

Gas sensing by epitaxial graphene is generally attributed to the adsorption/desorption of gaseous molecules which act as donors or acceptors on the graphene surface, leading to changes in graphene conductance [25]. Being essentially made of surface, where the whole volume can be exposed to surface adsorbents, graphene is highly sensitive to adsorbed molecules. In addition, graphene exhibits low Johnson noise due to its metallic conductivity and fewer crystal defects [15–17,26,27]. All these features are favorably combined in graphene to allow trace level detection of toxic gases.

2. Experimental setup

Graphene samples used in this study were grown epitaxially on CMP polished Si and C-faces of semi-insulating on-axis 6H-SiC substrates by sublimation at high temperature [28]. These substrates were annealed at temperatures ranging from 1300 °C to 1600 °C for 1 h under high vacuum ($<10^{-5}$ Torr) in a resistively heated SiC sublimation furnace lined with graphite insulation [28]. Silicon, due to its higher vapor pressure, sublimates off more easily than carbon and leaves a carbon rich surface behind, which rearranges on the hexagonal template provided by the substrate to form a few to several monolayers (MLs) of graphene. Growth was performed on 1 in. \times 1 in. pieces of SiC, which were then used in the sensing experiments.

Atomic force microscopy (AFM) was used to analyze the surface topology of these graphene samples, while Raman spectroscopy was used to estimate the crystal coherence length and layer thickness [27,28]. The AFM results revealed graphene films grown on the Si-face (rms roughness <1 nm) are smoother than their counterparts on the C-face (>1 nm). Fig. 1(a) and (b) illustrates the AFM images with scale bars for both the faces.

In order to estimate the thickness of our graphene films grown epitaxially on SiC substrate, we used a simple and noninvasive method using Raman spectroscopy, as described by Shivaraman et al. [28]. It was observed that the SiC substrate Raman signal gets attenuated in intensity by the graphene layers grown on top of it, and this attenuation depends on the graphene film thickness, which can be determined from X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). To distinguish the Raman spectra for grown graphene layers, the scaled spectrum of a pure SiC substrate was subtracted from the spectrum of graphene on SiC. Micro-Raman spectra were recorded using a Renishaw inVia Raman microscope with a 488 nm excitation wavelength. Further details of measurement technique can be found in Ref. [28].

Typical post-subtraction Raman spectra for the samples used in this study are shown in Fig. 1(c). Growth of epitaxial graphene on Si-face of SiC is rather slow and can continue only for short span of time at high temperatures, which ultimately results in thinner lay-

