



Hydrogen detection using platinum coated graphene grown on SiC

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ABSTRACT

The characteristics of hydrogen detection using epitaxial graphene covered with platinum are reported. The multi-layered graphene was grown by chemical vapor deposition (CVD) on a Si-polar 4H-SiC substrate. Surface morphology was characterized by scanning electron and atomic force microscopy. Current–voltage measurements and real-time monitoring of the current flow through the graphene/platinum device were used to confirm the response to hydrogen gas. The background temperature was varied from room temperature to 175 °C in order to measure the activation energy of hydrogen detection.

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1. Introduction

Graphene is a sheet of carbon atoms arranged in a honeycomb lattice via sp^2 bonds. Due to the delocalized $\pi(\pi)$ bonds of this crystal structure, charge carriers in graphene have zero rest mass and have mobility approximately three one thousandths of the speed of light [1,2]. The excellent crystal and electrical properties of graphene have produced an explosive interest in this material for numerous applications in recent years [3]. One of the promising areas that graphene can be used is in gas sensing. The two dimensional structure of graphene enables all carbon atoms to be exposed to the ambient. High surface-to-volume ratio combined with high conductivity translates into easy detection of molecular disruption on a sheet of graphene [4]. Numerous research groups have reported the use of graphene and related graphitic materials for the detection of gases and vapors. Hydrazine-reduced graphene oxide was used to detect H_2 and CO by Arsat et al. [5]; NO_2 , NH_3 , and dinitrotoluene by Fowler et al. [6]; HCN, chloroethylethyl sulfide (CEES), dimethylmethylphosphonate (DMMP), and DNT by Robinson et al. [7]. Using mechanically exfoliated graphene, Dan et al. [8] detected H_2O , NH_3 , octanoic acid, and trimethylamine, while Schedin et al. [9] studied the detection of NO_2 , H_2O , I_2 , NH_3 , CO, and ethanol. Jung et al. [10] and Lu et al. [11] focused on the detection of H_2O vapors,

and NO_2 respectively, by measuring changes in electrical resistance of reduced graphene oxide. Lastly, Al-Mashat et al. [12] used chemically synthesized-graphene/polyaniline nano-composite to detect hydrogen gas. To the author's knowledge, this is the first paper describing gas detection using epitaxial graphene. Reduced graphene oxide has residual epoxide and carboxylic groups that promote holes into the conduction band as stated in the study by Schedin et al. [9]. This was also confirmed by X-ray photoelectron spectroscopy results [13,14]. Epitaxial graphene does not have these functional groups on the surface [15], so different gas detection characteristics are expected.

H_2 is widely used in industrial applications such as fossil fuel production, metal refining, and hydrochloric acid production. In recent years, applications have emerged in next-generation, hydrogen-based zero carbon emission vehicle technologies. However, safety is a key concern when working with hydrogen. Since hydrogen is subject to explosion risk at concentrations above 4% by volume, it is vital to monitor hydrogen levels and shut down equipment accordingly. The demand for hydrogen sensors with fast response, large detection range, and capability to be deployed in city-scale networks will continue to rise. There are many published results of hydrogen sensors based on splitting of the H_2 molecule in the presence of a catalytic metal such as Pt or Pd [16–20]. Integrating these catalytic metals on graphene is an attractive approach for detecting hydrogen.

In this paper, the response of epitaxial graphene grown on SiC exposed to hydrogen gas is reported. Graphene covered with a thin film of Pt showed reduced resistance in response to the exposure

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to 1% hydrogen at various temperatures. From an Arrhenius plot, the activation energy of the resistance change was calculated.

