Encapsulation of Semiconductor Gas Sensors with Gas Barrier Films for USN Application

Hyung-Kun Lee, Woo Seok Yang, Nak-Jin Choi, and Seung Eon Moon

Sensor nodes in ubiquitous sensor networks require autonomous replacement of deteriorated gas sensors with reserved sensors, which has led us to develop an encapsulation technique to avoid poisoning the reserved sensors and an autonomous activation technique to replace a deteriorated sensor with a reserved sensor. Encapsulations of In_2O_3 nanoparticles with poly(ethylene-co-vinyl alcohol) (EVOH) or polyvinylidene difluoride (PVDF) as gas barrier layers are reported. The EVOH or PVDF films are used for an encapsulation of In_2O_3 as a sensing material and are effective in blocking In_2O_3 from contacting formaldehyde (HCHO) gas. The activation process of In_2O_3 by removing the EVOH through heating is effective. However, the thermal decomposition of the PVDF affects the property of the In_2O_3 in terms of the gas reactivity. The response of the sensor to HCHO gas after removing the EVOH is 26%, which is not significantly different with the response of 28% in a reference sample that was not treated at all. We believe that the selection of gas barrier materials for the encapsulation and activation of In_2O_3 should be considered because of the ill effect the byproduct of thermal decomposition has on the sensing materials and other thermal properties of the barrier materials.

Keywords: Encapsulation, gas barrier, gas sensor, ubiquitous sensor network (USN).

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I. Introduction

A gas sensor is a device used to provide concentration information of gas analytes through reactions between the analytes and the sensing materials of the gas sensor. The reaction comes with a change in the electrical property or chemical composition of the sensing material. These gas sensors can be classified into a semiconductor type, an electrochemical type, or an optical type, among others, based on their working mechanisms [1], [2]. In addition, various materials, such as metal oxides, polymers, CNTs, and graphenes, have been utilized as the sensing materials of various types of gas sensors [3], [4].

The cross sensitivities of gas sensors to water vapor with an analyte gas are an issue to be resolved considering that gas sensors operate under ambient conditions. An optical gas sensor overcomes the water vapor issue by adopting selective filters into the detectors, which enable the sensor to cut out the optical absorption band of water vapor from its full spectrum range [5]. However, this type of solution cannot be applied in semiconductor- or electrochemical-type gas sensors, as these types do not use optical filters. In semiconductor-type gas sensors, the amount of gas analytes in the environment can be determined based on the resistance changes resulting from the reaction between the gas analytes and the surface of the sensing materials. Recently, a semiconductor-type gas sensor consisting of NiO-doped SnO_2 showd a response with negligible humidity dependence owing to the selective adsorption of water into the NiO, resulting in a consistent reactivity of SnO_2 to carbon monoxide gas in various humid conditions [6]. However, it is still difficult to exclude the effect of water vapor and oxygen in an atmosphere in all semiconductor-type gas sensors.

