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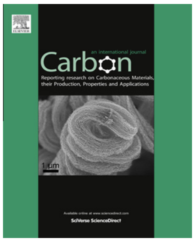

Asymmetric electron hole distribution in single-layer graphene for use in hydrogen gas detection

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ABSTRACT

We demonstrate a highly sensitive hydrogen gas sensor using single-layer graphene exfoliated from highly oriented pyrolytic graphite, which one side of it was covered by palladium. In this asymmetric graphene sensor, the electrons generated from reaction between palladium and hydrogen accumulate at the interface between palladium and graphene, and these accumulated electrons changed the carrier density of graphene beneath the palladium film from hole-dominated to neutralized graphene. This half-neutralized and half hole-dominant graphene showed asymmetrical I–V characteristics in a hydrogen atmosphere. Moreover, this device showed promising sensing performance in hydrogen gas including good sensitivity, a few second response time, and a few minute recovery time from 50 to 20,000 ppm hydrogen depending on the current direction. The fact that the response of the sensor satisfies Sievert's law, suggests that graphene with lithographically patterned palladium on one half can exhibit direction dependent asymmetrical electric current performance in a hydrogen atmosphere and also can act as a highly sensitive sensor for the quantitative detection of hydrogen molecules over broad concentration ranges.

1. Introduction

Graphene, i.e., an sp^2-bonded carbon monolayer sheet, has been of interest due to its astonishing physical properties covering all electrical and mechanical areas, such as crystal structure, ultrahigh electron mobility, minimal electron scattering, and extra high Young's modulus [1–3]. In addition, as one of only a few two-dimensional atomic layers, its unique structure and extremely large surface-to-volume ratio made it a promising candidate for atomic sensitive gas sensors with exceptionally low signal-to-noise ratios and high surface-to-volume ratios [4–6].

Many studies related to the chemical vapor sensing properties of graphene have been conducted with various toxic gases such as NO_X and NH_3, and these showed the high sensitivity of graphene, down to single molecule levels, and its comparable and reliable performance in ambient conditions [5,7]. The study of gas detection is crucial for not only a fundamental understanding of interactions of molecules and materials, but also engineering approaches for all environmental, energy and safety issues. Of the many topics of growing interest, one very important and pivotal issue is the detection of hydrogen gas (H_2). Detection of H_2 molecules has become an important issue regarding safety due to the widespread use of H_2 in bio- and nano-technology and its exceptional potential for applications to fuel cells or clean energy. In particular, the extremely high burning velocity, flammability and explosive characteristics of H_2, which is

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flammable at concentrations greater than 4% in air, demand the need for detection of minimal amounts of H_2 molecules.

To achieve high sensing performance, Pd has been studied actively as a sensor due to its high sensitivity and facile fabrication [7–10]. H_2 gas sensing properties of Pd itself have been applied in nanowire structures fabricated by electron beam lithography, and these operate by absorbing H_2 gas molecules [8]. Moreover, CNTs modified with Pd nano-particles (PdNPs) prepared by different methods such as electrodeposition [9], electron beam evaporation [10], and chemical methods [11] shows that Pd can also act as an excellent catalyst for hydrogen absorption in gas sensors. To date, many research groups have studied the catalytic properties of Pd in graphene-based H_2 gas sensors [12].

The present study shows novel H_2 sensing properties of a graphene–Pd system. This work is motivated by prior studies of each material individually, that graphene showed promising characteristics in gas sensing and palladium showed its benefits in terms of H_2 detection. With all of those benefits, we studied H_2 gas sensors with graphene exfoliated from highly oriented pyrolytic graphite (HOPG) which have lithographically patterned Pd on one side, and we suggest how graphene–Pd systems work as a H_2 gas sensor. Graphene is obtained by mechanical cleavage from HOPG, which ensures its unique crystal structure with smooth edges and almost defect-free properties. Moreover, we have found a mechanism of electrical reaction between Pd and graphene, wherein electrons from hydrogen-absorbed Pd accumulated on the graphene surface and neutralize graphene layer. This half-neutralized graphene under the Pd allows for highly sensitive hydrogen sensing by current direction dependent measurements. Further, the good sensing performance, which follows Sievert's law, confirms that this sensor can exhibit reliable sensor characteristics for quantitative H_2 gas detection in broad concentration ranges.

