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Resistive Hydrogen Detection Sensors based on 2 Dimensions – Molybdenum Disulfide Decorated by Palladium Nanoparticles

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***Abstract*—This research presents a resistive-type hydrogen (H_2) gas sensor based on a composite of palladium nanoparticles (Pd-NP) decorated on 2D-molybdenum disulfide (MoS_2) layer. The sensor fabrication involves synthesizing MoS_2 and coating Pd by DC sputtering technique. MoS_2 has been adopted for its high selectivity for H_2, wide operating temperature range, reliability, and low power consumption. Pd has high catalytic properties for H_2 and performs a H_2 adsorption mechanism through resistance transition. In this study, we propose a Pd-decorated MoS_2 structure and introduce the chemical resistance mechanism within the channel. The limit of detection (LOD), sensitivity and response time of the fabricated H_2 gas sensors are optimized and analyzed. Finally, the nanocomposites network based H_2 sensor can promote the utilization of various industries and discuss the issues in sensor applications.**

***Index Terms*—Hydrogen, gas sensor, palladium nanoparticles, molybdenum disulfide**

I. INTRODUCTION

Importantly, the depletion of fossil fuels and emissions of hazardous gases such as NO_x and CO_x have highlighted alternative energy fuels. Various fuels are being developed, but the development of high-performance fuels is insufficient. Recently, H_2 fuel energy is rapidly gaining attention as a clean energy source. H_2 has colorless and odorless properties when the concentration in the atmosphere is 4% or higher, making it difficult for human senses to detect explosiveness [1-3]. H_2 gas has wide flammability and metal corrosiveness. Therefore, real-time sensing and monitoring of H_2 leaks in various H_2 infrastructures and fields are important. In addition, the sensitivity and response/recovery time in detecting H_2 under various environment & temperature conditions are critical issues that need to be addressed.

H_2 sensing technology has been extensively studied based on catalytic combustion, electrochemical, and semiconductor metal oxide (SMO) sensors. Table 1. describes the characteristics and mechanisms of each sensor. To improve the sensing parameters of H_2 sensors, various strategies have been developed for nanomaterial-based H_2 gas sensors, which have gained attention for their high sensing performance and simple structure [12, 13]. Firstly, Pd-NP [14], palladium nanowires (Pd-NW),

Table 1. Comparison of various H_2 gas sensors

Type	Mechanism	Features/Remarks	Ref.
Catalytic combustion	Changes in resistance according to combustion heat of surface catalyst of combustible gas	• Excellent to high concentration • Low sensitivity and stability • Difficult to measure low concentration H_2 • Long life time (over 5 years) • Simple device structure	[4]-[5]
Electrochemical	Changes in resistance due to adsorption of combustible gas and metal oxide surfaces	• High sensitivity, good linearity • Silicon poisoning (short life time) • High power consumption • Low selectivity	[6]-[9]
SMO-based	Electromotive force formation and resistance change by ionization and ion migration of combustible gases	• Excellent to low concentration • Low reliability & Short life time • High influence on temperature and humidity • Low selectivity	[10]-[11]

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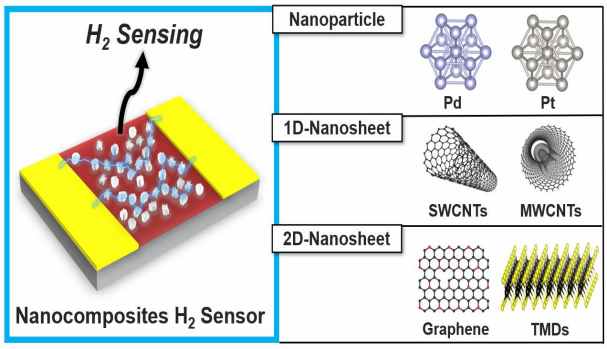

Fig. 1. Proposed nanocomposites H_2 gas sensor structure.

