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Epitaxially grown graphene based gas sensors for ultra sensitive NO_2 detection

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ABSTRACT

Epitaxially grown single layer and multi layer graphene on SiC devices were fabricated and compared for response towards NO_2. Due to electron donation from SiC, single layer graphene is n-type with a very low carrier concentration. The choice of substrate is demonstrated to enable tailoring of the electronic properties of graphene, with a SiC substrate realising simple resistive devices tuned for extremely sensitive NO_2 detection. The gas exposed uppermost layer of the multi layer device is screened from the SiC by the intermediate layers leading to a p-type nature with a higher concentration of charge carriers and therefore, a lower gas response. The single layer graphene device is thought to undergo an n-p transition upon exposure to increasing concentrations of NO_2 indicated by a change in response direction. This transition is likely to be due to the transfer of electrons to NO_2 making holes the majority carriers.

KEYWORDS

Epitaxial graphene, Gas sensor, NO_2, SiC.

1 INTRODUCTION

Sensor devices utilizing epitaxially grown graphene have the potential to bypass the cumbersome removal of graphene and its subsequent re-deposition onto a substrate, thus allowing for simple and reproducible devices. Single layer graphene sensors have every atom at the surface and demonstrate sensitivity down to single molecular level, functioning as low power, room temperature sensors [1]. Their sensitivity is due in part to their high metallic conductivity, even when very few charge carriers are present [2,3]. Thus, changes in number of even a few charge carriers can cause notable changes in conductivity and sensor signal [1]. The high conductivity and few crystal defects of graphene leads to low Johnson [3, 4] and thermal switching noise also referred to as flicker or low frequency (1/f) noise [5]. Recent advances in epitaxial graphene growth [6] may enable mass produced gas sensors with ultra high sensitivity to be realised due to the successfully demonstrated epitaxial growth of single layer graphene on whole SiC wafers.

Graphene exhibits a strong field effect [7] thus making graphene based FET sensors of interest as a method to control carrier concentration and ultimately, sensor sensitivity. Whilst the first layer of carbon in epitaxially grown graphene on SiC has no graphitic electronic properties and acts as a buffer layer, the subsequent graphene layers are n-type due to charge transfer from the SiC substrate to the graphene layers [8], this charge transfer introduces a band gap [9, 10]. With each subsequent graphene layer the band gap decreases from 0.26 eV for the layer closest to the SiC, to negligible by layer four due to shielding of the charges at the interface between the graphene and the SiC substrate [10, 11].

2 MATERIALS AND METHODS

2.1 Graphene growth

The single layer epitaxial graphene used in this study has been shown by low magnetic field measurements to be n-doped due to charge donation from SiC, with the measured electron concentration lying in the range 5×10^{11} to 10×10^{11} cm^{-2} [12]. The concentration of electrons was reduced yet further

by exposure of the graphene to atmospheric oxygen which has been demonstrated to be the atmospheric agent responsible for the p-type nature of carbon nanotubes [13]. Here, multi layers and single layers of graphene were grown on the Si face of 4H-SiC (0001), produced by annealing at 2000 ^{o}C under a gas pressure of 1atm of Ar, as described in Ref. [6]. The production of carbon on the Si face of SiC is slower and more readily controlled than on the C face which allows for homogeneous monolayer graphene, atomically uniform over more than 50 μm^2. AFM studies reveal the carpeting effect of the graphene, which follows the step edges and preserves the structural integrity of the SiC [6]. The multi layer graphene sample was measured by photoelectron spectra to be 30 nm thick, equivalent to 10 atomic layers of graphene. AFM studies revealed that the multi layer graphene is also continuous over the SiC surface and like the single layer graphene, carpets the step edges of the SiC [14].

2.2 Device fabrication

Prototype resistive sensors were fabricated from epitaxially grown single and multi layer graphene. The multi layer devices were prepared by evaporation of interdigitated Cr/Au contacts, 10/250 nm respectively, through a shadow mask. No cleaning was undertaken before contact deposition and no photo resist was required, which may leave a residue on the graphene surface and possibly affect the sensing properties of the graphene [15]. The low adhesion of the graphene to the buffer layer on the SiC surface under the large bond pads led to their detachment along with the underlying graphene layers upon attempting to gold wire bond. This manual removal of bond pads and underlying graphene results in patterning of the graphene and Ti/Au bond pads were subsequently re-deposited on the patterned areas as can be seen in part a of Figure 1. Reliable wire bonding remains challenging due to residual carbon contamination on the SiC surface, as such, for the devices presented, gold bond wires were attached with silver epoxy to the bond pads. Single layer epitaxial graphene devices were also fabricated by adhesion of gold bond wires with silver epoxy, however, without the deposition of interdigitated finger electrode structures onto the graphene. The approximate spacing between electrodes of the multi layer device was 200 μm and 4 mm for the single layer device (See Figure 1). Both devices showed linear