2. Experimental

2.1. *Sample preparation*

Monolayer graphene was prepared by mechanical cleavage from HOPG on a Si/SiO_2 wafer with a 300 nm of SiO_2 layer. Using optical microscopy, we observed a graphene, which size is about 10 micrometer of width and height for convenient micro fabrication process. Raman spectra were used to define certain layers of graphene by the shape of the G peak and intensity of the 2D peak of graphene sheets at a wavelength of 633 nm. The graphene in this study is a clearly monolayer, as shown in Fig. 1(c). Fig. 1(b) shows an atomic force microscope (AFM) image of a graphene, which has a smooth-edge and a height of about 0.38 nm. Photolithography using negative photoresist AZ5214, a photo mask and AZ300MF developer was used to pattern the gold electrodes first, which were designed to reduce resistance on the contact sides of the graphene edge and electrodes. The pattern was deposited using an electron beam deposition system at 10 Å/s ratio with a base pressure of 4×10^{-5} torr for 400 nm of gold deposition, after deposition of a few nanometers of Ti for adhesion. After an annealing process for better adhesion, a sample of graphene with gold electrodes on both sides then went through a photolithography process again for proper patterning of Pd deposition. After patterning, about 30 nm of Pd was deposited on the top of the patterned device using an ultra-high vacuum DC magnetron sputtering system at 4×10^{-8} torr with a discharge power of 200 W and 14 sccm argon gas injected into the deposition chamber. Fig. 1(a) shows a scanning electron microscope (SEM) image of the fabricated device. The device, which is shown not only in Fig. 1(a), but also the inset of Fig. 2(b), was fabricated in a chip for simple and convenient two-point electrical measurements. After fabrication, the device on the wafer was attached to a printed circuit board (PCB) chip and connected by Al wire.

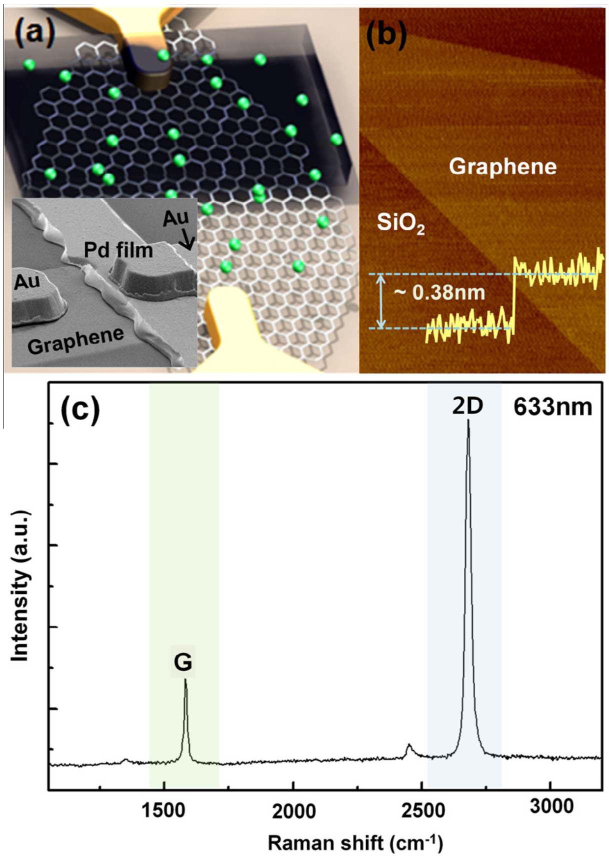

Fig. 1 – (a) Schematics of our sensor device of mechanically exfoliated monolayer graphene embedded on a silicon wafer with Au electrodes and deposited Pd (black). Hydrogen molecules (green) flow on the device. Inset shows the SEM image of the sensor device. (b) AFM image of monolayer graphene from mechanical cleavage and its height analysis. (c) Raman spectrum of graphene used for the sensor device. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. *Measurement*

