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Pd-dot-size dependence of hydrogen sensors based on graphene FET for breath analysis

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Abstract

We have fabricated a palladium-modified graphene field-effect transistor for hydrogen detection. The negative-voltage shift was observed with exposure to hydrogen gas. Moreover, the sensitivity characteristics were investigated using sensors with two types of Pd-dot size. Hydrogen concentration dependence of the sensors was measured from 5 to 2,700 ppm. The results indicate that the device with larger surface area of Pd has more highly sensitivity.

1. Introduction

In recent years, a breath analysis of diabetes-drug effect has attracted attention owing to invasive treatment to the patient. Expired air has been studied for the detection of disease, such as colorectal cancer, stomach cancer, pulmonary disease, diabetes etc. Particularly, previous research revealed that diabetic who took a medicine (α-GI) includes hydrogen at concentration of 13 ppm in their breath. on the other hand, diabetic who didn't take includes hydrogen at concentration of 5 ppm [1]. Thus, the continuous monitoring of hydrogen is useful for patients. However, conventional measurement needs an expertise, and takes long analysis time and unable to measure repeatedly. In this study, we focused on graphene field-effect transistors (G-FETs) for hydrogen detection. As graphene is a two-dimensional crystal consisting of carbon atoms and the graphene channel is exposed to the air directly, graphene is a promising material for the highly sensitive gas sensor [2].

In this abstract, we fabricated G-FETs modified with two different sizes of Pd dots and measured the voltage shift to compared their sensitivity.

2. Fabrication process

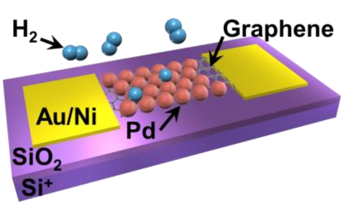

Fig. 1. Schematic illustration of a hydrogen sensor based on a Pd-modified G-FET.

Figure 1 shows a schematic illustration of a G-FET modified with Pd dots. First, CVD-grown monolayer graphene was transferred on a SiO_2/Si substrate and Au/Ni electrodes were formed to fabricate a G-FET. Then, Pd (1 nm) was deposited on the fabricated G-FET using electron-beam or thermal evaporation for hydrogen detection. We measured the electrical characteristics over time at each concentration of hydrogen gas and voltage shifts of the transfer characteristic after exposed to hydrogen in a vacuum chamber.

3. Results and discussions

Figure 2 shows transfer characteristics in a Pd-modified G-FET before and after exposed to hydrogen at 50 ppm, where Pd was deposited using electron-beam evaporation. The result reveals that the transfer characteristic shifted in the negative gate-voltage direction of 35 V after exposed to hydrogen. However, the transconductances were not changed between before and after introduction of hydrogen, indicating that the effect of scattering owing to hydrogen adsorption can be ignored.

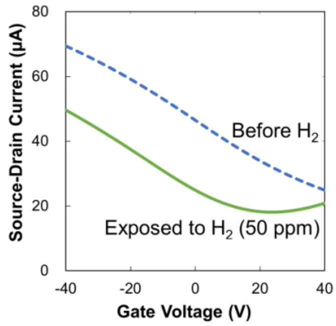

Fig. 2. Transfer characteristics of G-FET modified by electron beam deposition Pd. The green and blue lines show before and after exposed to hydrogen gas, respectively.

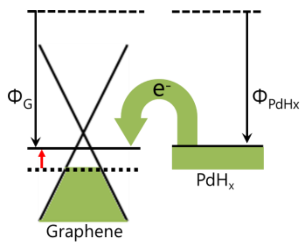

Fig. 3. Energy diagram of the Pd-modified G-FET after hydrogen exposure.