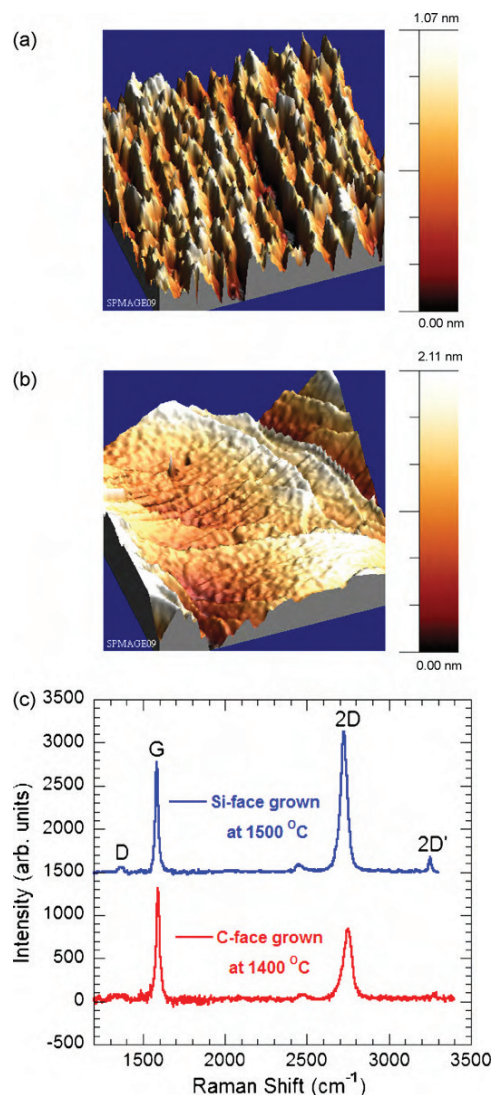


Fig. 1. Atomic force micrographs with height scales for epitaxial graphene films grown on (a) C and (b) Si-face of 6H-SiC. Raman spectrum for epitaxial graphene films grown on (c) C and (d) Si-face of SiC clearly shows graphene peaks, which are used to determine the thickness of the films used in this study.

ers (1–5 MLs) of graphene. On the other hand, graphitization on the C-face of SiC does not self-limit, so relatively thicker layers (5–50 MLs) of epitaxial graphene can be achieved [29]. From the Raman data, the thickness of the Si-face graphene was found to be 4 MLs or less, while that on the C-face was 12–20 MLs. The Raman spectra for the films showed prominent characteristic graphene peaks at ~ 1580 cm^{-1} (G) and ~ 2730 cm^{-1} (2D) along with a minor D peak at ~ 1370 cm^{-1} . The ratio of intensities of the D and G peaks indicates the quality of the material, with lower I_D/I_G corresponds to larger crystal coherence lengths [27]. For all samples grown in this study, the ratio I_D/I_G is <0.1 , with the best samples approaching <0.02 .

2.1. Setup for amperometric measurement

In this work, the sensitivity and selectivity of epitaxial graphene (grown on both Si and C-faces of SiC) for NO_2 detection was investigated by both potentiometric and amperometric measurements. For amperometric measurements, the gas sensing mechanism is

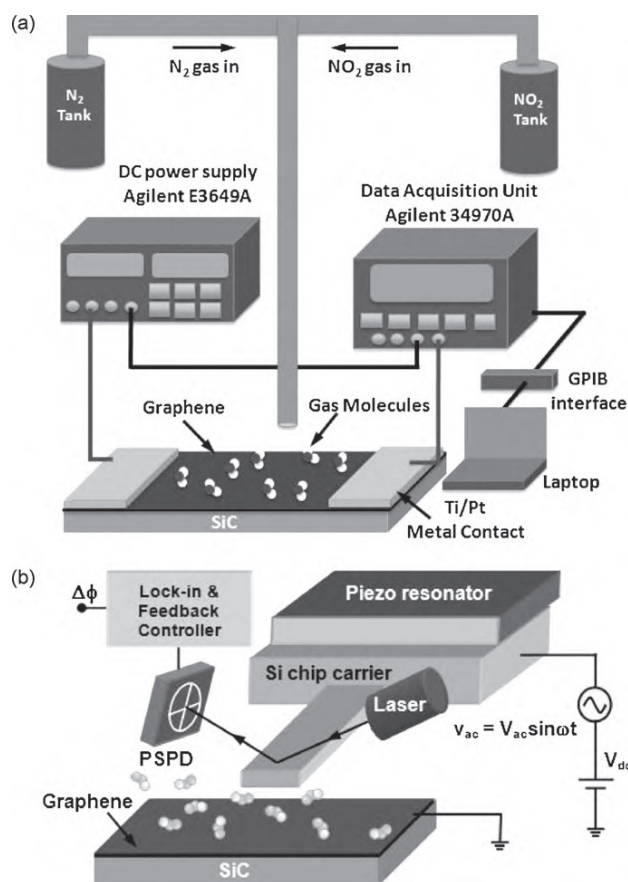


Fig. 2. (a) Amperometric and (b) potentiometric measurement setup for NO_2 sensing.

based on the change in conductivity of the graphene sheets. The measurements were performed on epitaxial graphene layers grown on both the Si and the C-faces of semi-insulating SiC. The sensor devices were fabricated very simply by electron beam deposition of two metal contact pads ($1 \text{ mm} \times 2.5 \text{ mm}$) of Ti (10 nm)/Pt (100 nm) at the two ends of the epitaxial graphene film. The contact pads were connected to the measurement system using spring-loaded mechanical press contacts and coaxial cables. The I–V characteristics for the contacts were found to be linear indicating good ohmic contact formation.