IV characteristics. The devices were glued to a ceramic (Al_2O_3) substrate, containing a thin resistive-type Pt wire, to enable heating of the sensor device. The ceramic heater was mounted onto a 16 pin header with gold plated contacts. The heater is suspended above the header to enable rapid changes in temperature to be made. A Pt100 temperature sensor was also mounted onto the ceramic heater for control of the operating temperature. The devices were contacted through gold wires to gold contacts on the pins of the header. The final devices are shown in Figure 1, c and d.

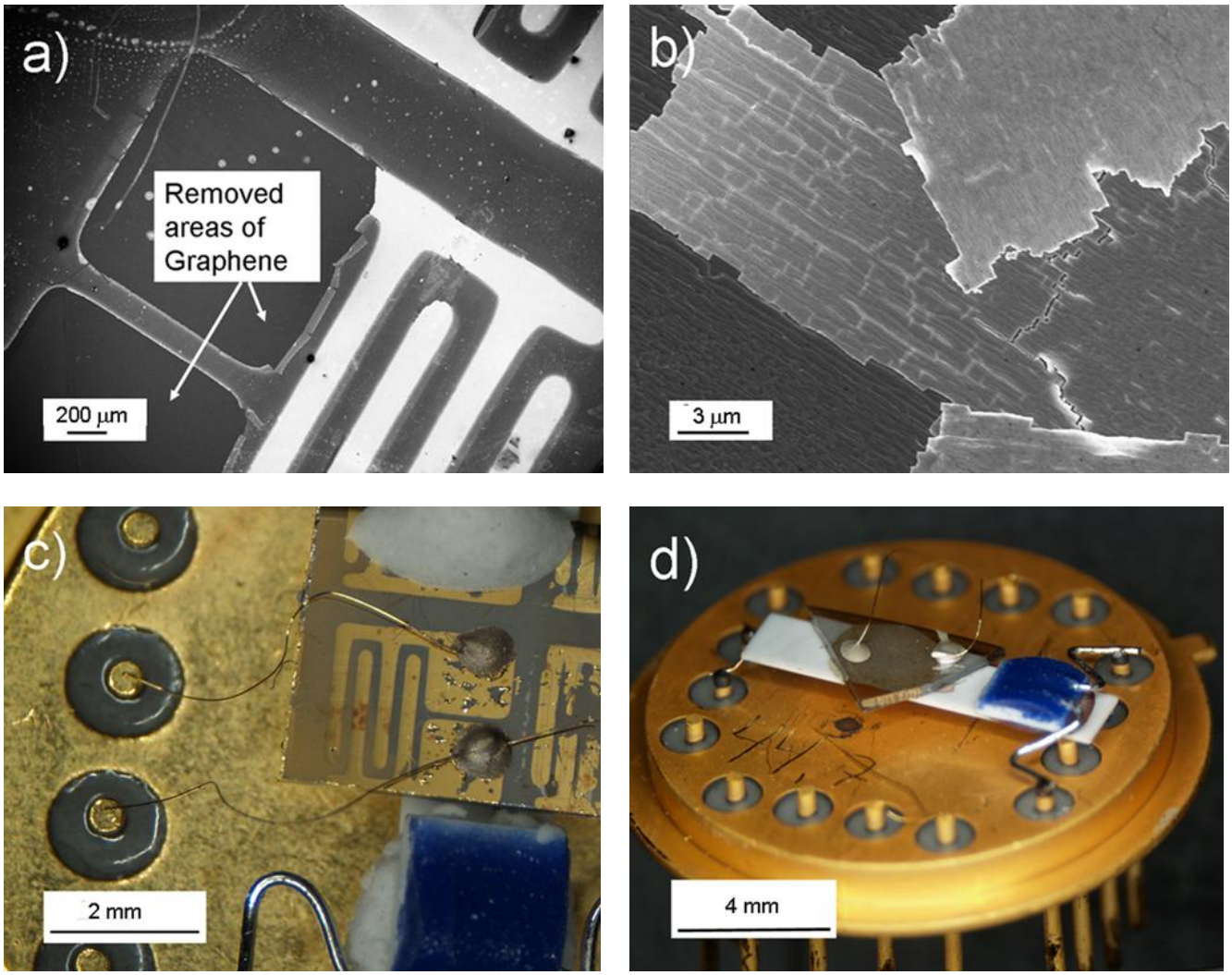

Figure. 1: SEM images showing; a) interdigitated finger electrode structure on multilayer graphene with bond pads and underlying graphene removed. b) SEM image showing flakes of multi layer graphene (light grey) at edge of removed bond pad showing SiC underneath (dark grey). The step edges of the SiC are just visible. c) wire bonded multi layer device on header showing heater and temperature monitor (blue). d) wire bonded single layer device.