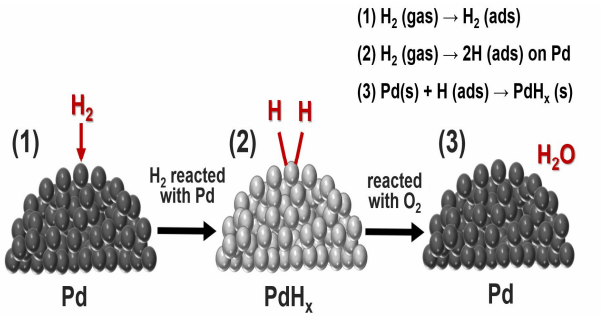

Fig. 2. Pd-H_2 of reaction mechanism.

and palladium nanotubes (Pd-NT) have been developed as a Pd network not only reduce the activation energy of H_2 adsorption but also exhibit high catalytic properties for H_2 sensing [15]. Secondly, SMO (TiO_2 [10], Nb_2O_5 [16], ZnO)-based H_2 gas sensors are known to have high reactivity and catalytic activation to detect H_2. Lastly, 1D single-walled carbon nanotubes (SWCNTs) and 2D transition metal dichalcogenides (TMDs) nanosheet-based H_2 gas sensors also show excellent H_2 sensing performance at low operating temperatures and promising detection platforms in practical H_2 applications [17-19].

In this study, Fig. 1 presents nanocomposites H_2 gas sensor decorated with Pd on MoS_2 layer as a channel. We analyze the H_2 sensing mechanism according to MoS_2 synthesis and Pd coating techniques.

II. NANO MATERIALS

Nanomaterial technology is being actively researched in various industries and applications. Among the various infrastructures, MoS_2 of 2D materials is also attracting attention in the field of gas sensors. MoS_2 nanosheets allow gas molecules to penetrate and diffuse between layers through van der Waals forces. MoS_2 is also highly reactive to toxic gases due to its high surface area-to-volume. However, MoS_2 is insensitive to nonpolar molecular sensing such as H_2 gas [20]. To effectively detect H_2, Pd with high catalytic properties for H_2 was decorated. Fig. 2 illustrates the operation of Pd-H_2 detection. When H_2 is injected into a gas sensor, the absorbed H_2 reacts with Pd to produce a Pd hybrid (PdH_x), which combines with O_2 in the air to form H_2O. The technology based on Pd nanoparticles operates on the principle that H_2 is dissociated within the lattice of Pd to form PdH_x and induce a change in resistance. Also, the Pd-H_2 mechanism enables a fast response time for H_2 detection through electrochemical modulation. As the high sensing specific surface area of MoS_2 increases, it exhibits high sensing sensitivity and excellent selectivity for H_2 detection. Moreover, the high electron mobility of MoS_2 activates the reaction of H_2 as it induces rapid oxygen ionization within the MoS_2 channel. Fig. 1(a) proposed an H_2 sensor by applying a nanocomposite of Pd-MoS_2. The optimization of Pd decoration and MoS_2 synthesis is critical. If the Pd deposit thickness is as 1 nm, Pd molecules on MoS_2 interfaces may be unclear and Pd nanoparticles may have low coverage density [22]. When Pd nanoparticles are deposited more than 8 nm, the distance between particles disappears and the H_2 reaction volume immersion decreases. The formation of Pd nanosheets not only reduces the H_2 detection area of MoS_2 but also weakens the H_2 sensing characteristics. The bandgap changes according to the number of MoS_2 deposited layers. Monolayer MoS_2 is a semiconductor with a direct bandgap of 1.8 eV, whereas multilayer MoS_2 has an indirect bandgap that decreases to 1.2 eV as the number of layers increases. Additionally, the number of layers in MoS_2 controls the interaction properties of electrons and the electrical conductivity characteristics. In the case of multilayer MoS_2, there is increased electron mobility, leading to a decrease in the bandgap and improved electrical properties. Through the optimization of the fabrication process, various Pd-MoS_2 gas sensor samples were fabricated, and I-V characteristics and sensing I-T curve were analyzed.

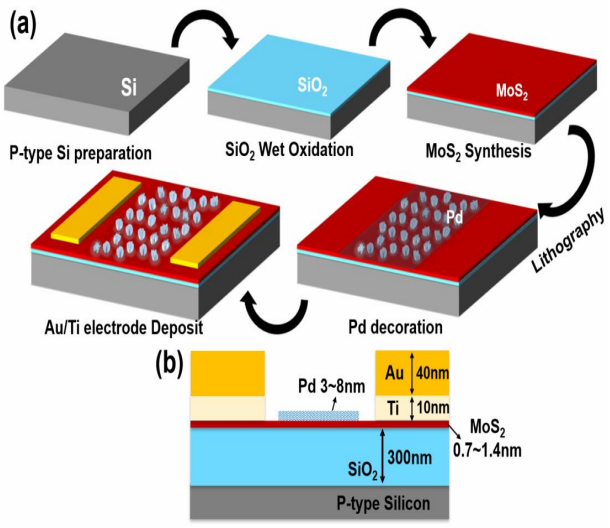

Fig. 3. (a) The fabrication process flow of Pd-MoS_2 network gas sensor; (b) The schematic drawing of proposed H_2 gas sensor structure.