The temporal changes in conductivity of the sensor device were recorded upon its interaction with the test gases. The schematic diagram of the test setup is illustrated in Fig. 2(a). The test gases were passed at the rate of 500 sccm using a gas flow fixture with cross-sectional area of 1.5 cm^2 , positioned within a few mm above the graphene surface. The sensor response (percentage conductance change) is calculated as $(I_g - I_0)/I_0$, where I_g and I_0 are the current between the electrodes with and without the presence of the test gases, respectively.

2.2. Setup for potentiometric measurement

The main advantage of the potentiometric technique is that it is entirely based on the surface properties of the sensing materials. We performed potentiometric measurements using a highly sensitive resonant microcantilever whose oscillation amplitude changes due to adsorption induced SWF changes of the sensing layers. A commercial AFM setup (Autoprobe M5, made by Thermomicroscope) with gold coated tipless Si microcantilever (resonant

frequency 12 kHz and a quality factor of 35) was used to carry out the potentiometric sensing experiments. The experiments were performed under ambient conditions where a piezo-actuator was used to excite the cantilever at a frequency of 13 kHz. The measurement technique has been described in more detail elsewhere [30,31].

In the potentiometric sensing experiments, the desired NO_2 concentrations were again prepared by intermixing calibrated commercial NO_2 with purified N_2 at specific ratios using mass flow controllers (MKS Instruments) as in the amperometric technique. However, the test gases were flown at a lower rate of 200 sccm using a gas flow fixture with cross-sectional area of 1.5 cm^2 which was positioned within a few mm of the sample. The cantilever-sample distance during measurements was kept $10 \mu\text{m}$ during the measurements. The measurement setup with an external ac bias, piezo-actuator, cantilever, and the gas flow tubes are shown schematically in Fig. 2(b).

3. Results and discussion

In our amperometric measurements, large changes in conductance of the epitaxial graphene layers were observed with the flow of different concentrations of NO_2 . Fig. 3(a) shows the percentage conductance change for graphene layer grown on the Si-face of SiC sample with the flow of 18 ppm, 12 ppm, 6 ppm, and 500 ppb of NO_2 . In ambient conditions, 18 ppm NO_2 caused 10% reduction in conductance while for much lower concentration of 500 ppb, the change is 2.5%, which clearly indicates the large sensitivity of graphene layers to NO_2 . Similar high sensitivity was also observed for graphene grown on the C-face where, however, the conductance increased with the flow of different concentrations of NO_2 . As illustrated in Fig. 3(b), 18 ppm of NO_2 increased the conductance

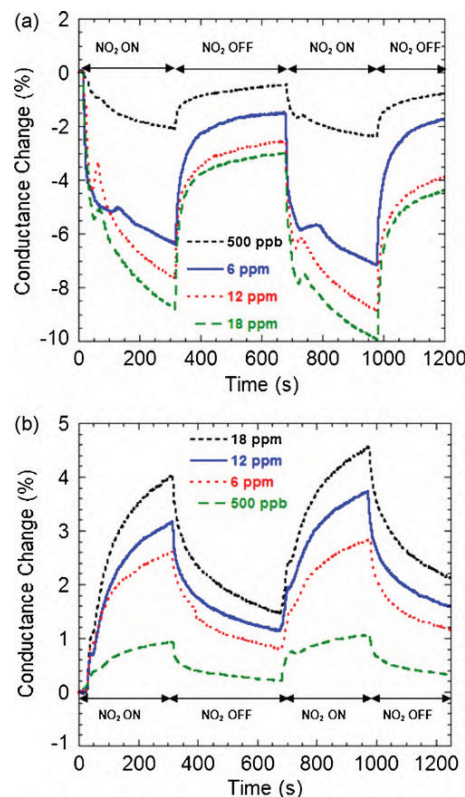


Fig. 3. The percentage conductance changes of epitaxial graphene layers grown on (a) the Si-face, and (b) the C-face of SiC for the flow of different NO_2 concentrations.