2.3 Gas measurements

The devices were exposed to NO_2 in a carrier gas of N_2 and 20% O_2. The gases were mixed with an in-house built gasmixer system comprising of Bronckhorst flow controllers. The devices were held in a stainless steel container with a head space of 1 cm^3 into which the gases were flowed in and out. The flow rate during gas exposure testing was maintained at 200 $mlmin^{-1}$. The resistance of the devices was monitored using a Keithley SourceMeter. A constant current of 0.1 A was maintained over the sensors and the resistance change was recorded. The gasmixer program was controlled using Labview, and the electronics and heating were controlled using in-house built electronics cards with programming carried out in Labview. After each series of gas exposures the devices were heated to encourage desorption of NO_2 from the graphene surface until the resistance was stable, then cooled to 25 ^oC to ensure the original base line resistance had been achieved.

3 RESULTS AND DISCUSSIONS

3.1 Effect of temperature on device resistance

The temperature of the multi layer device was swept between 25 and 150 ^oC at a ramp rate of 10 ^oC per minute under a gas flow of N_2 with 20% O_2 at a flow rate of 100 $mlmin^{-1}$. The resistance of the multi layer device decreased with increasing temperature as shown in Figure 2.

The multi layer device exhibited good stability on sweeping the temperature with only a small shift observed in resistance after the first heating sweep. This initial shift may be due to desorption of adsorbed gases on the surface or annealing of the contacts. In the room temperature range the resistance of graphite is generally thought to decrease with increasing temperature and increase again at temperatures above 1000 ^oC [16]. In some reports the initial resistance decrease is sub linear and in some cases super linear, reversals of the trend are also observed at differing temperatures with the difference probably due to varying defect concentrations arising from the differing production methods