The electrical measurement of the device was conducted using a Keithley 236 power supply, which was connected to the test chamber. During I–V measurement, a voltage from −1.0 to 1.0 V was applied and a constant voltage of 0.5 V

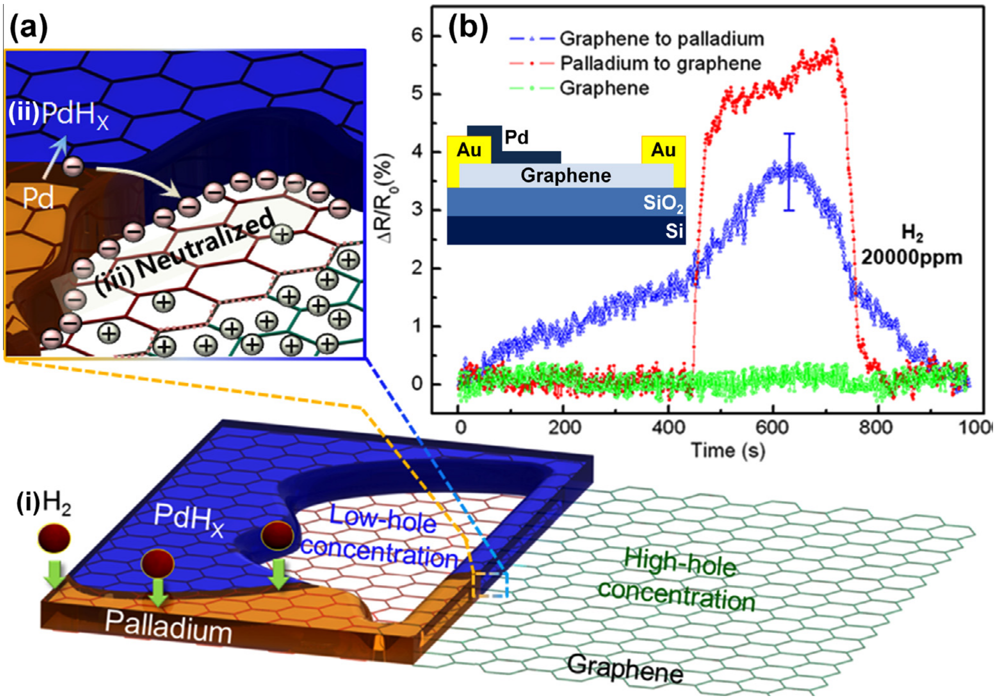

Fig. 2 – (a) Schematics of the sensor mechanism. (b) Response of pure graphene and current-dependent graphene–Pd composite to H_2 gas.

was applied in resistance measurements. The chamber was equipped with a mass flow controller (MFC) that monitored the inlet/outlet ratio of H_2 and dry air, and the real time electrical resistance response to H_2 was measured at room temperature. The test chamber had inlet lines for the flow of different gases and an outlet line for purging with pure air. All data acquisition was carried out through a general purpose interface bus (GPIB) interface card.