by 4.5%, while a lower concentration of NO₂ of 500 ppb showed a conductance change of 1%. The significantly higher percentage of conductance change for the Si-face compared to the C-face can be attributed to the presence of lesser number of graphene layers on the Si-face compared to the C-face.

It is worthwhile to compare the performance of the current sensor with NO₂ sensing results obtained with graphene films prepared by thermally reducing graphene oxide, and mechanically exfoliated ones. Mechanically exfoliated graphene has shown ~4.3% increase in conductance for 1 ppm NO₂ [25], whereas a conductance change for reduced graphene oxide (GO) of 12% has been reported upon 40-min exposure to 2 ppm NO₂ [32]. Assuming a linear relationship between conductance change and NO₂ concentration, the conductivity change can be expected to be ~2.1% in the former case, and 3% for the later, for 500 ppb NO₂. Our results indicate a change of 2.5% for 500 ppb with 5 min exposure time. Comparing these results, it is quite obvious that our overall sensor performance utilizing epitaxial graphene is better than those utilizing mechanically exfoliated graphene or reduced graphene oxide. Incidentally, the change in conductance is also much larger than that observed earlier using mechanically exfoliated graphite layer coated on a ceramic substrate, where the conductance only changed by ~2.5% for 8 ppm NO₂, and 1.1% for 1.5 ppm NO₂ [33,34].

The opposite conductance change due to NO₂ observed for the Si and C-faces, needs to be examined in more detail. Graphene is a zero bandgap material where the Fermi level may encroach either the conduction or the valence band, resulting in ambipolar presence of charge carriers [9]. Its n-type or p-type behavior is determined by the charge carriers that play a dominant role in conduction. NO₂ 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. As per our observation for the Si-face (Fig. 3(a)), this causes decrease in the conductance which leads us to infer that graphene layers on the Si-face display an n-type sensing behavior. On the other hand, for the C-face, the conductance increases due to NO₂ adsorption [Fig. 3(b)], which indicates a p-type sensing nature of graphene layer. However, Hall measurements performed on the graphene films indicate that the carrier types on each face of graphene can be either p-type or n-type, with most samples demonstrating an n-type nature. Different conductivity types of epitaxial graphene grown on SiC have also been reported earlier although no specific trend could be observed [35]. Therefore, any correlation between sensing behavior and nature of carriers for a particular face is at best inconclusive at this point. Another notable aspect of Fig. 3(a) and (b) is the effect of NO₂ concentration on recovery time. Although the high concentration of NO₂ resulted in higher conductance change and faster response time, the recovery time was increased, which is most likely due to slower desorption kinetics of the adsorbed molecules, which are adsorbed at much larger numbers for higher NO₂ concentration.

Sensing experiments were also conducted at higher temperatures to investigate the role of temperature on gas sensing. A commercial hot plate (made by Thermo Scientific) was used to vary the temperature from 25 °C to 300 °C. For graphene on both the Si and the C-faces, faster responses with large changes in conductance were observed with increasing temperature as illustrated in Fig. 4(a) and (b). We observe that the change in conductance for the Si-face graphene reaches saturation for the measurement performed at 300 °C. From Fig. 4, the response times (defined as the time taken to reach 90% of the saturation value) are found to be 50 s and 100 s for the Si-face and C-face, respectively, for the 300 °C transients. Moreover, the recovery times (defined as the time taken to reduce 90% of the maximum value) were found to be shorter for higher temperatures, which can be attributed to faster desorption of NO₂ molecules as the temperature increases. An interesting fea-