2. Materials and methods

Epitaxial graphene layers were grown on a Si-polarity 4H-SiC(0001) semi-insulating sample which was placed in a commercially available horizontal chemical vapor deposition (CVD) hot-wall reactor (Aixtron VP508), inductively heated by an rf generator [21]. In situ etching of substrate in the mixture ($\text{H}_2\text{-C}_3\text{H}_8$) was performed prior to growth at 1600 °C temperature range under 100 mbar in order to obtain mono-atomic terraces on the substrate surface. Then, epitaxial graphene was formed by CVD technique on SiC sample using propane gas as the carbon precursor. The growth description as well as characterization results of the graphene including Raman, ARPES, STM methods were published in details previously [22]. The deposition resulted in 2–3 carbon atom layers on the SiC substrate, confirmed by ellipsometry [23]. The conductivity of the graphene layer measured by single post-dielectric resonators [24] was approximately $5 \times 10^5\text{--}5 \times 10^6$ S/m. Fig. 1(a) shows an AFM image of the surface of the bare graphene sample. The surface root mean square roughness measured was 1.827 Å. Metal contacts composed of Ti/Au (10 nm/200 nm) were deposited in an e-beam evaporator through a hexagonally shaped TEM grid (Ted Pella). The side of each hexagon was 160 μm long and each hexagon was separated by a 10 μm gap. Fig. 1(b) is an optical microscope image of the sample after the metal contact deposition. After the contacts were formed, a 5 nm Pt film was deposited to function as a catalyst layer. The sheet resistance of the Pt film was found to be 1000 Ω/square by using a four point probe, which was obtained by loading a glass slice with the same Pt deposition of the real sample. This Ti/Au hexagon pattern and Pt coatings were also deposited on glass slides, so we could measure the responses of hydrogen detection platinum films alone. The graphene device was then mounted on a TO header and wire-bonded for electrical connections. The gas sensing experiments were performed in a sealed quartz tube that has electrical feed-through connections to an HP 4145B parameter analyzer. The resistance change of the sensor was measured upon exposure to nitrogen and 1% hydrogen gases in N_2 while a constant bias was applied. A tube-furnace was installed around the quartz tube to modulate the background temperature during measurements. Gas flows into the tube were controlled by mass flow controllers.

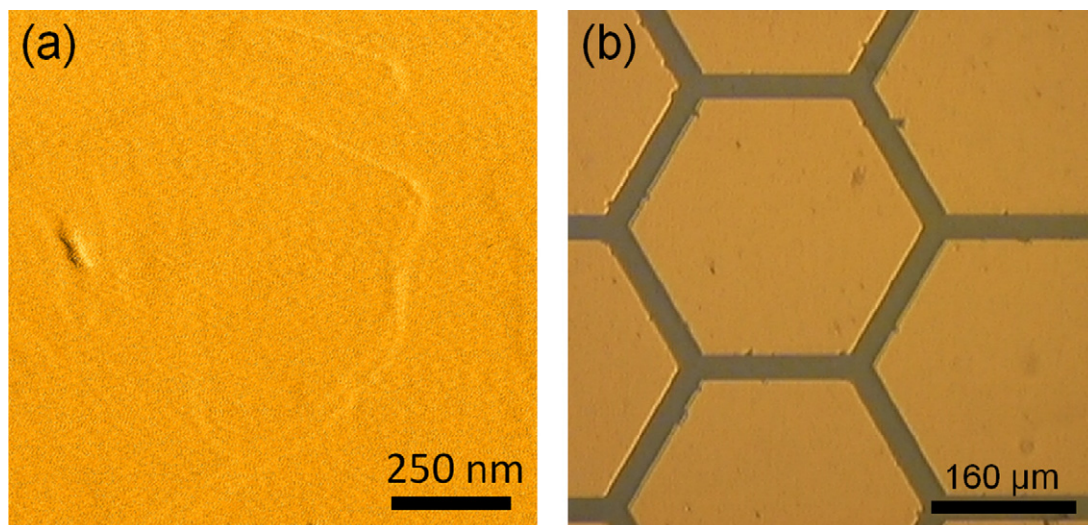


Fig. 1. (a) AFM image of the graphene sample and (b) optical microscope image of the graphene/Pt device.

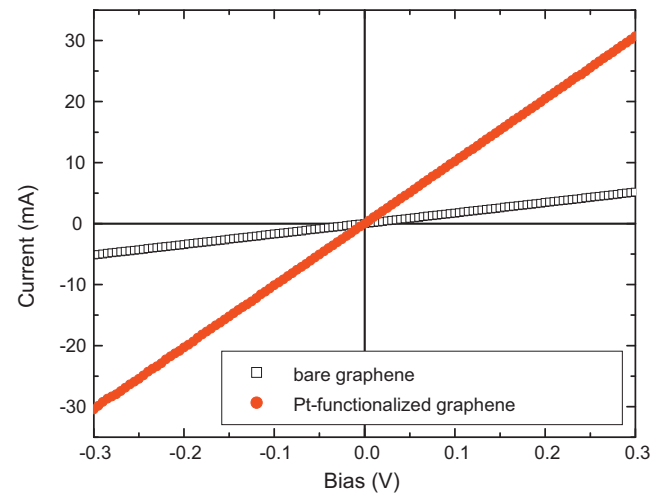


Fig. 2. I–V characteristics of graphene before and after Pt deposition.