3. Mechanism of the device

Fig. 2(a) and (b) schematically present the mechanism of this sensor. The Pd is known to inject holes into graphene and extract electrons from graphene. [13] On the other hand, when Pd is exposed to H_2 gas, each dissociated hydrogen atom is adsorbed onto the Pd surface, [14] and Pd is converted to PdH_X, as presented in Fig. 2(a)(i). This reaction of Pd and hydrogen results in one excess electron, as shown in Fig. 2(a)(ii), and those electrons are accumulated at the interface between Pd and graphene, as presented as Fig. 2(a)(iii) [15]. These accumulated electrons change the carrier density in graphene, which were originally found to be p-type in ambient conditions, [16] by neutralizing holes in graphene and reducing effective hole concentration, as shown in Fig. 2(a). This mechanism causes electron density asymmetry on single-layered graphene, as the side with Pd becomes neutralized by electrons donated from hydrogen-absorbed Pd, while the other side of the pure graphene remains p-type. This asymmetrical effective hole-electron concentration causes single-layer graphene to behave direction dependent electrical current. Based on this study, we confirm that, when Pd is exposed to hydrogen, neutralization of graphene by accumulating electrons is more dominant than hole injection of Pd itself. This asymmetric hole-electron distribution in single-layer graphene is a current direction dependent reaction, as shown in Fig. 2(b). The signal of graphene with and without Pd is shown in the inset of Fig. 2(b). We first measured the response of intrinsic graphene to hydrogen gas without depositing palladium and found there was no response as a green-line in Fig. 2(b) [17]. With hydrogen, the detection currents between graphene to Pd and Pd to graphene were totally different as the resistance change of Pd to graphene was significantly higher than that of graphene to Pd.

In the measurement, higher hydrogen concentration decreased the effective hole concentration of graphene and increased the virtual resistance of the device. Therefore, a reverse bias of p-type-like graphene to n-type-like neutralized graphene is not as fluent as that in the opposite direction. The opposite bias of n-type-like neutralized graphene to p-type-like graphene experiences some increase in resistance, because even though the current direction is reliable, the quantity of electrons was not sufficient, and this resulted in a slight increase in resistance. This means that the reverse bias form of the sensor can obtain a higher resistance change and is more suitable for H_2 gas sensing. Moreover, by continuous study, we confirmed that higher hydrogen concentrations made graphene's effective electron/hole concentrations more asymmetrical by increasing changes in resistance. This may be due to higher electron concentrations on the interface of Pd and graphene as a result of higher neutralization characteristics following higher hydrogen concentration.

Fig. 2(b) shows the responses of graphene and graphene-Pd composites with different current directions to H_2 gas with a concentration of 20,000 ppm. Even though the hydrogen concentration is fairly high, the pure graphene response seems to be very poor, while the graphene-Pd device shows a fair response. Based on the mechanism, the data showed a current-direction-dependent signal such that the Pd to graphene signal showed higher resistance changes. Also, the signal from graphene to Pd was comparatively poor due to its low sensitivity and also low signal to noise ratio.

4. Results and discussions

4.1. *I–V characteristics*

Fig. 3(a) describes I–V characteristics of the sensor from −1.0 to 1.0 V. The source was connected to the Pd sight, and the drain was connected to the graphene region, as shown in the inset of Fig. 2(a). The region −1.0–0.0 V describes I–V characteristics of the graphene-to-Pd direction (Region 1), and 0.0–1.0 V shows I–V characteristics for the Pd-to-graphene direction (Region 2). In this figure, the red line describe response from sensor after 10 s of hydrogen exposure and green line indicates what from 1 min of hydrogen exposure. As shown in Fig. 2(b), the sensor exhibits increased resistivity properties for both regions. Fig. 3(c) describes I–V characteristics for Region 2, in which both graphs (H_2 gas 1 min after flow and 1s after flow) are well separated. This may be due to the high signal-to-noise ratio (observed from Fig. 2(b)) as a result of the increased resistivity for discrete exposure time of H_2 gas. Fig. 3(b) describes I–V characteristics for Region 1, in which both graphs are merged together, and may be due to the low signal-to-noise ratio and slow response time (discussed in Fig. 2 (b)). In addition, these results imply asymmetric current dependent behavior for different voltage directions since the current values changed from 1.8 to 2.3 μA for the Pd-to-graphene direction, while that for the graphene-to-Pd direction was from 2.0 to 2.5 μA. The difference of about 10% in current flow dependent its direction indicates this device performs asymmetric current. [18,19] Fig. 3(d) represents the voltage–current relationship after a 10 min exposure of H_2 gas, where the y-axis represents the measured current flow difference between Region 1 and Region 2. The x-axis represents the absolute voltage value taken from Fig. 3(a), which exhibits different current directions for the same voltage value. Fig. 3(d) illustrates that the current flow in Region 1 (graphene-to-Pd) always exceeds that of Region 2 (Pd-to-graphene). Moreover, this clearly implies the asymmetric current dependent properties for different voltage directions.