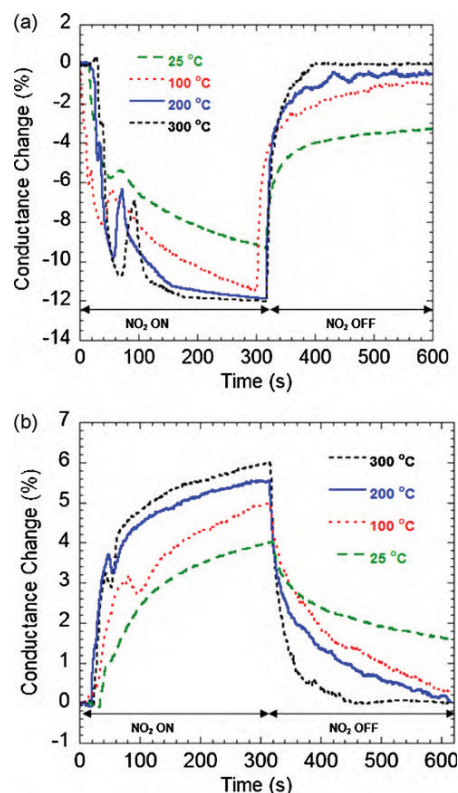


Fig. 4. The temporal conductance change in graphene layers on (a) the Si-face, and (b) the C-face at different temperatures with a flow of 18 ppm NO₂.

ture in Figs. 3 and 4 is the presence of kinks, which were observed shortly after the NO₂ flow started. These are more pronounced and wider at higher temperatures. At this point we are not sure of the reasons for their appearance, however, they are most likely related to the presence of trap states at the surface. More investigations are underway to fully understand this phenomenon. In addition to NO₂, the adsorption of other commonly interfering gases was also investigated. Fig. 5(a) and (b) illustrates the responses of CO₂ (20%), H₂O (saturated vapor), NH₃ (550 ppm), pure O₂, and N₂ on epitaxial graphene layers. The responses are found to be significantly smaller (changed the conductivity by a maximum of 2%), and opposite in sign compared to the NO₂ response.

Further experiments were performed to determine the selectivity of NO₂ detection compared to other major interfering gases. For this, a series of sensing experiments involving various gases were performed at a temperature of 300 °C. Fig. 6(a) and (b) illustrates our sensors response to different gases typically present in an automobile exhaust. In order to determine possible interference from gases in the exhaust, N₂, NH₃, CO₂, O₂ and H₂O were flown over the sensor sequentially, and the changes in conductance were measured. For the Si-face, the effect of these gases on the conductance is not very significant, typically increasing 0.5% for O₂ and N₂, 1.5% for NH₃ (550 ppm), about 1% for CO₂ (20%) and less than 2.5% for saturated H₂O (Fig. 6). However when NO₂ was flown at the end and the conductance changed drastically in the opposite direction. In addition, the transient for NO₂ is much faster compared to the other gases. Although the NO₂ sensor response was not measured when the interfering gases are present simultaneously, considering the magnitude and direction of the sensor response to NO₂ in comparison with the interfering gases, we expect that highly sensitive and selective detection of NO₂ would be possible even when the interfering gases are present simultaneously. Graphene on the