3. Results and discussion

Current–voltage (I – V) characteristics measured before and after Pt deposition are plotted in Fig. 2. The device showed Ohmic characteristics, indicating that contact resistance is not a dominant factor. In comparison, previous reports of hydrogen sensors that were based on Pt deposited on SiC showed Schottky characteristics [25]. Interestingly, the conductivity of the device increased significantly after Pt was deposited on the graphene surface. The sheet resistance of the deposited Pt film suggests that the conductance of the deposited Pt film is negligible compared to the conductivity of graphene. Therefore, the conductance increase of the graphene device could be a result of doping. Giovannetti et al. [26] used density functional theory calculations to study the doping of graphene resulting from adsorption of metals such as Al, Co, Ni, Cu, Pd, Ag, Au, and Pt. In the case of Pt/graphene interfaces, the weak interaction preserves the electronic structure of graphene. However, the Fermi-level of graphene is shifted downwards in order to reach equilibrium with Pt. This means that holes from the metal are donated to the graphene, resulting in p-type doping of graphene [26].

In order to accurately estimate the hydrogen detection sensitivity of the Pt coated graphene, the contribution of the hydrogen

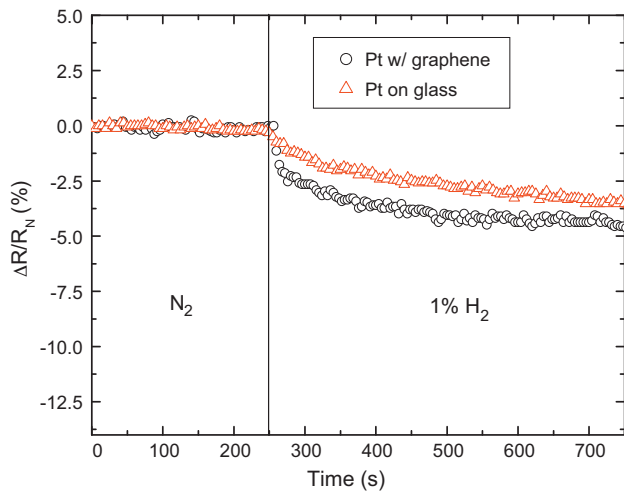


Fig. 3. Resistance change as a function of time for the graphene sensor coated with Pt and reference sensor by depositing Pt on a glass slice during the exposure of the sensors to 1% hydrogen at 175 °C.

detection from the Pt film itself needed to be excluded. Fig. 3 shows a comparison of resistance changes that occurred after exposure to 1% hydrogen for Pt on graphene and Pt on glass. The measurements were conducted at 175 °C under 0.025 V bias. The Pt integrated with graphene had a higher sensitivity towards hydrogen. This result proves that the integration of Pt with graphene enhances the hydrogen sensitivity than bare Pt.

Fig. 4(top) shows the resistance change of the device due to 1% hydrogen at varying background temperatures. The results indicated that exposure to hydrogen decreased the resistance of the device. Dissociated hydrogen atoms will accumulate at the surface of Pt and diffuse into the graphene/Pt boundary. According to a recent review of gas adsorption on graphene by Wehling et al. [27], hydrogen atoms form covalent bonds with graphene. Graphane, which is the hydrogenated form of graphene, will have an increased work function of $\Phi=4.97$, which is 0.2 eV larger than graphene [28]. Possibly the separation distance increase between graphene and Pt can also cause the Fermi-level shift to become larger [26]. Therefore, the free carrier concentrations will increase, raising the conductance of the graphene/Pt device. Results from the work done by Shafei et al. [29], who used a Schottky diode composed of SiC and reduced graphite oxide to detect hydrogen also supports this hydrogen transport mechanism. Hydrogen adsorbed on Pt can form platinum hydride which has a lower work function than Pt [30]. This can possibly reduce the overall conductance change due to hydrogen but is not sufficient to overcome the effects at the graphene/Pt boundary. Further studies are needed to investigate the hydrogen detection response with bare graphene.

The Arrhenius plot shown in Fig. 4(bottom) was used to investigate the activation energy, E_a of hydrogen detection. There were three E_a observed depending on the background temperature: 0.832 eV for 30–60 °C, 0.396 eV for 60–100 °C, and 0.057 eV for 100–170 °C. Hydrogen to graphene binding energies have been published in literature and range from 0.43 eV to 1.44 eV with the majority of the values in between 0.6 eV and 0.85 eV [31]. For lower temperatures, 30–60 °C, the activation energy is within the range of published values. However, E_a becomes reduced at higher temperatures. One possibility for the reduced activation energy at higher temperatures is desorption of hydrogen from graphene. According to the work published by Ryu et al. [32], chemisorbed hydrogen can be detached from graphene by thermal annealing at 100–200 °C. As temperature increases, the number desorbing hydrogen atoms could grow to become similar to the number of adsorbing hydrogen.