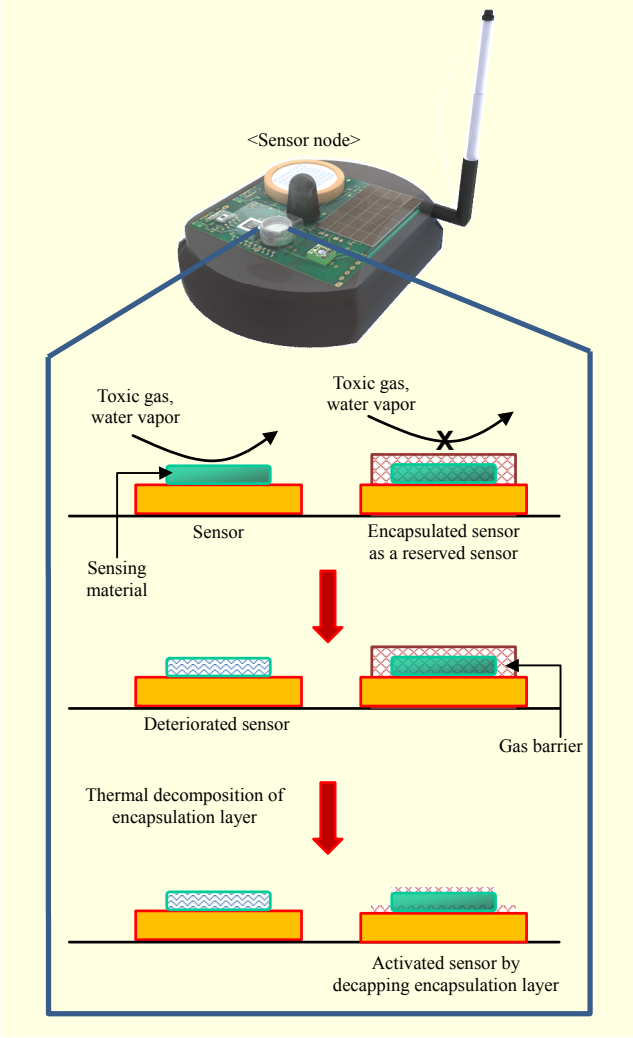

Fig. 1. Schematic diagram of encapsulation and activation of semiconductor-type gas sensor consisting of In_2O_3 nanoparticles.

Many researchers have attempted to develop semiconductor-type gas sensors with low power consumption [7]-[10] and apply these sensors into portable gas monitoring devices and ubiquitous sensor networks (USNs) [11]-[14]. The reliability of USNs can be established from the robustness of the sensors integrated into the sensor nodes. However, the application of these gas sensors into USNs has been limited owing to the poisoning phenomena of the sensing materials resulting from reactions with toxic gases and water vapor.

In this paper, we report on the encapsulations of the sensing materials of these gas sensors using gas barrier polymer layers to avoid a poisoning (suffering a loss of response) of the sensing materials by a toxic gas or water vapor. The encapsulating material of the sensing materials is adopted from food packing [15] and display encapsulation [16] research. Furthermore, the activation of sensing materials by removing the barrier layers through a thermal decomposition is demonstrated, as shown in Fig. 1. These encapsulations of the sensors by the gas barrier films and the activations of the sensors by the thermal decomposition of barrier films can be carried out through a simple heating of the sensors, which makes it possible for the autonomous operation or programmed operation in the USNs to replace a deteriorated sensor with an encapsulated sensor as a reserved sensor. This operation can be expected to increase the robustness of the sensor node incorporating the gas sensor against the poisoning phenomena.

II. Experiments

1. Preparation of Semiconductor-Type Gas Sensor

An In_2O_3 paste as a sensing material of a semiconductor-type gas sensor was deposited on an alumina substrate on which the Pt electrodes were screen-printed. A thick film heater made from Pt/Pd alloy was printed on the reverse side of the substrate. The fabricated gas sensor devices were thermally treated at 850°C for 1 hr to ensure solidification of the sensing material and the removal of alpha-terpineol, which is used for paste formation with the In_2O_3 nanoparticles, from the paste.

2. Encapsulation of In_2O_3 with Gas Barrier

The encapsulation films of the sensing materials were selected by considering the gas barrier property. Poly(ethylene-co-vinyl alcohol) (EVOH) has been known as an effective gas barrier material against oxygen and water vapor and is used for food packing material [15], [17]. EVOH containing 27 mol% ethylene fractions was purchased from Sigma-Aldrich. Polyvinylidene difluoride (PVDF) was selected as another candidate for the gas barrier material owing to its inertness against other toxic chemicals as well as its hydrophobicity. The PVDF (Mn = 70,000) was also purchased from Sigma-Aldrich.

EVOH and PVDF pellets were transformed into films through hot pressing at 150°C to 180°C, and the thickness of the films were adjusted to around 50 μm. The resulting EVOH and PVDF films were placed on top of the sensing material while heating at 160°C to 190°C to encapsulate the gas-sensing materials with barrier films.

3. Removal of Gas Barrier from Gas Sensors

Encapsulation films as a gas barrier from the surface of the sensing materials made from the In_2O_3 nanoparticles were removed through the thermal decomposition of the barrier film at 600°C for 10 minutes. The encapsulated layer composed of a PVDF was removed from the sensor, resulting in a dark-

colored stain. On the other hand, the encapsulated layer with the EVOH disappeared without leaving a colored stain. SEM and EDX analyses were carried out to check the influence of the thermal decomposition of the encapsulated layers on the sensing material.

4. Measurement of Gas Sensing Property of Sensor

The effectiveness of the gas barrier films, PVDF and EVOH, on the gas sensing property can be confirmed by investigating the response behaviors of the sensors for the analyte gas. The electrical resistances of the gas sensors encapsulated with PVDF and EVOH, as well as the reference sample, were monitored because the response of the gas sensor can be defined as

$$\text{Response}\ (\%) = (R_a - R_g)/R_a \times 100, \quad (1)$$

where R_a is the resistance of the sensor upon exposure to air, and R_g is the resistance of the sensor upon exposure to such analyte gas as formaldehyde.