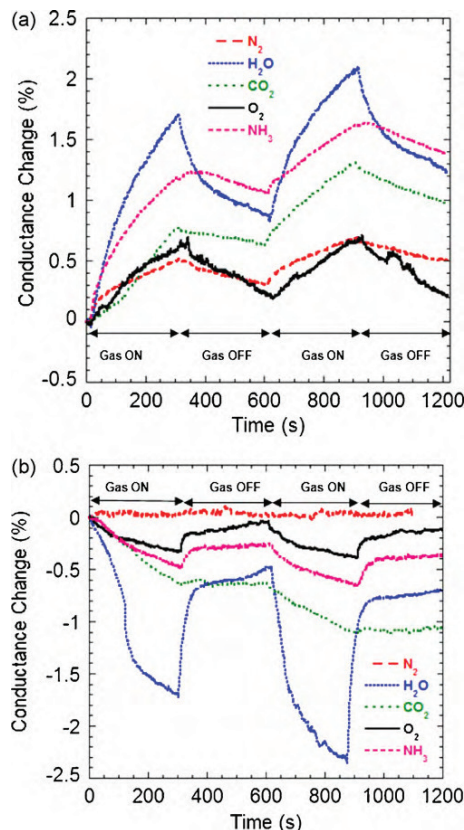


Fig. 5. The change in graphene conductance for (a) the Si-face, and (b) the C-face with the flow of major interfering gases such as N_2 (pure) NH_3 (550 ppm), CO_2 (20%), O_2 (pure), and H_2O (saturated).

C-face of SiC resulted in somewhat lower sensitivity for the test gases, with the conductivity changing in opposite direction for any particular gas.

From Fig. 6 we find that the response of two oxidizing gases NO_2 and O_2 are opposite to one another, which appears contradictory. The interaction of NO_2 with graphene is usually understood based on charge transfer from graphene to NO_2 , as the Dirac point of graphene is higher than the lowest unoccupied molecular Orbital (LUMO) of NO_2 [36]. However, since O_2 is physisorbed on the graphene surface, no charge transfer is supposed to occur between them [37]. Nevertheless, it is possible that flow of pure dry O_2 changes the environment around the sensor from ambient air (containing water vapor and a variety of other gases) to pure O_2 , which produces a small response for the sensor in the opposite direction. Very similar changes are observed by flowing pure N_2 (see Fig. 6), which is another non-interacting gas, corroborating the above argument.

In our potentiometric measurements, we found that the SWF changed significantly when gases were flown through the system. Fig. 7(a) and (b) illustrates the change in SWF of the epitaxial graphene layers with the flow of 18 ppm NO_2 and 500 ppm NH_3 , respectively. We find that the changes occur in opposite directions for NH_3 and NO_2 , which is expected because NH_3 functions as an electron donor contrary to NO_2 [36]. In addition, the magnitude of the change is larger for NO_2 than for NH_3 . For NO_2 , the change in SWF was 155 meV for the Si-face, and 135 meV for the C-face. On the other hand, NH_3 caused only 72 meV and 40 meV changes on the Si and C-faces, respectively. Significantly, the response for either NO_2 or NH_3 for both the Si and the C-face are in the same direction, indicating similar charge interaction

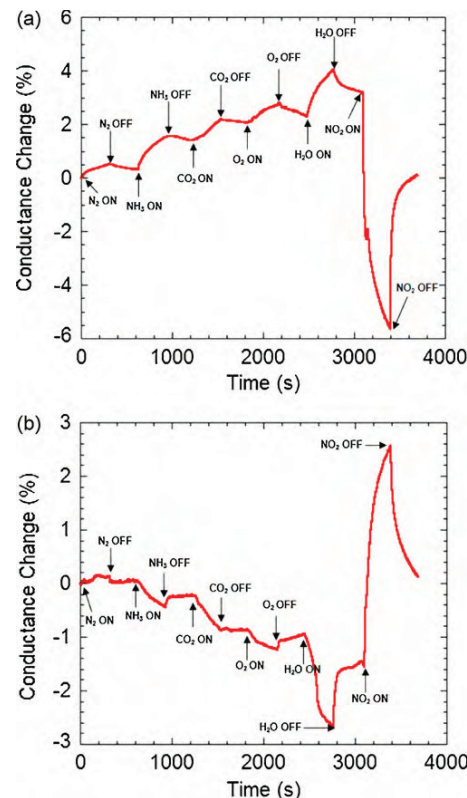


Fig. 6. Highly-selective NO_2 detection using epitaxial graphene films on (a) the Si-face, and (b) the C-face, in the presence of major interfering gases such as N_2 , NH_3 (550 ppm), CO_2 (20%), O_2 (pure), and H_2O (saturated).