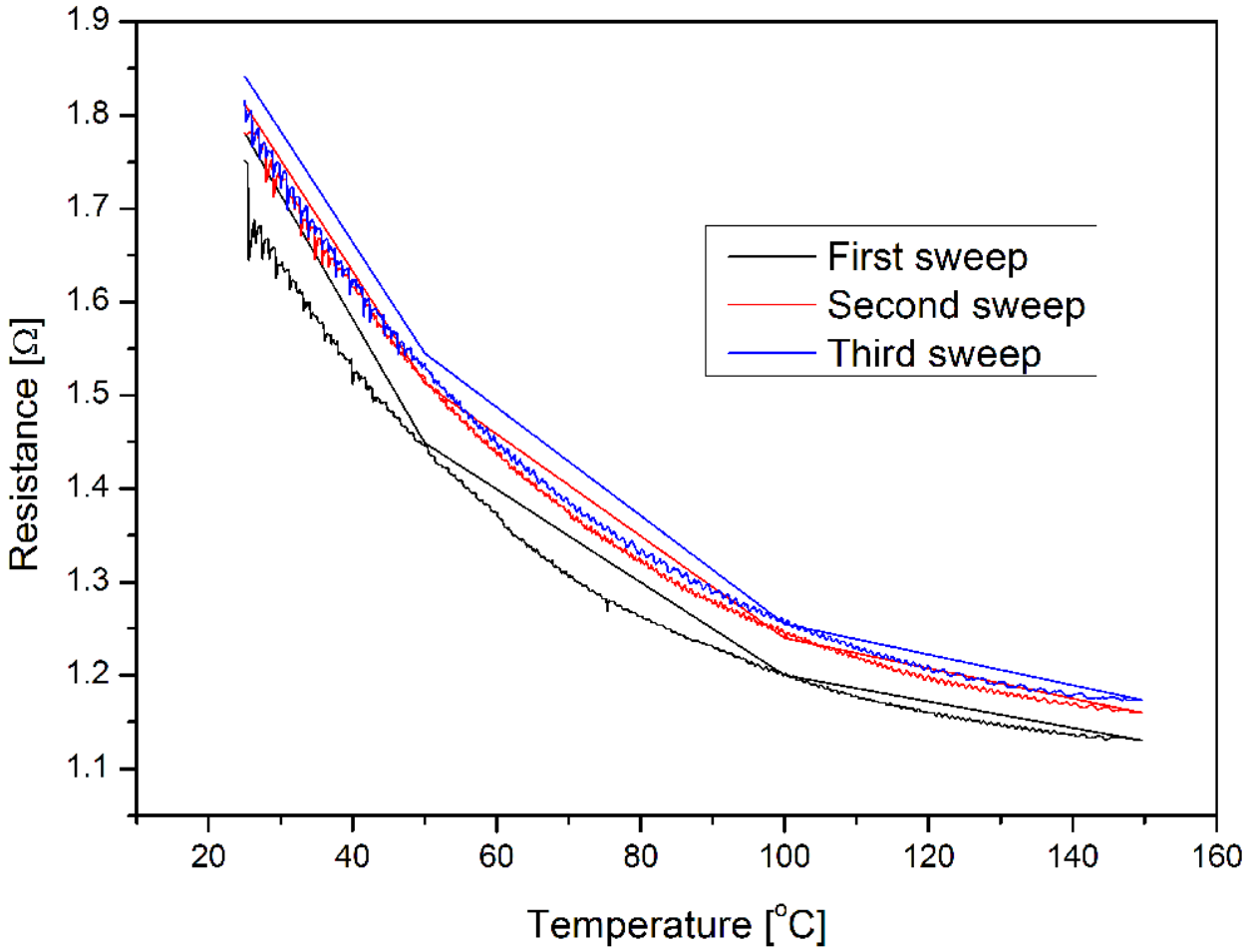

Figure 2: Plot showing change in resistance with temperature of the multi layer device. The heating rate was 10 ^{o}C min^{-1}. The resistance was then recorded on returning to 100, 50 and 25 ^{o}C

[16,17]. A decrease in resistance with temperature is characteristic of intrinsic semi conductors and is generally agreed to be due to the increase in thermally generated electron-hole pairs.

The single layer sensor was slower to respond to changes in temperature than the multi layer sensor and required several hours to stabilise completely at any drastically new temperature making sweeping of the device temperature difficult. The reason for this drift in resistance with changing temperature is not understood at present. The temperature of the single layer graphene device was left to stabilise in N_2 with 20% O_2 at 25, 50 and 95 ^{o}C before measuring gas response (Section 3.3). Unlike the multi layer graphene device the single layer device first increased in resistance then decreased at temperatures above ~80 ^{o}C.

Resistivity measurements on single and double layer graphene on SiO_2 exfoliated from highly ordered pyrolitic graphite and high-temperature, high-pressure grown materials were recently reported [17]. The resistivity was shown to drastically reduce upon heating from 300-500 K [17] with the results obtained for single layer graphene in good agreement with theory [18]. The decrease in resistance at room temperature and above has been proposed to originate from the thermal generation of carriers whilst the shape of the resistance curve is determined by hole scattering on the long and short range disorder and acoustic phonons [18]. Differences in the reported single layer temperature dependant conductivity to that measured here on single layer epitaxial graphene on SiC may be due to changes in electronic band structure of the graphene arising from the differing substrates.

3.2 Multi layer device response towards NO_2

Upon exposure of the multi layer device to NO_2 a decrease in resistance, indicating the device has a majority hole carriers (p-type material), is observed at all attempted temperatures and concentrations. A decrease in response, but improved response and recovery time is observed with increasing temperature see Figure 3 where, in order to compare between responses at different temperatures, the sensor response is plotted as the resistance in test gas/ the resistance in carrier gas (R/R_0). There is a degree of shift to increasing resistances upon NO_2 exposure at elevated temperatures (~100 ^oC). This increase in resistance is permanent and may be due to oxidation of the edges of the graphene sheet.

The response towards 2.5 ppm NO_2 of the multi layer sensor after 1 hours exposure time at 25 ^oC is ~0.01Ω. In comparison the epitaxially grown single layer graphene on SiC sensor (Figures 4 and 5) gave a response of ~ 550 Ω after 1 hours exposure time at 25 ^oC. It is thought that the low response is due to a screening effect whereby current flows through non-exposed carbon layers in the multi layer sensor. It is assumed that the interdigitated finger electrode structure contacts only the uppermost graphene layer as the Ti/Au was deposited through a shadow mask and no high temperature annealing was carried out. The bond pads however may contact several, or possibly all, of the graphene layers as they were deposited over the edge of patterned graphene. Interlayer coupling in multilayer graphene FETs as

compared to single layer graphene FETs has recently been discussed [19] with an increase in current observed in multi layer devices due to contribution from additional parallel conduction paths (graphene layers). The concentration of charge carriers in the uppermost graphene layer may also play a role in the reduced sensitivity of this device. Substrate effects are felt less strongly with each subsequent graphene layer from the SiC and by layer four the graphene no longer has an induced band gap and is no longer expected to be electron doped [10]. Hole doping from atmospheric oxygen [13] adsorbed onto the uppermost layer leads to an increased number of charge carriers reducing the sensitivity of the multi layer device compared to the single layer device, which has only very few carriers [12]. The response of the multi layer graphene device is comparable to nanocrystalline graphitic materials epitaxially grown on SiC [20].