The gas sensors were located in a steel chamber fitted with inlet and outlet ports for the gas flow. Air as a balanced gas was used at a 2,000 cc/min flow rate, and formaldehyde (HCHO) gas of 20 parts-per-million (ppm) was used as the analyte. The desired analyte concentration was controlled by mixing HCHO gas with balanced gas to achieve a concentration of 0.2 ppm to 2 ppm using mass flow controllers (MFCs). The measurements of gas sensitivity were carried out at 400°C by applying power into the heater integrated into the sensors. The reaction periods were controlled by flowing HCHO gas with the desired concentration into the reaction chamber for two minutes, followed by flowing only balanced gas into the chamber for three to four minutes to recover the gas sensors. These response measurements of the sensors were carried out before and after removing the encapsulating materials from the gas sensing materials to investigate the encapsulating and the decapping efficiencies.

III. Results and Discussion

An EVOH film has been reported as an efficient barrier material that blocks the permeation of oxygen and water vapor. Semiconductor-type gas sensors are easily affected by oxygen, water vapor, and toxic gas, resulting in the instability of the reference resistance of the sensor [18], [19]. HCHO is one of the gases giving rise to the sick building syndrome occurring in newly-built apartments or remodeled houses, as its emissions irritate the eyes and mucous membranes in the nose and throat. In addition, the gas is classified as a carcinogen, which means that HCHO can be considered as a toxic or reactive gas. Therefore, we tried to encapsulate In_2O_3 as the sensing material

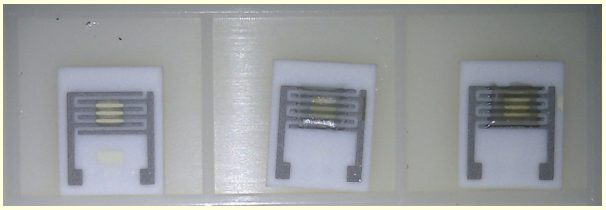

Fig. 2. Gas sensor device (a) without an encapsulation layer as reference sample, (b) with PVDF encapsulation layer, and (c) with EVOH encapsulation layer.

with EVOH film as the gas barrier layer to investigate the efficiency of the encapsulated layer to monitor the sensor response to HCHO gas. We selected EVOH as a gas barrier film owing to its high moisture barrier efficiency of 1.4-5.4 gram-mil/100sq per 24 hrs in an atm at 40°C and 90% relative humidity (RH) and because of its thermal stability during the encapsulation and decapping processes [15]. When we apply a polymer as the gas barrier film of a gas sensor, the polymer should melt at a low temperature during the encapsulation process and decompose at a low temperature during the decapping process. PVDF was also selected as a gas barrier film, as it is a known gas barrier material and is expected to be robust against toxic gases [15], [20]. The encapsulation process was carried out at 160°C to 190°C by heating 50 μm thick EVOH and PVDC films on gas sensor devices to encapsulate the In_2O_3 nanoparticles of the gas sensor, as shown in Fig. 2.

The gas sensors encapsulated with EVOH and PVDF were investigated in terms of the response to HCHO gas to check the gas barrier efficiency. The sensors were located in a gas reaction chamber and exposed to HCHO gas with controlled concentrations of 0.2 ppm to 2.0 ppm. The reference sample showed a 28% response through a reaction with HCHO at a 1 ppm concentration. On the other hand, the encapsulated sensors with the EVOH or PVDF showed a negligible response to HCHO gas through concentrations of 0.2 ppm to 2.0 ppm, which means the sensing materials were isolated or well encapsulated from the HCHO gas by the EVOH or PVDF barrier layer, as shown in Fig. 3. The fluctuation in the sensitivity of the gas of the encapsulated sample at 1.0 ppm to 2.0 ppm comes from the temperature changes resulting from the HCHO analyte gas injecting on and off the sample. We can confirm that the encapsulation process of the gas sensors with the EVOH and PVDF were effective to protect the sensing materials from the HCHO gas by comparing the responses of the reference sample and the encapsulated sensors to the HCHO gas.

