

Nanoscale, Low-energy Molecular Sensors for Health Care and Environmental Monitoring

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ABSTRACT

In the era of the internet of things (IoT), low-energy, small-size sensors are in strong demand. Low-energy physical sensors such as gyro, sound, and optical sensors have been integrated in mobile electrical terminals such as smart phones. However, chemical sensors such as gas sensors have not been implemented in small-size electronic systems, due to issues regarding size and energy consumption. In this feature article, two types of recently developed molecular sensors are introduced; a voltage-controlled multimolecular sensor consisting of Pd-functionalized, suspended graphene, and a Pt nanosheet, which can detect ppm-level hydrogen in expired air, are presented.

INTRODUCTION

Currently, numerous electrical products are connected to the internet. Some may download the newest software from servers and others may provide global positioning system (GPS) information to improve services. We have observed great progress in artificial intelligence (AI) technologies, by which numerous kinds of valuable information for individuals and for society at large are inferred from various kinds of data. In order to enhance the accuracy of the inference, the quantity as well as the variety of the data are critical. Therefore, various kinds of sensors are expected to be implemented in every electrical product that has internet access capabilities. We anticipate that their data will be utilized actively in the “big data” societies of the future. In fact, low-power physical sensors such as temperature, gyro, and optical sensors have been already integrated into mobile terminals such as smart phones. However, chemical sensors for mobile

terminals are still under development and have not been integrated in mobile devices or devices driven by energy harvesters, because of their relatively large size and energy consumption.

In this feature article, we will introduce two types of sensors recently developed by our group; a Pd-functionalized graphene sensor activated by Joule heating [1], and a Pt nanosheet sensor [2] that can detect hydrogen in breath, are presented.

PD-FUNCTIONALIZED GRAPHENE SENSORS

The analysis of the molecules in human breath is a promising diagnostic technique because a number of compounds in human breath are considered to be related to various kinds of diseases [3-5]. The H₂ concentration of breath is a good indicator of disorders in small intestine, including bacterial overgrowth, colonic fermentation, abnormal fermentation, and carbohydrate intolerance. [3,6-8] The typical H₂ concentration ranges from a few ppm to several hundred ppm. However, breath contains many disturbing substances, such as a high concentration of water. [6,9] Thus, to develop an easy, ubiquitous, H₂-based breath diagnosis method, H₂ sensors should be able to detect low and wide ranges of H₂ concentrations, should be small, and should show humidity robustness and low power consumption.

Recently, we fabricated Pd-functionalized suspended graphene sensors, where heat transfer from the self-heated graphene to the substrate was successfully avoided. The graphene was suspended on the electrodes using a poly-

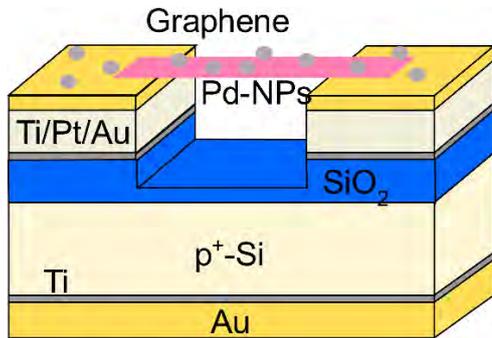


Fig. 1: Schematic of fabricated Pd-functionalized graphene sensor. The graphene was suspended over two electrodes; one is a source that is grounded and the other is a drain that is biased with drain voltage (V_D).

dimethylsiloxane (PDMS) stamp method. [10,11] By utilizing Joule heating within the suspended graphene, we explored the possibility of selective sensing of hydrogen/humidity by applying an appropriate bias voltage in realistic gas environments, in which small changes in the H_2 concentration and large variations in the relative humidity (RH) were induced.

Figure 1 shows the fabricated Pd-functionalized graphene sensor. The 300-nm-thick SiO_2 thermally grown on the p-type Si substrate was used as the substrate. After the formation of Ti/Pt/Au electrodes on SiO_2 , HOPG was exfoliated using Nitto tape (SPV224-R) and placed on commercially available PDMS (Gel-Film® WF-20×4 6mil). The PDMS was used to transfer the graphene on the electrodes. The graphene was transferred by a PDMS stamping method. After cleaning, 0.3-nm-thick Pd was deposited and agglomerated by annealing at 400 °C for 30 min. The suspension was confirmed by scanning electron microscopy (SEM) and the multi-layer structure and high quality of suspended graphene was checked by Raman spectroscopy. In addition, using transmission electron microscopy (TEM), we confirmed that Pd was placed on graphene as nanoparticles (NPs) and that there were eight graphene layers. One might consider eight-layer graphene to be too thick to work with as a transducer. However, it is reported that the electrical conductivity of eight-layer graphene can be well modulated by external electric fields. [12] Therefore, eight-layer graphene can work as a transducer of hydrogen-induced changes.