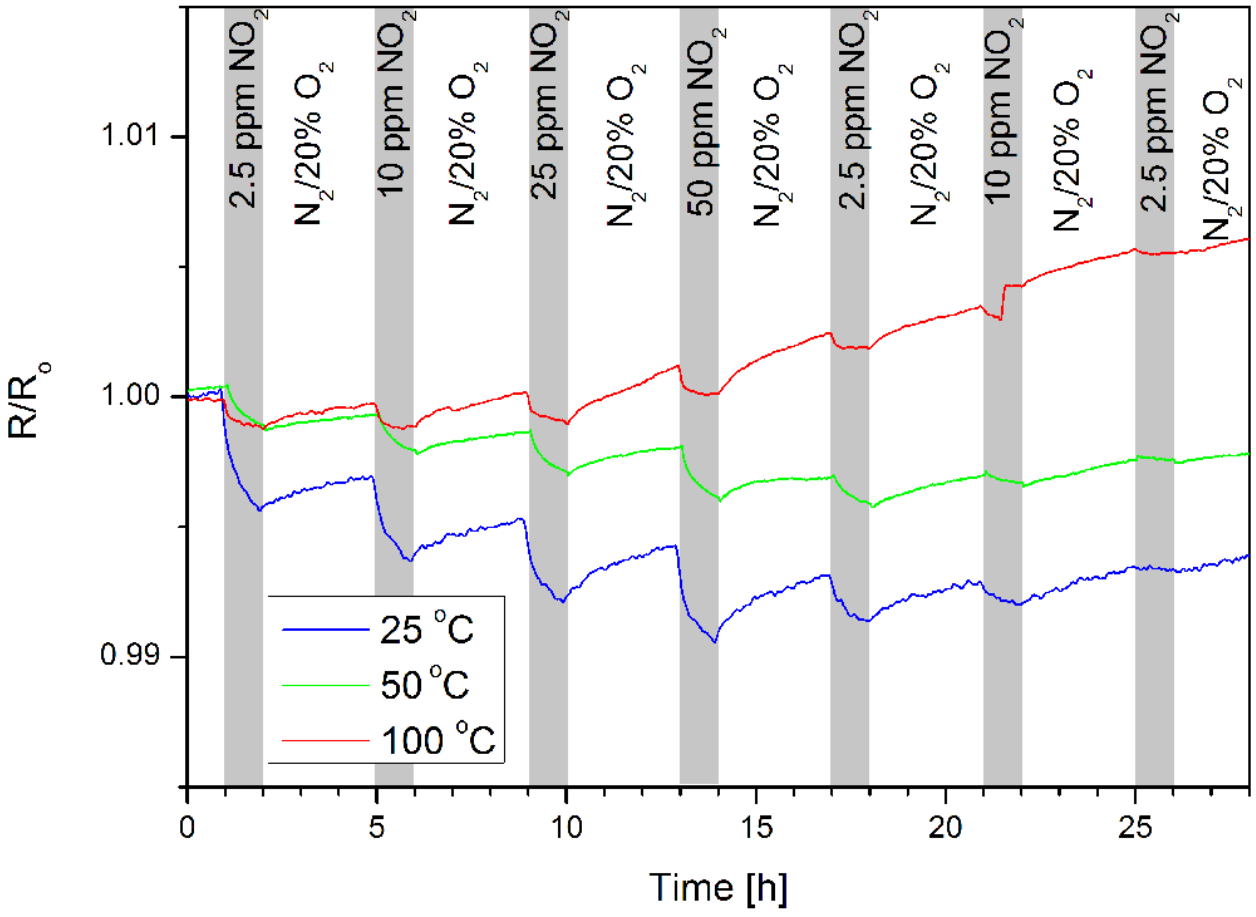

Figure 3: Response of multi layer graphene sensor towards NO_2 pulses at 25, 50 and 100 °C in a carrier gas of N_2 with 20% O_2.