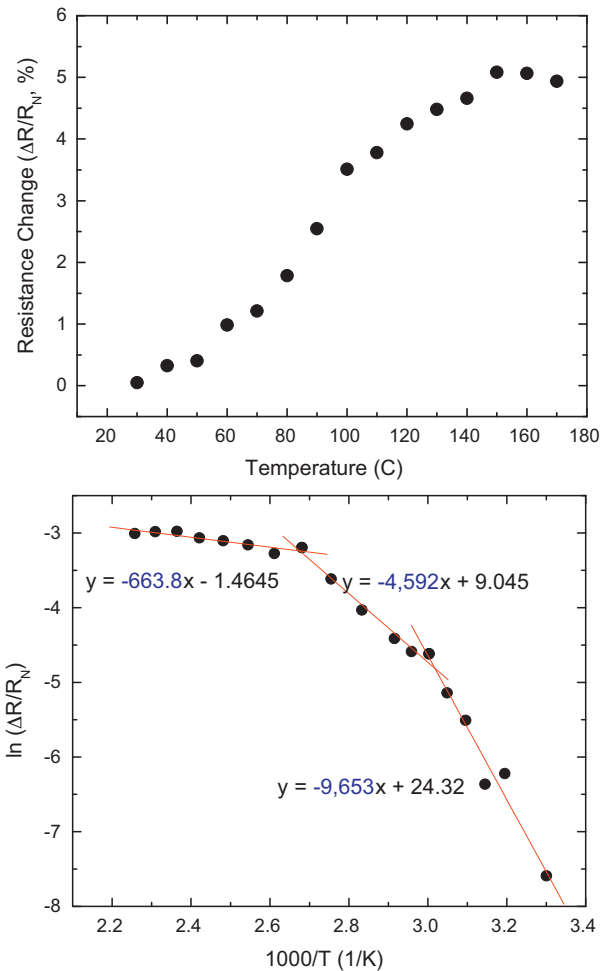


Fig. 4. (Top) Resistance change of sensor at various temperatures. (Bottom) Arrhenius plot showing the graphene sensor activation energy for the sensor response to 1% hydrogen.

Therefore, there is a reduced improvement of hydrogen sensitivity as the temperature is raised.

Drain current change as a function of time in response to 1% hydrogen at a constant bias of 0.05 V and 175 °C background temperature is illustrated in Fig. 5. Initially, the chamber is purged with

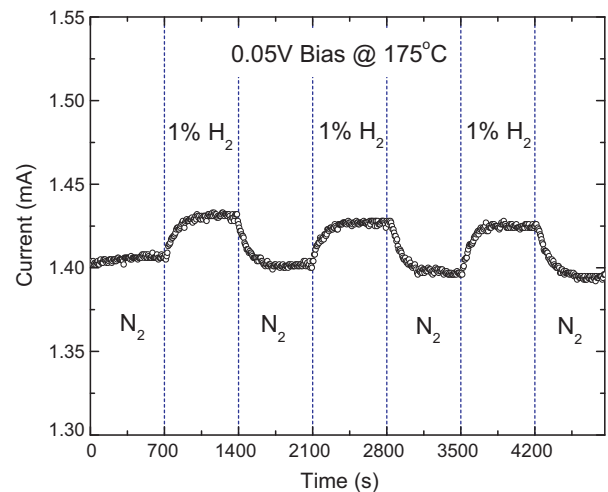


Fig. 5. Current vs. time measurement of the device showing response to 1% hydrogen at 0.05 V constant bias.

pure nitrogen until at 700 s, 1% hydrogen gas began flowing into the gas testing system. The sensor immediately shows a response and the current continues to increase until equilibrium was reached. At 1400 s, the hydrogen feed was cut off, and pure nitrogen was flowed through the quartz tube again. Immediately following the end of hydrogen gas flow, the current started decreasing until it finally reached back to the initial current level. This process was repeated two more times to test the repeatability of the sensor. All three peaks due to hydrogen gas have similar heights and response time.

4. Conclusion

In conclusion, epitaxial graphene deposited by CVD on SiC was coated with platinum to detect hydrogen gas. *I–V* comparisons showed that platinum acted as a dopant and increased the conductance of graphene. Gas testing results showed that exposure to hydrogen decreased the resistance of the graphene/Pt and three activation energies were observed depending on the temperature range. Real-time measurement of the sensor suggests that it has robust and repeatable response to hydrogen.

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