Figure 2a shows the sensor response, which is defined by the resistance change (ΔR) relative to the original resistance (R_0), to 100-ppm H_2 as a function of time at

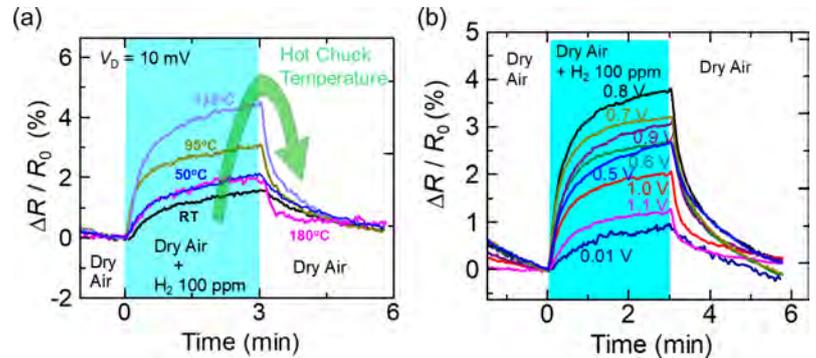


Fig. 2: (a) Temperature dependence of the sensor response. The device was heated by an external heater. (b) Sensor response as a function of time at various drain voltages.

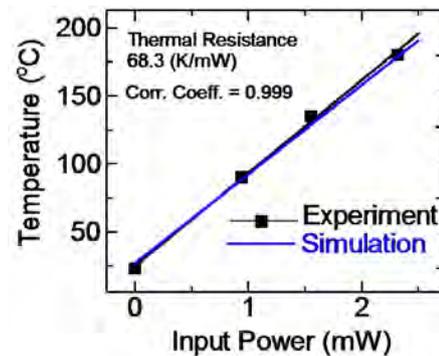


Fig. 3: Temperatures as a function of self-heating power. Experimental temperatures were extracted by comparing V_D -dependent and temperature-dependent sensor responses. Simulation data were obtained using multi-physics finite element method simulator with graphene-gold thermal contact resistance of $2500 \mu m^2 \cdot K/mW$.

various operating temperatures from room temperature (RT) to 180 °C. The sensor response increases as the operating temperature increases to 135 °C, due to the promoted dissociative adsorption of H_2 . However, the sensor response decreases at 180 °C because of the desorption of hydrogen from Pd. Figure 2b shows the time dependence of the sensor response to 100-ppm H_2 , where the device was operated at various V_D from 0.01 V to 1.1 V at RT. The sensor response increases as V_D increases to 0.8 V, and then gradually decreases as V_D continues to increase from 0.9 V to 1.1 V. This tendency of the V_D -dependent sensor response is almost the same as that of the temperature-dependent sensor response, which clearly suggests that V_D -induced self-heating was successfully achieved. To calibrate the graphene channel temperature when the self-heating technique was utilized, the sensor responses to 100 ppm of H_2 using the self-heating technique and hot chuck were compared. We also verified the rela-

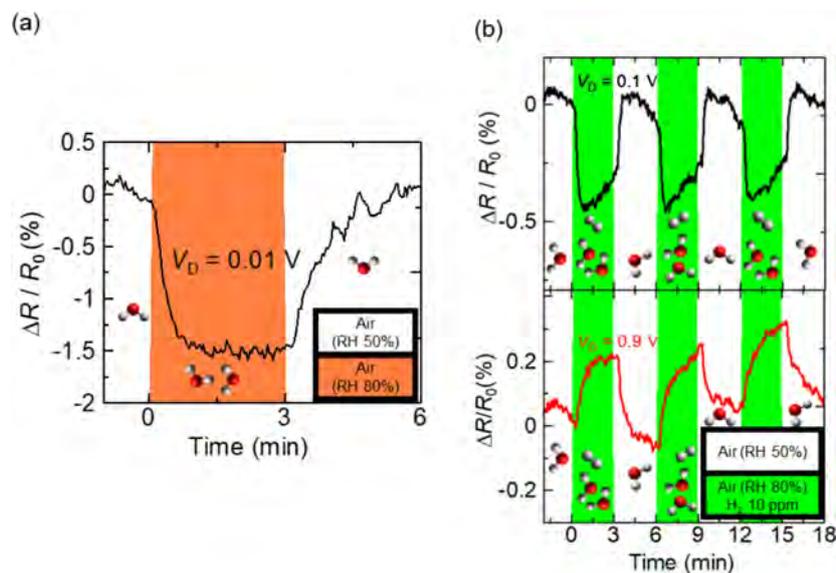


Fig. 4: (a) Room-temperature time dependence of the sensor response to a relative humidity (RH) change from 50% to 80% at V_D of 0.01 V. (b) Room-temperature time dependence of the sensor response to 10 ppm of H_2 with a RH increase from 50% to 80% at V_D of 0.1 V (upper) and 0.9 V (lower).

relationship between the input power and temperature in the graphene sensor using numerical simulations. The simulation data agree well with the experimental data as shown in Figure 3. Figure 3 demonstrates that a temperature of 100 °C was achieved by small power consumption of 1 mW by Joule heating.