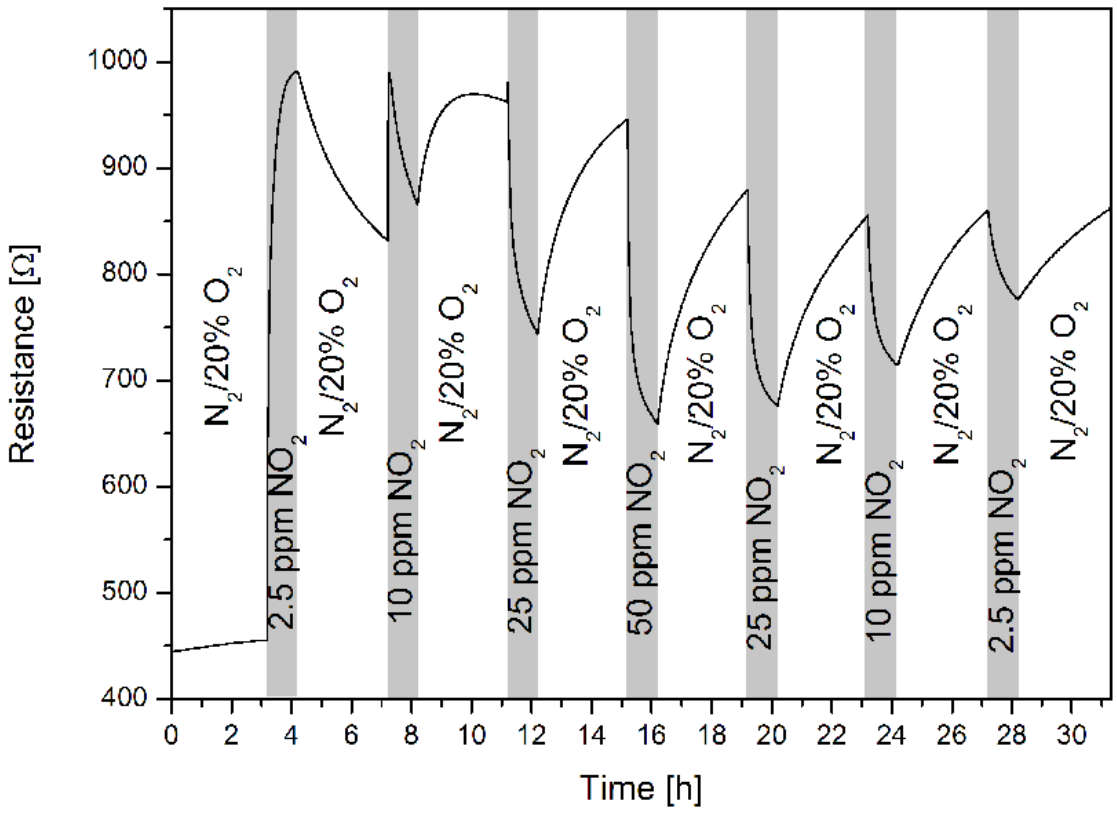

Figure 4: Response of single layer graphene sensor towards NO_2 in a carrier gas of N_2 with 20% O_2 at 25 ^oC. Plot shows change in response direction during the first 10 ppm NO_2 pulse.

3.3 Response of the single layer device towards NO_2

Figure 4 shows the response of the single layer device towards 30 minute pulses of NO_2. At low NO_2 concentrations the device demonstrates an extremely large response, however, a change of response direction is observed upon exposure to more concentrated NO_2. This change in response direction indicates an n-p type shift of the material. It is interesting to note that the direction of recovery after exposure to 2.5 ppm NO_2 is towards lower resistances, however, after exposure to 10 ppm NO_2 (after the shift in response direction is clearly observed) the resistance on flushing with carrier gas first increases then decreases slightly, indicating recovery to the initial response direction upon NO_2 desorption. After sufficient desorption of NO_2 the sensor device reverts back to the response direction expected for an n-type material. The n-p type shift occurs at the same concentration at all attempted

temperatures, see Figure 5, which shows step-wise exposure of the device to increasing concentrations of NO_2.