4.2. *Response of the device as hydrogen sensor*

Fig. 4(a) presents graphene–Pd sensor response to various H_2 gas concentrations in reverse bias-like measurements in the Pd-to-graphene direction. The sensitivity was carried out using Sensitivity (%) = $(R_{H2}-R_{Air})/R_{Air} \times 100$. As in Fig. 4(a), we confirm that the detection limit of this sensor was reliable up to 50 ppm, which implies that asymmetrical electron density in pure graphene can be detected by Pd–hydrogen systems in that condition. Fig. 4(b) shows the sensor's sensitivity to 10,000 ppm of H_2 gas, which indicates that the sensor is capable of recovering its original condition and can repeat the same performance with continuous inlet and outlet of H_2 gas and air. Even though the measurements were carried out with various air conditions and concentrations of gas, the sensor's recovery time, which is less than 5 min, is comparable with previous reports [9–11]. The recovery time

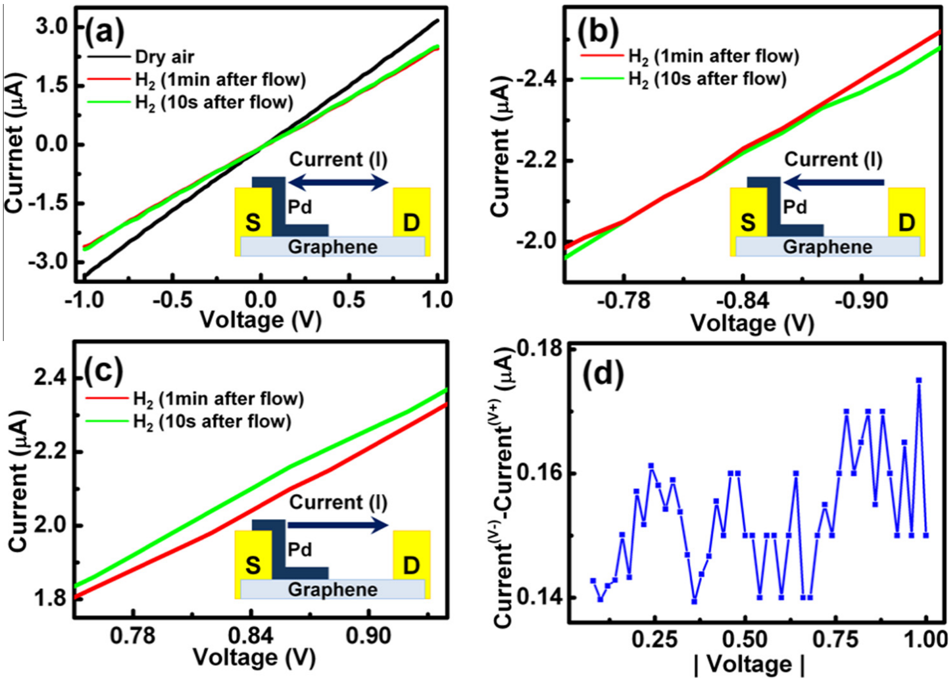

Fig. 3 – (a) I–V characteristics of the device from −1.0 to 1.0 V. (b) I–V characteristics of the device from −0.92 to −0.75 V. (c) I–V characteristics of the device from 0.75 to 0.92 V. (d) Voltage–current relationship depends on current direction (*y*-axis represents the current flow differences between the current directions, *x*-axis represents the absolute voltage value).