Finally, voltage-controlled multi-molecule detection by self-heating was demonstrated. Figure 4a shows the time dependence of the sensor response to humidity at a V_D of 0.01 V. The reference and test gases were humid airs with relative humidity (RH) of 50% and 80%, respectively. The sensor resistance decreased under the higher humidity of 80%, because water molecules were adsorbed on the oxidized Pd and acted as acceptors (hole donors) for the graphene operating in the hole regime. As a result, the graphene resistance was decreased. Figure 4b shows the sensor response to 10 ppm H_2 balanced with RH-80% humid air. Humid air with a RH of 50% was used as the reference gas. As demonstrated in Figure 4b, the sensor function can be switched by changing V_D . The upper figure shows that at a V_D of 0.1 V, at which the sensor operates at RT, the sensor responded to humidity. On the other hand, the lower figure shows that at a V_D of 0.9 V, at which sensor operates at approximately 135 °C, the sensor responded to 10 ppm H_2 even when a large RH variation from 50% to 80% occurred simultaneously. Therefore, self-heating successfully prevented the effect of humidity and resulted in the detection of a low con-

centration of H_2 . These results led to the conclusion that the sensor function can be changed using applied voltages, thanks to the self-heating effects as shown in Figure 5. This multi-functionality realized with self-heating is extremely useful as it reduces the space requirements for sensors in small electrical terminals.

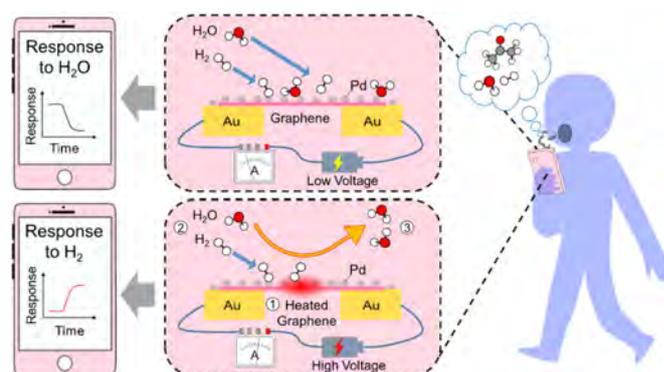


Fig. 5: Schematics illustrating the concept of a voltage-controlled multifunctional molecular sensor utilizing Joule heating of nanomaterials.

PT-NANOSHEET HYDROGEN SENSORS

We have developed another hydrogen sensor that utilizes a Pt nanosheet. The experimental results indicate that the Pt nanosheet sensors can detect ppm-level hydrogen in expired air. The hydrogen and oxygen adsorption/desorption kinetics on the Pt surface were utilized to

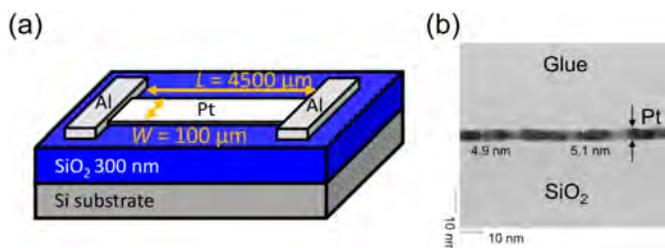


Fig. 6: (a) Schematics of Pt nanosheet sensor. (b) Cross-sectional transmission electron microscopy (TEM) image of a Pt nanosheet.

quantitatively model the sensor response of the Pt nanosheets, based on the surface hydrogen coverage ratio.

Pt nanosheets were deposited using the electron beam deposition method on Si substrates covered with a 300-nm-thick SiO₂ layer on the top. Aluminum electrode formation followed. Figure 6a shows the schematic of the sensor structure. Figure 6b shows the sectional TEM image of the Pt nanosheets. Polycrystalline Pt films with cracks were observed.