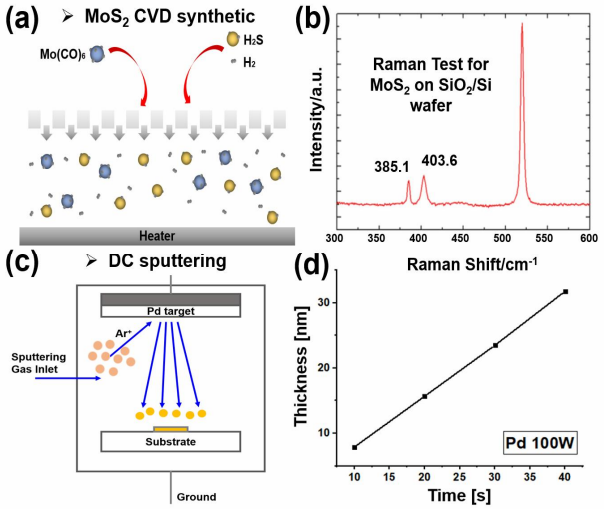

Fig. 4. (a) The schematic diagram of MoS_2 synthetic method; (b) Raman spectroscopy of the MoS_2 on SiO_2/Si, showing a distribution from 350-450 cm^{-1}; (c) The schematic diagram of DC sputter fabrication; (d) Pd thickness conditions as deposition time for DC sputtering.

III. Fabrication Method

Fig. 2(a) shows an overview of the fabrication process of the Pd-MoS_2 based H_2 sensor. Fig. 3(b) shows the channel and metal electrode deposition size of the fabricated nanocomposites H_2 gas sensor. After P^+ (Boron) implantation a Si wafer substrate, SiO_2 layer thickness of 300 nm was accumulated on the Si body by wet oxidation. To deposit the channel, MoS_2 is synthesized through chemical vapor deposition (CVD). Monolayer MoS_2 was deposited approximately 4 layers (~0.7 nm) and multilayer MoS_2 was deposited about 8 layers (~1.4 nm). Fig. 4(b) measured a sample of H_2 gas sensor by Raman spectroscopy of MoS_2. After the pattern is formed through a lithography process, Pd is decorated on MoS_2 using DC sputter as shown in Fig. 4(c). The sputtering process is conducted under two conditions: 4 seconds and 10 seconds at 100 W and Ar flow rate of 30 CC. If the Pd thickness exceeds 10 nm, the Pd nanoparticles are formed into Pd nanosheets. As shown in Fig. 4(d), Pd nanoparticles were decorated with 3 nm and 8 nm. As the last step, a two-terminal Ti/Au electrode is deposited with thicknesses of 10 nm/40 nm.

IV. Gas Sensor Mechanism

A detailed H_2 sensing mechanism is presented in Fig. 5. Prior to the injection of H_2 gas, oxygen molecules are adsorbed onto the surface of MoS_2 and converted into oxygen ions. When the gas sensor is exposed to H_2 gas, the Pd coating on the surface adsorbs H_2. As the concentration of H_2 gas increases, H_2 diffuses from Pd to the MoS_2 surface through the spillover effect. Subsequently, the oxygen ions and H_2 within the MoS_2 channel react, resulting in the production of H_2O and electrons. These chemical reactions induce changes in resistance in the MoS_2 channel. When observing the MoS_2-Pd network gas sensor, the Schottky barrier is lowered, allowing current to flow in response by H_2 injection.