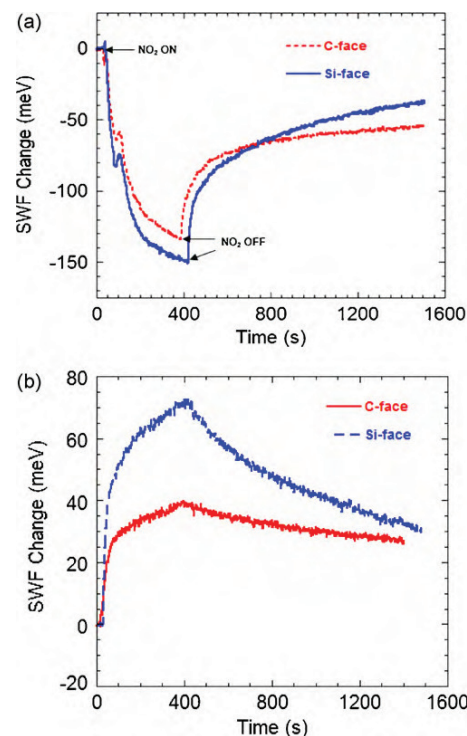


Fig. 7. The SWF changes of epitaxial graphene layers grown on both Si and C-faces of SiC for the flow of (a) 18 ppm NO_2 , and (b) 500 ppm NH_3 .

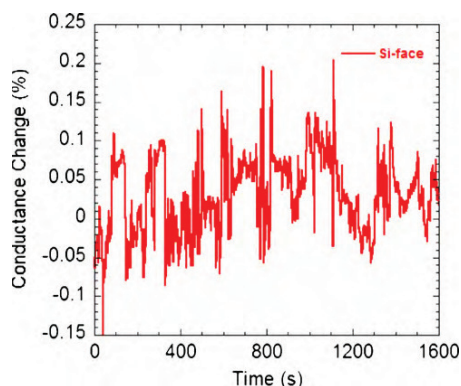


Fig. 8. Noise and stability data for the epitaxial graphene samples (grown on both the Si and the C-faces of 6H-SiC) used in this study.

between graphene and a particular gas. Details will be presented elsewhere.

In order to determine the noise limited sensitivity of the sensors, fluctuation in conductance due to the random system noise was measured. The results are shown in Fig. 8. The peak-to-peak changes were found to be within $\pm 0.2\%$ while the rms noise was 0.05% . Since 500 ppb NO_2 produces a conductance change of 2.5% for the Si-face, the rms noise limited resolution of the sensor is calculated as $\sim 10 \text{ ppb}$. This is more than sufficient for application in automotive exhaust sensing since typical concentration of NO_x gases present in automotive exhaust range from 1 ppm to 10 ppm . The reliability of the sensor was evaluated by monitoring its response over a period of several hours under constant operating conditions. It was observed that the response was very stable confirming the possibility of using it for sensing application.

4. Conclusions

NO_2 sensing experiments utilizing amperometric and potentiometric measurements have demonstrated epitaxial graphene to be an excellent material for developing NO_2 sensors. Graphene layers grown on both faces of 6H-SiC demonstrated sensitivities down to parts-per-billion levels, and showed high selectivity for NO_2 detection with respect to typical interfering gases. Sensing experiments conducted at higher temperature showed faster response and recovery times for the sensor, confirming its robustness and ability to operate in harsh environments at high temperatures. The rms noise limited sensitivity was calculated to be $\sim 10 \text{ ppb}$, which, to our knowledge, is better than any commercial gas sensor available at present. In summary, epitaxial graphene on 6H-SiC exhibited high detection sensitivity, selectivity, and fast response time for NO_2 detection, which makes it a very attractive candidate for automobile exhaust gas sensing applications.

Acknowledgements

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