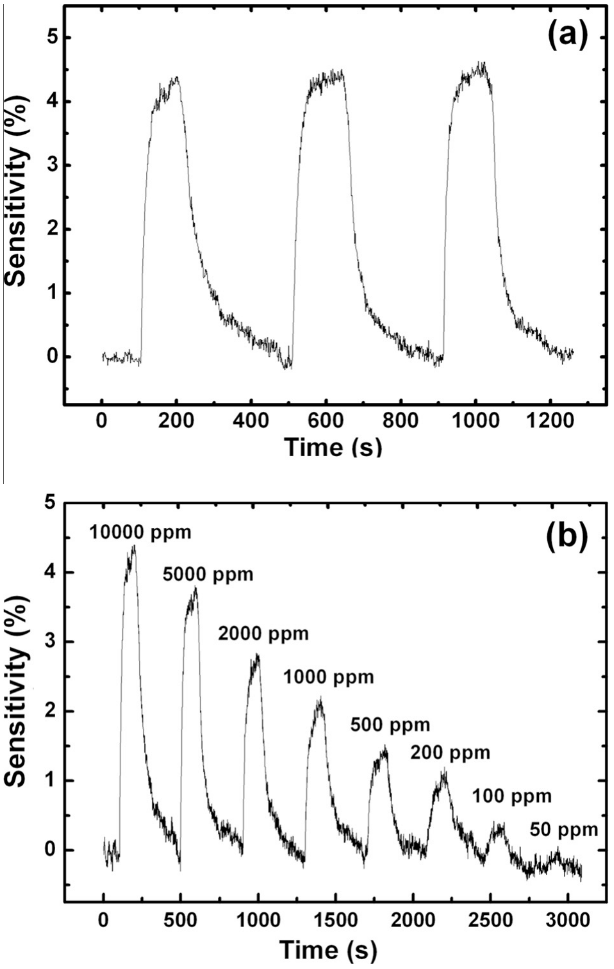

Fig. 4 – (a) Reliable and renewable response of sensors with similar sensitivity, and proper recovery with continuous inlet of 10,000 ppm H_2 gas and outlet of dry air. (b) Response of sensor with continuous altering inlet gas with H_2 and air.

of H_2 gas sensors by electrodeposition of PdNPs on single-walled carbon nanotubes [9] and single-walled carbon nanotubes grafted with PdNPs [11] were reported to be about 5–10 min.

Fig. 5(a) presents the sensitivity and response time of the sensor in various H_2 gas concentrations. The sensitivity was carried out using Sensitivity (%) = $(R_{H2}–R_{Air})/R_{Air} \times 100$, as Fig. 4, and the response time is defined as the time it takes to reach 36.8% (=e^{-1}) of the total change of the electric resistance at a given H_2 gas concentration [11,20]. Our sensor's sensitivity was also comparable with other studies conducted with devices with rigid forms of Pd, such as Kim et.al. [21] or Jeon et.al. [8]. The Pd sensor can show different performance based on whether or not Pd is free to expand, because hydrogen atoms diffuse until they occupy the interstitial sites of the Pd lattice and cause a certain amount of lattice expansion [22–23]. This reaction, which causes mechanical expansion of Pd, resulted in different sensitivities between freely expanded Pd and rigid patterned Pd. Therefore, we compared those studies conducted with devices containing rigid forms of lithographically fabricated Pd. Our sensor showed a similar sensitivity of 5% at 20,000 ppm of H_2 as other sensors with rigid Pd. This comparison also implies the high sensitivity of the electron from H_2 absorbed on Pd neutralized the graphene beneath Pd. The response time was about 8–47 s, which is shown in Fig. 5(a); this was also comparable to other sensors with similar response times, including those of Y. Sun et.al. [10], which shows 3.8–55 s, and S. Jua et.al. [11], which is about 10–90 s. This comparison shows that electron neutralization on the surface of graphene is not only sensitive, but also highly active.