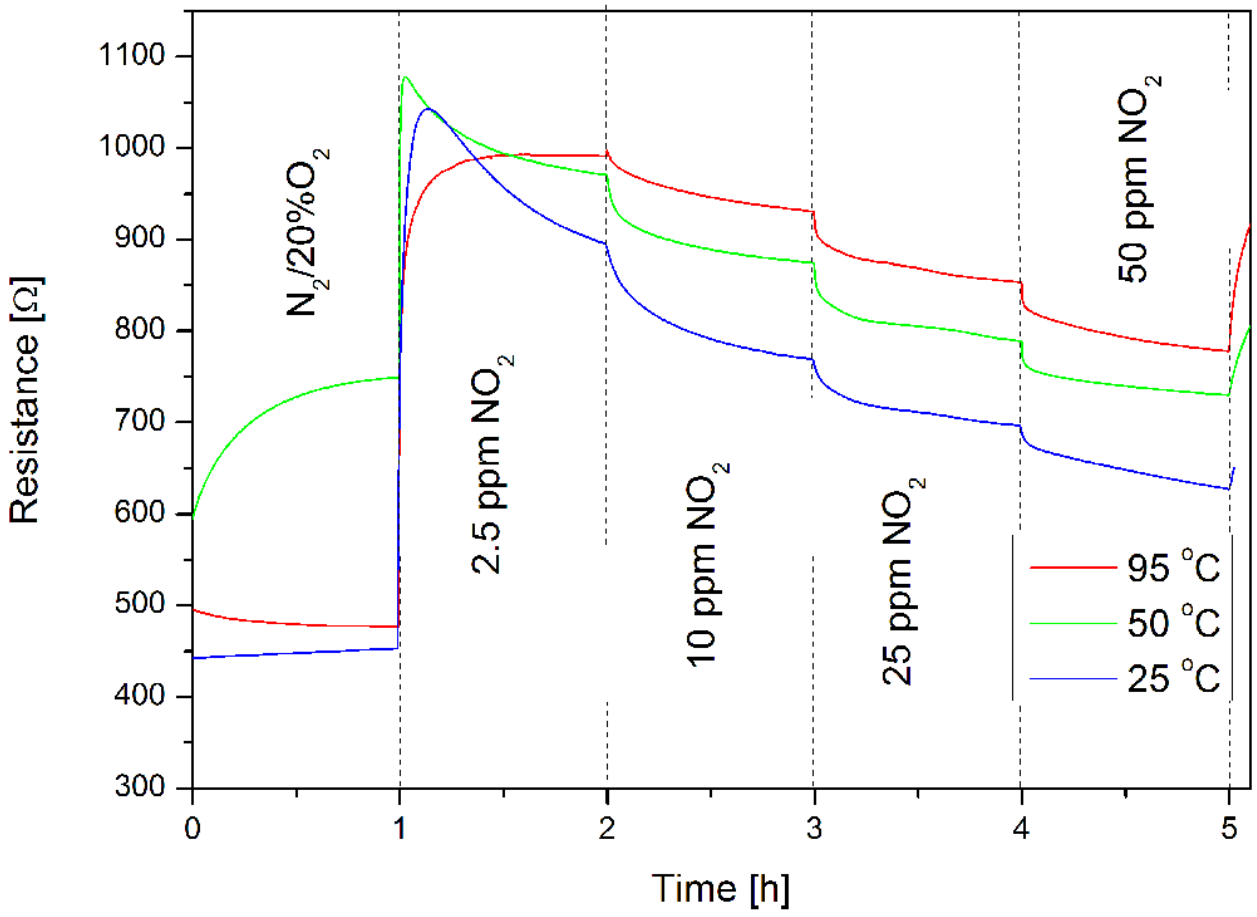

Figure 5: Response of single layer graphene sensor towards stepwise increases in NO_2 in a carrier gas of N_2 with 20% O_2. Plot shows change in response direction with increasing NO_2 concentration.

A decrease in resistance upon exposure to NO_2, indicative of a p-type material, is reported for both CNT sensors [21] and few layer graphene devices at 1 to 10 ppm NO_2 [1]. The single layer graphene measured here is n-type when not exposed to gases due to electron donation from the SiC substrate, albeit with a low carrier concentration [12]. Whilst oxygen binds on the surface removing electrons from the conduction band of carbon materials [13], the single layer epitaxial device remains n-type in nature, but with a yet further reduced carrier concentration. It is thought that this low carrier concentration in the single layer graphene device allows for extremely sensitive detection of low concentrations of NO_2.

Hall measurements have shown that NO_2 adsorption on graphene dopes the graphene with holes [1]. It is postulated here that sufficient electrons are bound on exposure to low concentrations (less than 10

ppm) of electron withdrawing NO_2 to make holes the majority carriers. Indeed it has been theorized that upon NO_2 adsorption on graphene the acceptor states are almost entirely localized at the adsorbed NO_2 molecule and the associated electrons have a considerably lower mobility than those in the graphene bands [22]. The acceptor level is reported to be fully occupied with one electron effectively transferred from the graphene layer for each adsorbed molecule of NO_2 [22]. Furthermore, n-p transitions for a top gated FET structure fabricated from single layer graphene on the Si face of SiC have been reported when the gate voltage was swept to below -20 V [23]. A bias induced n-p shift was also theorized for epitaxial graphene FETs but was reported to only occur on C terminated SiC face [24]. However, the work reported here is to the best of our knowledge the first study of a reversible n-p transition on epitaxial graphene caused by adsorption of an electron withdrawing gas.