The decapping processes of the encapsulated gas sensors were carried out by removing the EVOH or PVDF layers from

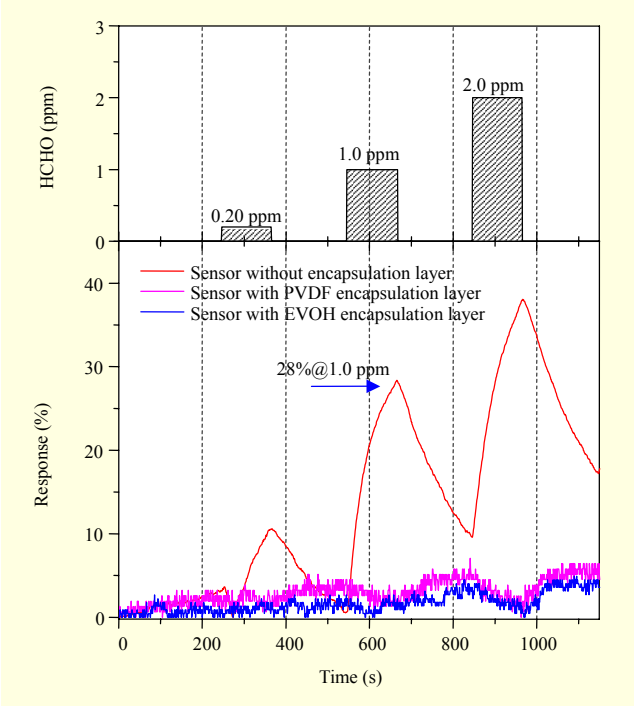

Fig. 3. Responses to HCHO gas of reference sample, sensor encapsulated with PVDF, and sensor encapsulated with EVOH at concentrations of 0.20 ppm to 2.0 ppm at 400°C as measurement temperature.

Fig. 4. (a) Reference sample without encapsulation after heating at 600°C, and removal of (b) PVDF encapsulation layer and (c) EVOH encapsulation after heating at 600°C.

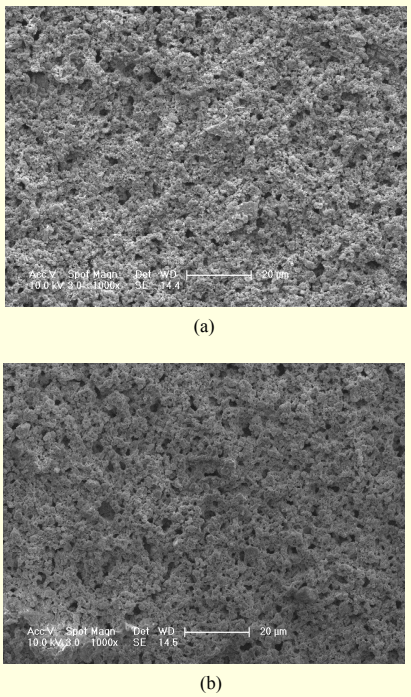

Fig. 5. SEM images In_2O_3 surface of (a) reference sample and (b) activated sensor after removing EVOH.

the gas sensor devices through the thermal decomposition of the films, which allowed the sensing materials to be exposed to the gas analytes. The gas barrier materials are composed of only polymer, void of any metal or clay. Thus, the gas barrier materials can be removed by relatively mild heating compared to the annealing condition of sensing materials, which has a temperature of around 700°C to 900°C and a duration of several hours to several days, and they are not expected to affect the sensing materials' property by remaining after the thermal decomposition. The decapping process of the gas sensor was carried out by heating the barrier materials at 600°C for 10 minutes, which was effective for removing the EVOH and PVDF layers through thermal decomposition, as shown in Fig. 4.

These decapping processes of the barrier layers can be carried out autonomously by using an integrated heater in the sensors. Therefore, the activation processes can be applied in the sensor nodes of the USNs to replace a deteriorated sensor with a reserved sensor that was encapsulated with the gas barrier layers.

The sensor encapsulated with a PVDF showed color changes in the sensing materials after the activation process. According to [21], this phenomenon was a result of a side reaction with the In_2O_3 nanoparticles and fluorine coming from the PVDF thermal decomposition, which was well matched with the F element found through an energy-dispersive X-ray spectroscopy analysis (EDX) of the sensor activated by removing the PVDF. In a semiconductor-type gas sensor, the electrical property of the sensing materials is one of the important factors because the sensor's responses to gas are determined by the electrical resistance changes of the sensing materials. This fluorine doping of the In_2O_3 can affect the response of the gas sensor after removing the PVDF barrier layer. On the other hand, the sensor encapsulated with EVOH did not show any color changes after the activation process. The EVOH is composed of only carbon, oxygen, and hydrogen, and, thus, the remaining materials after thermal decomposition are expected to be only CO_2 and H_2O. These byproducts can be vaporized at 600°C on the surface of the