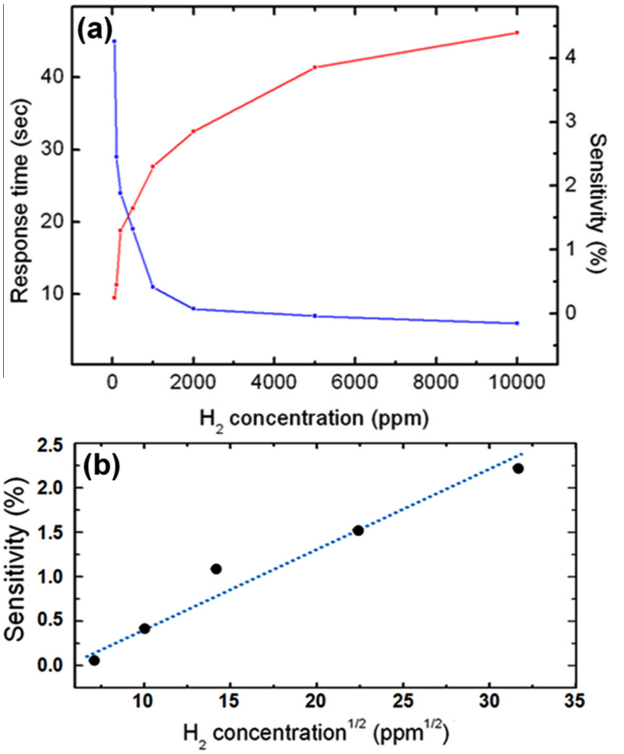

Fig. 5 – (a) Response time and sensitivity of graphene–Pd sensor due to changing hydrogen concentration. (b) Sensor's sensitivity in low concentration (10–1000 ppm), which follows Sievert's law.

Fig. 5(b) shows our sensor's sensitivity was fairly reasonably represented by the fundamental Sievert's law, Sensitivity $\propto [H]/[Pd] = 1/KS\ (pH_2)^{1/2}$, where [H] and [Pd] are the concentrations of hydrogen atoms and Pd atoms, respectively [24,25]. When Pd is exposed to H_2, hydrogen molecules are adsorbed onto the Pd surface and are dissociated into hydrogen atoms. The hydrogen atoms are adsorbed onto the Pd surface and diffuse into the Pd lattice. Then, the resulting lattice expansion causes the formation of Pd hydride, which leads to the resistance increase in the Pd. The magnitude of the resistance increase is proportional to the atomic fraction of absorbed hydrogen atoms to Pd atoms, as expressed by Sievert's law [24,25]. In that equation, KS is the temperature-dependent Sievert's constant, and H_2 is the partial pressure of H_2 in the environment. From the above equation, it can be observed that sensitivity is correlated to the relative concentration of hydrogen and with the square root of the hydrogen partial pressure. The correlation of our response and concentration of H_2 gas was found to be in good agreement with this law in the range of 50–1000 ppm. This ensures that our sensor's quality is based on the laws of physics and can be used as a sensor to quantitatively detect hydrogen molecule concentration.

5. Conclusion

In conclusion, the graphene-palladium system is a promising candidate for hydrogen gas sensors. Gas sensing was measured by flowing H_2 and Air over the graphene-palladium system at atmospheric pressure and room temperature. The sensor properties due to resistivity change of graphene, which is increased by H_2 adsorption on the graphene surface due to the presence of palladium, were comparable to other H_2 sensors using palladium. The sensor's similar response to a continuous hydrogen inlet shows it can be applied to renewable sensors, while the broad detection range down to 50 ppm H_2 confirms its high sensitivity. Also, we suggested one mechanism of electrical action between graphene and the palladium–hydrogen system, namely, that electrons from the palladium–hydrogen reaction transfer to the graphene surface and seem to neutralized graphene's effective hole concentration even in single-layer graphene. This resulted in asymmetric current performance up to 50 ppm of H_2 flow. This mechanism also suggests one possibility for applying graphene to future diodes with simple chemisorption of a palladium–hydrogen system, even the single crystal structure of graphene. Further study will focus on the sensing ability of graphene–palladium systems with chemically derived graphene, which will ensure its commercial applications, and also careful analysis for understanding the doping-like effect of graphene for more extreme electrical asymmetry even in electron-dominant conditions for its application to future diode devices.

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