The sensor response, which is defined by the electrical current change (ΔI) relative to the original electrical current (I_0), of a Pt nanosheet was found to be robust against humidity, as shown in Figure 7a. The substrate was heated at 150 °C. Compared to these Pt nanosheets, Pd nanosheets are much less robust as hydrogen sensors. For hydrogen concentrations from 500 ppb to 200 ppm, the response of the Pt nanosheet sensor was measured at RH = 0%, 50% and 90%. The same linear sensor response as a function of hydrogen concentration was obtained as shown in Figure 7b. Since room air typically contains 550 ppb hydrogen [13], expired air contains more hydrogen than typically in the atmosphere. Thus, the response of the Pt nanosheets tested here indicates

sensor response sufficient for hydrogen detection in expired air. Furthermore, sensor response under expired air is shown in Figure 7c. Apparent increases of the sensor response just after the lunch as well as seven hours after the lunch were observed. These increases of sensor response are correlated with increases of hydrogen after ingesting foods; it is known that hydrogen concentrations increase approximately six hours later when food is taken by examinees [14,15]. Therefore, this experiment clearly demonstrates that the present Pt nanosheet sensor responded to low-level hydrogen in air expired by a healthy human.

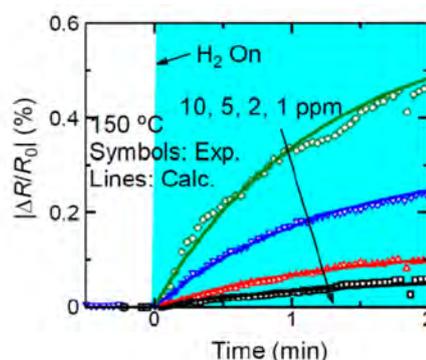


Fig. 8: Comparison of sensor response as a function of time between experimental data (symbols) and simulated data (lines).

We simulated the dependence of the sensor response on hydrogen concentration and time, by taking into account the time-dependent molecular coverage change [2]. The time-dependent sensor response at a hydrogen concentration of lower than 20 ppm was successfully reproduced by our model, as shown in Figure 8. However, at higher hydrogen concentrations, the calculated time dependence slightly deviates from the experimental data. We consider that the deviation was caused by catalytic water formation, which is not taken into account in our pres-

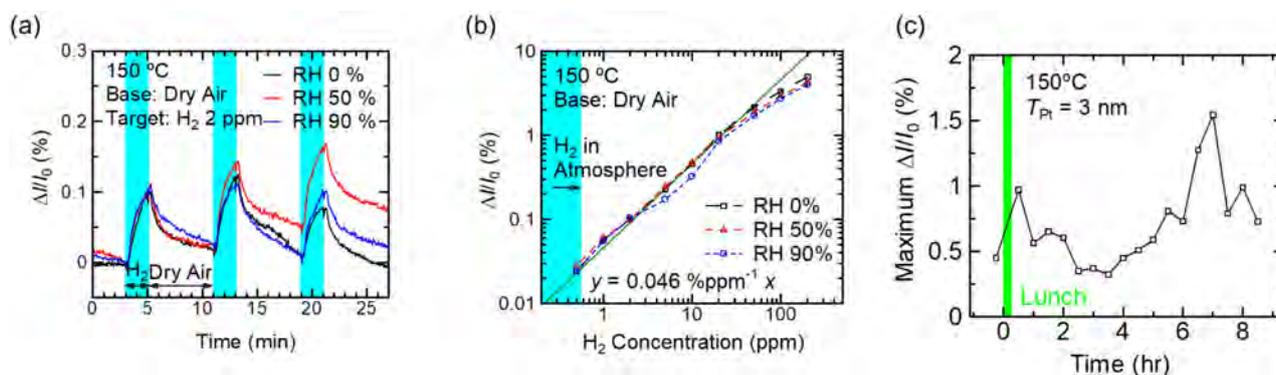


Fig. 7: (a) Sensor response of the Pt nanosheet. (b) Hydrogen concentration dependence of the sensor response. (c) Time dependence of the sensor response to expired air.

ent model, on the Pt surface. At a hydrogen concentration of less than 20 ppm, the surface coverage change is dominated by oxygen desorption. Therefore, the sensor response is precisely predicted by adsorption and desorption of hydrogen and oxygen, which are fully considered in the model. The robustness against humidity in hydrogen sensing is attributed to the small contribution of water to the hydrogen surface coverage.

CONCLUSION

In this article, two types of molecular sensors that we recently developed were introduced; a voltage-controlled multimolecular sensor consisting of Pd-functionalized, suspended graphene, and a Pt nanosheet that can detect ppm-level hydrogen in expired air were presented. In the Pd-functionalized, suspended graphene sensor, Joule heating is successfully utilized as a low-energy activator of chemical reactions. Although the Pt nanosheet sensor introduced in this article was heated up by an external heater, the same Joule heating method should be applicable to lower the energy consumption of sensors. We believe that these small-size, low-energy sensors will become extremely useful in the “big data” societies of the future.

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