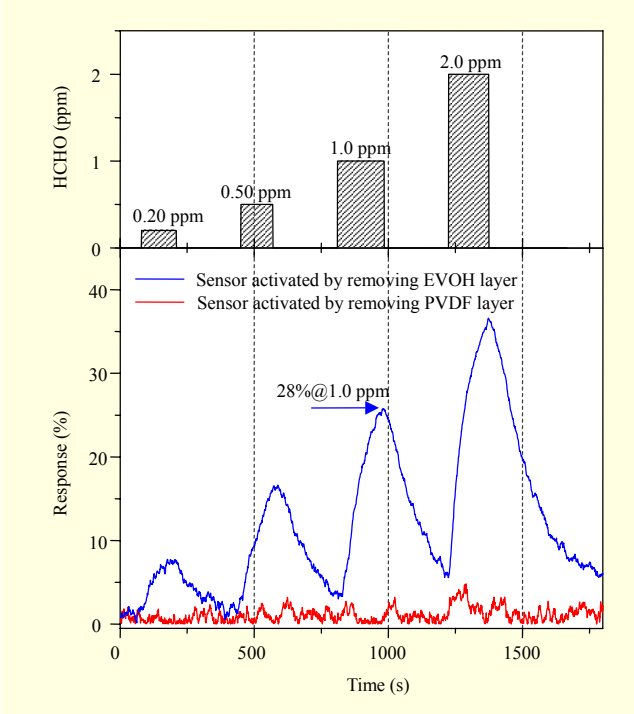

Fig. 6. Responses to HCHO gas in sensors activated again by removing EVOH and PVDF barrier films at concentrations of 0.20 ppm to 2.0 ppm at 400°C as measurement temperature.

In_2O_3 and removed efficiently without any effects on the property of the In_2O_3. At this point, the differences of the thermal decomposition phenomena of the gas barriers can be utilized for the selection of the gas barrier layers. The gas barrier can be selected on the basis of the fact that the byproduct of the thermal decomposition of the barrier layers should be inert or removed completely without affecting the property of the gas sensing materials.

We investigated the resulting sensing materials after the removal of gas barrier materials through thermal decomposition using SEM, as shown in Fig. 5. We found that several hundreds of micrometer-sized In_2O_3 particles and macroporous cavities were reserved after thermal treatment at 600°C to remove the EVOH. Furthermore, there was no significant difference between the sensing materials of the reference and the activated sample after removing the EVOH through EDX.

The gas sensors activated by removing the EVOH and PVDF from In_2O_3 were again investigated in terms of the response to the HCHO gas to check the effect of the barrier removal process at 600°C on sensing materials, as shown in Fig. 6. After the removal of the PVDF, the activated sensor showed no response to the HCHO gas. We thought that this result may be related to the side reaction of In_2O_3 with fluorine coming from the decomposition process of the PVDF. Fluorine-doping of In_2O_3 can change the electrical property of the In_2O_3 nanoparticles significantly as fluorine atoms show a high electro-negativity. Therefore, we think that PVDF is not suitable as an effective barrier material to In_2O_3 nanoparticles.

After the removal of the EVOH, the activated sensor showed a similar response (sensitivity 26%) to HCHO compared to the reference (sensitivity 28%), shown in Fig. 3. Therefore, we found that EVOH can be an effective gas barrier material to HCHO gas and can be applied as an encapsulation material, as this did not accompany any electrical property changes of the sensing material after the activation process.

IV. Conclusion

We reported the encapsulation of In_2O_3 with EVOH or PVDF used as a gas barrier layer. We found that the EVOH and PVDF played a role in protecting the In_2O_3 from the HCHO gas. In addition, the activation process of the In_2O_3 achieved by removing the EVOH through a thermal decomposition was found to be effective. However, the thermal decomposition of the PVDF affected the sensing property of the In_2O_3 in terms of the response to gas. From these results, the selection of the gas barrier material should be considered for a reaction between the sensing material and the side product of its thermal decomposition, as well as gas permeation property, glass transition temperature, melting temperature, and decomposition temperature. The encapsulation of the sensing materials with the gas barriers and the activation of the gas sensors can be applied in a wireless sensor node, as a gas sensor contains an internal heater that can be utilized for the activation process with autonomous processes within the wireless sensor nodes. We expect that an autonomous or programmed operation in the USNs can replace a deteriorated sensor with an encapsulated sensor as the reserved sensor, which should increase the reliability of the gas sensor nodes regarding the poisoning phenomena.

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