4. CONCLUSIONS

In summary, simple resistive multi and single layer epitaxially grown graphene devices were fabricated and tested for NO_2 sensitivity. The multi layer device demonstrates a lower sensitivity which is proposed to be due to conduction through not only the gas exposed uppermost layer. The low sensitivity of the device may also be due to a higher number of charge carriers in the uppermost graphene layer which is screened from the electron donation of the SiC substrate and hole doped by atmospheric oxygen. The single layer graphene device is extremely sensitive to low concentrations of NO_2 and exhibits a switch in response direction, thought to be an n-p type shift of the material, upon exposure to higher concentrations of NO_2. The extreme sensitivity is thought to be due to the low concentration of charge carriers in epitaxially grown SiC. The shift to a direction of sensing of a p-type material at higher NO_2 concentrations is likely to be due to hole doping from the adsorbed NO_2 molecules with the sensing direction of an n-type material regenerated by the desorption on NO_2. It is demonstrated that tuning of graphene's electronic properties is possible by electron donation from the substrate, which can be utilised to achieve extremely sensitive gas detection at the required concentration range.

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VITAE

Ruth Pearce was awarded her Ph.D in 2008 from Imperial College London for research on carbon nanotube gas sensors, as part of which, she worked as an EU funded Marie Curie young researcher at Linköping Univeristy Sweden. Since completing her Ph.D she has been employed at Linköping University Sweden as a post doctoral researcher working in the field of gas sensors.

Mike Andersson received his Ph.D. in applied physics at Linköping University 2007 and completed a Post Doc in sensor science in 2009. He is currently working as a research scientist within the sensor science group at Linköping University as well as within SenSiC AB. His main research interests concern chemical sensors for high temperature and environmental applications.

Lars Hultman, born 1960**,** is head of the Thin Film Division at Linköping University, Sweden. He received a Ph.D in materials physics 1988 from Linköping, did a post-doc at Northwestern 1989, and was as a visiting professor to University of Illinois at Urbana 2004-06. Professor Hultman directs Center-of-Excellence programs in materials science and nanotechnology and is an ERC Advanced Research Grant Awardee. He is an ISI Most cited researcher with 400 publications. In 2003, he was announced Excellent Researcher by the Swedish Research Council. He is Editor of *Vacuum*, Fellow of AVS and FZD-Rossendorf, and elected member of the Royal Swedish Academy of Science.

Anita Lloyd Spetz received her PhD in 1989 at the Laboratory of Applied Physics in Linköping. In 2004 she was appointed Professor in Sensor Science, especially Chemical Sensors. From 1995-2006 she was a project leader at S-SENCE, Swedish Sensor Centre (centre of excellence). From 2007 she is the Vice Director of the VINN Excellence centre, FunMat, Functional nanostructured Materials. Her research group works on development, sensing mechanism and applications of silicon carbide based field effect high temperature sensors. She is also involved in the development of resonator sensors and soot sensors. The applications are performed in projects together with industry (Volvo Technological Development, Volvo Cars, Ford Innovation Center, Selmic Oy, SenSiC, Alstom Power Systems). She is also member of the board in a spin off company, SenSiC AB, for commercialisation of silicon carbide based field effect gas sensors. Anita Lloyd Spetz has published more than 150 papers in scientific journals and referenced conference proceedings, 10 book chapters, she has given 20 invited talks at international conferences and she has 4 patents.

Rositza Yakimova holds a professor position in material science, Linköping University (LiU). She has many years of experience in growth and characterisation of epitaxial layers and nanostructures of wide band gap materials such as SiC, AlN and ZnO. She is an internationally recognized expert in this field and she has been invited to several world recognized universities to share her competence. Since 1993 she has had a leading role in the development of the sublimation growth process of SiC in Sweden. In 2004 Yakimova was awarded a prestigious Individual Grant by the Swedish Foundation for Strategic Research to start up ZnO activities. Yakimova has pioneered a novel method for fabrication of large area epitaxial graphene on SiC. The high quality of this graphene has been evidenced by demonstrating quantum resistance standard based on it [Nature Nanotechnology 5 (2010) 186].

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