V. Measurement Result

Fig. 6 shows the I-V characteristics of the fabricated Pd-decorated MoS_2 gas sensor. The I-V curves of the typical sensor in air exhibit obvious nonlinear operation at room temperature by vacuum probe station. A voltage DC sweeps of -5 V to +5 V was applied to the two-terminal electrodes. A significant difference of 1,000 times [3 orders] was observed when comparing the two devices coated with Pd 3 nm, with multilayer MoS_2 showing a larger difference compared to monolayer MoS_2. The number of MoS_2 layers not only affects the bandgap but also leads to different resistance values. Moreover, Pd 8nm decorated multilayer MoS2

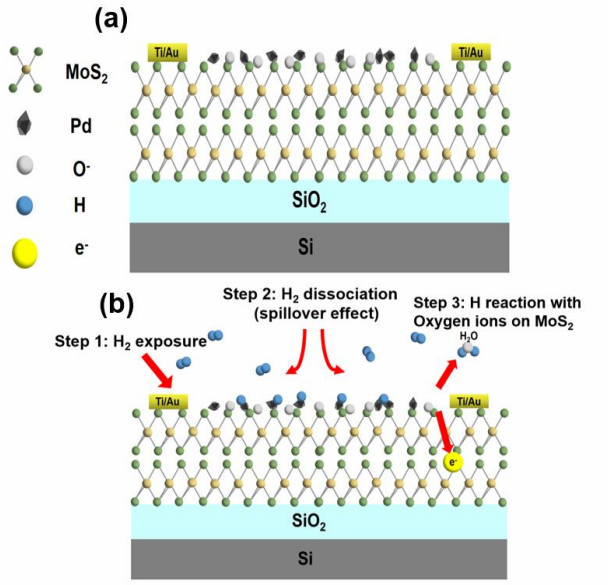

Fig. 5. H_2 sensing mechasim of Pd decorated MoS_2 gas sensor: (a) When H_2 gas is not exposed to the sensor; (b) When H_2 gas is injected to the sensor.

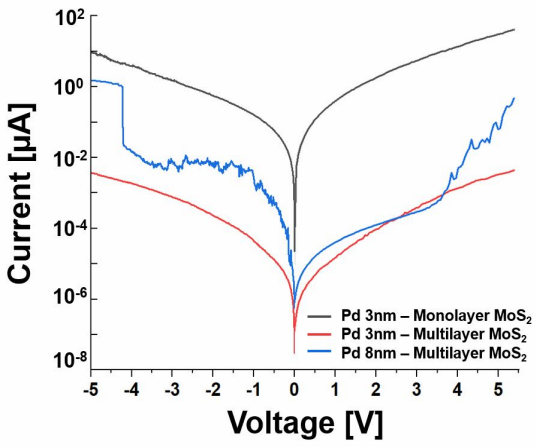

Fig. 6. I-V characteristics of the Pd decorated MoS2 network gas sensors measured by a typical DC double sweep.

demonstrates characteristics similar to a selector device in resistive random-access memory.

Fig. 7(a) and 5(b) are the results of extracting H_2 detection responses of monolayer MoS_2 and multilayer MoS_2 deposited with Pd 3 nm. To perform I-T curve measurements, a nanocomposite H_2 gas sensor was placed inside the gas probe station chamber. The N_2 gas was injected for 1 minute at a flow rate of 100 standard cubic centimeters per minute (SCCM) to minimize the reaction with other gases. When injecting H_2 gas at a 20 SCCM, all gases were controlled by a mass flow controller (MFC). During the measurement, a voltage of 3 V was applied to the Au/Ti electrode at room temperature. The gas concentrations were supplied at 10000 ppm, 20000 ppm, 30000 ppm, and 40000 ppm to detect the LOD. The sensitivity was calculated as R_0/R_g, where R_g denotes the channel resistance value of the sensor after H_2 gas injection, and R_0 presents the resistance of the gas sensor in the presence of an N_2 gas without H_2. To extract the response time, N_2 is injected to stabilize the resistance. To extract the response time, N_2 was injected to stabilize the resistance. The response time was measured as the time exceeding 90% of the initial resistance change from the injection of H_2 gas.

With the supply of H_2 gas, Fig. 7(a) shows that the sensitivity of the Pd 3 nm - monolayer MoS_2 gas sensor is about 22.19 and the response time is about 77.4 sec. In Fig. 7(b), the sensitivity of the Pd 3 nm - multilayer MoS_2 gas sensor was 6.513, and the response time was extracted as 220.8 sec. Therefore, it may be seen that MoS_2 as multilayer structure has excellent reaction characteristics of H_2 gas. On the other hand, Fig. 7(c) shows that there is no reactivity to H_2 gas when the Pd thickness is 8 nm. If deposited as Pd nanosheets rather than Pd nanoparticles, the reaction area of the sensing gas is reduced, and the catalytic properties of H_2 are degraded [21].