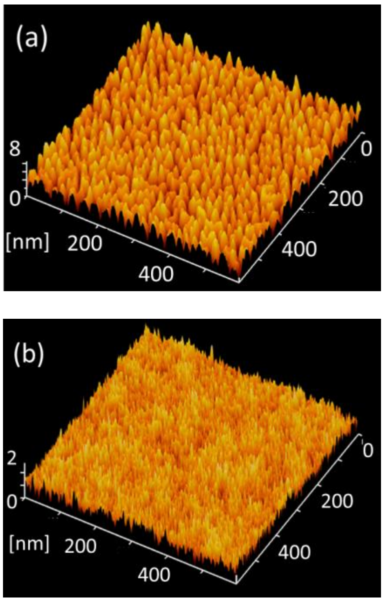

Fig. 4. AFM images of Pd deposited by (a) thermal and (b) electron-beam evaporations.

A hydrogen-detection mechanism in Pd-modified G-FET can be explained using the change in work functions as follows (Fig. 3). After hydrogen exposure, the Pd changes to PdH_x. The work function of PdH_x is smaller than intrinsic Pd. Thus, after hydrogen exposure, electrons are transferred from PdH_x to graphene and the transfer characteristics shifted to negative direction, as show in Fig. 2.

Next, the sensitivity characteristics were investigated for sensors modified by Pd using two types of evaporation methods. The Pd surface morphology of each device was observed using AFM measurement, as shown in Fig. 4. The AFM image in Fig. 4(a) reveals that the density of Pd dots was estimated to be 1,400 dots/μm^2 for Pd deposited by thermal evaporation. On the other hand, the density of Pd dots was estimated to be 9,400 dots/μm^2 for Pd deposited by electron beam evaporation [Fig. 4(b)]. The density of Pd dots formed by electron beam evaporation was higher than that by thermal evaporation. Thus, Pd dots formed by electron beam evaporation had lager surface area.

Figure 5 shows the hydrogen-concentration dependence of the gate-voltage shifts using two types of devices. In the measurement, the hydrogen concentration was adjusted from 5 to 2,700 ppm. The voltage shift was calculated with the transconductances and the current change measured at 0 V of the back-gate voltage. The results reveal that the voltage shift $(\Delta I/G_m)$ increased rapidly at low concentration and was saturated as the concentration increased, indicating that hydrogen react to the only surface region of Pd dots. Thus, we graphed Langmuir's adsorption isotherm [eq. (1)] fitting curve with the solid lines [3].

$$\frac{\Delta V}{\Delta V_{max}} = \frac{C_{H_2}}{C_{H_2} + K_D} \qquad (1)$$

Here, ΔV is voltage shift, ΔV_{max} is maximum of voltage shift, C_{H2} is the concentration of hydrogen, K_D is the dissociation constant. These results are well fitted to Langmuir's adsorption isotherm. The results reveal that the device with Pd using electron beam deposition had a larger shift than that using thermal evaporation, indicating that the former has higher sensitivity. The higher sensitivity can be explained by the difference in the surface area of the Pd dots.

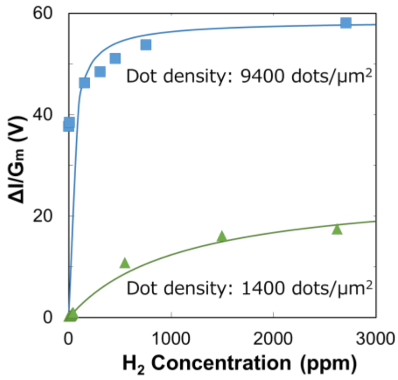

Fig. 5. Hydrogen-concentration dependence of the voltage shifts in two type of devices with different Pd deposition methods. The green and blue solid lines were obtained using Langmuir's adsorption isotherm.

4. Conclusions

To develop highly sensitive hydrogen sensor, we fabricated Pd-modified G-FETs. By exposing to hydrogen, the transfer characteristics shifted in the negative gate-voltage direction. The hydrogen-concentration dependence of voltage shift was monitored using two devices modified by Pd using thermal and electron-beam evaporation. The voltage shifts using electron-beam evaporation became larger owing to increasing the surface area of the Pd dots. We demonstrated the response of the sensors exposed to different concentration of hydrogen gas ranging from 5 to 2,700 ppm. Thus, Pd-modified G-FETs are one of the promising sensors for breath analysis.

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