V. CONCLUSIONS

In this study, we proposed a resistive-type H_2 gas sensor with Pd-NP decorated on MoS_2 as channel network. Then, the chemiresitive H_2 detection mechanism in the sensing layer according to MoS_2 CVD synthesis and Pd nanoparticles coating technique is introduced. The sensitivity and response time of the fabricated H_2 gas sensors are measured through the input voltage signal. We demonstrated high H_2 reaction volume density properties through deposition of Pd nanoparticles. In addition, we compared the sensing parameters of H_2 gas following the interaction of electrons according to different energy band gaps with MoS_2. Finally, the H_2 sensor was optimized through Pd nanoparticle application technology, and the electrical H_2 gas sensing behavior according to the number of MoS_2 layers was confirmed through the input voltage.

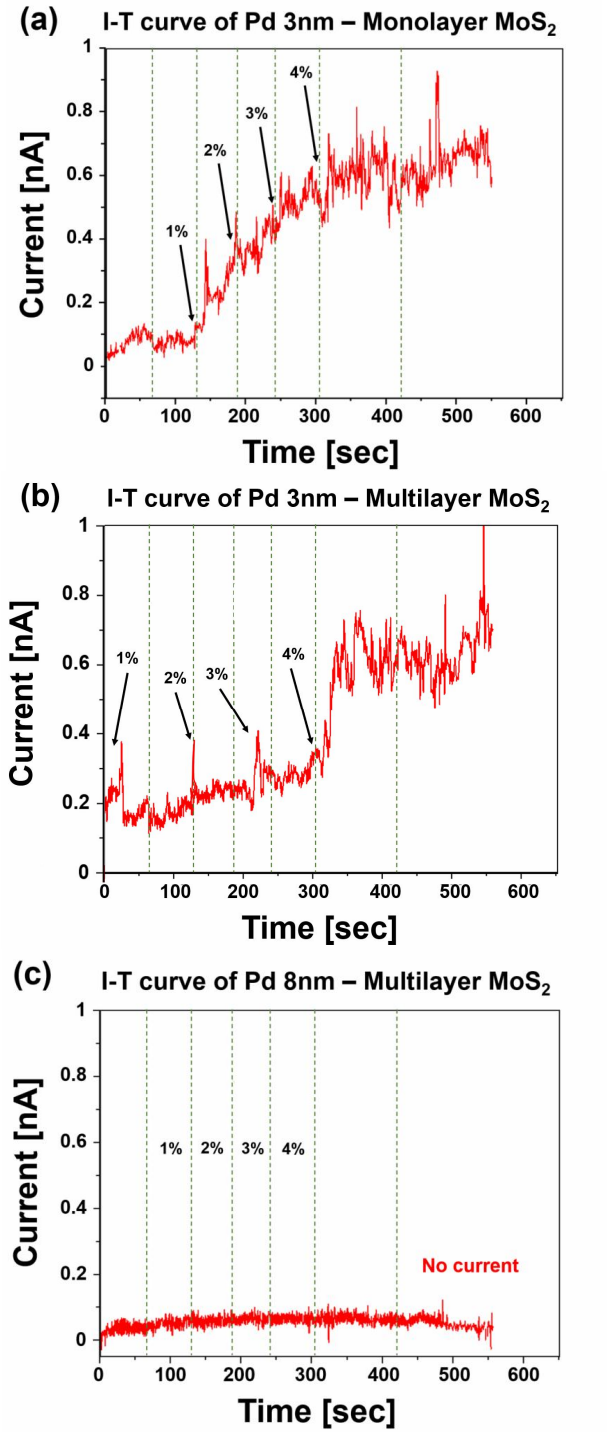

Fig. 7. Dynamic I-T curves of (a) Pd 3 nm – monolayer MoS_2 gas sensor; (b) Pd 3 nm – multilayer MoS_2 gas sensor; (c) Pd 8 nm – multilayer MoS_2 gas sensor as 1% to 4% H_2 concentration sensing.

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