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A Hydrogen Sulfide Sensor Based on a Surface Acoustic Wave Resonator Combined with Ionic Liquid

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Abstract:

This paper describes a hydrogen sulfide (H_2S) gas sensor using ionic liquid (IL). In this sensor, a reservoir for the IL was integrated above a surface acoustic wave (SAW) resonator. The IL serves as an absorber for H_2S gas. Mass change due to this absorption is detected as a frequency-shift of the resonance. In this study, we fabricated and demonstrated the sensor using the $LiNbO_3$ SAW resonator with the resonant frequency of 38 MHz. The integrated reservoir was filled by the IL 1-butyl-3-methlimidazlium tetrafluoroborate ([BMIM]-[BF_4]). As experimental results, we could observe the linear correlation between the amount of the frequency-shift and the exposure time of the sensor to the H_2S gas.

Key words: H_2S, SAW, ionic liquid, gas sensor

Introduction

Hydrogen sulfide (H_2S) gas is one of the common toxic gases in our life today. Since 2008, there has been a burgeoning of suicide attempts using the H_2S gas, and the fad is escalating into a chain reaction in Japan [1]. The H_2S gas is made from household chemicals in the bath or toilet, and is synthesized voluminously more than what is required for an individual suicide. So, it is very deleterious not only for the suicide but also for his family, neighbors, and rescuers. Recently, high sensitive detection of the H_2S gas becomes important to make our society safe and comfortable.

In this study, we developed a new type H_2S gas sensor based on the surface acoustic wave (SAW) resonator. The SAW technology is mature to detect the mass change and widely accepted as a high sensitive sensor [2-8]. In addition, the SAW resonator is suitable for size shrinkage, suppression of power consumption and integration with RF systems. These advantages are attractive to construct the wireless sensor network to monitor the generation of the H_2S gas as a distribution.

To develop the H_2S gas sensor, the material to trap the H_2S gas and give the mass change to the SAW resonance is a key. The ionic liquid (IL) was spotlighted for such absorber in this study. The IL is molten salts that are liquid over a wide temperature range including ambient temperatures. It has high thermal and electrochemical stability since a vapor pressure of the IL is negligibly small. One of the active research areas of the IL is an application to trap and remove the acid gas (CO_2 or H_2S) from sour natural gas [9]. Especially, 1-butyl-3-methlimidazlium tetrafluoroborate ([BMIM]-[BF_4]) has been reported as a useful H_2S absorber [10].

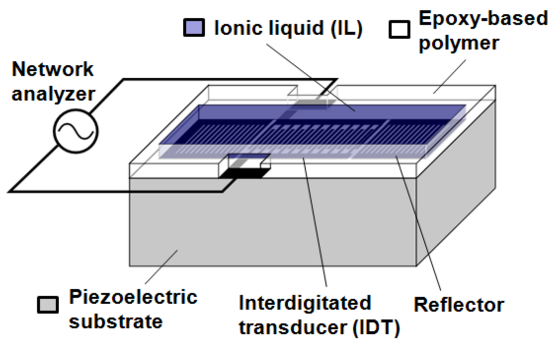

Fig. 1. Schematic illustration of the SAW based H_2S gas sensor combined with ionic liquid.

Using this IL [BMIM]-[BF_4] for the absorber on the SAW resonator, the sensor can obtain the high selectivity for the H_2S gas, and high stability against a temperature and a pressure in operating environment.

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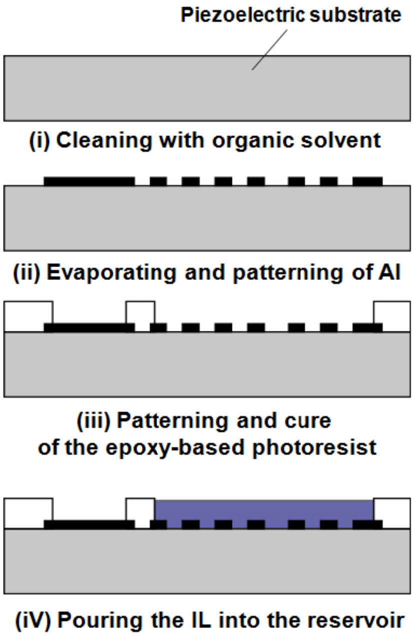

Fig. 2. Fabrication flow of the H_2S gas sensor.

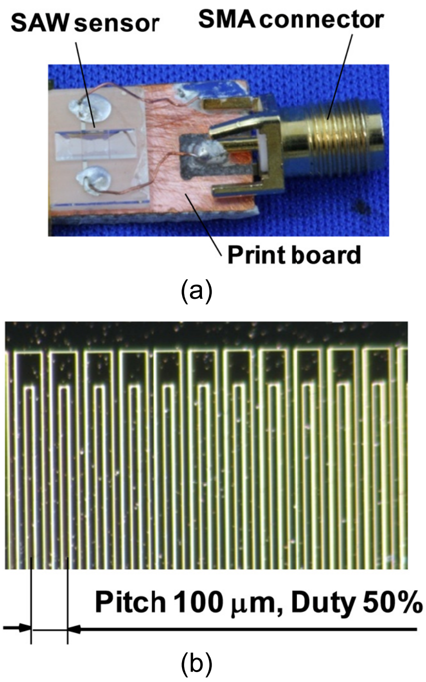

Fig. 3. Optical micrographs of the H_2S gas sensor.

Fabrication

Figure 1 shows a schematic illustration of the H_2S gas sensor we propose. In this sensor, a reservoir for the IL was integrated above a SAW resonator using micro electromechanical systems (MEMS) based technologies. In the SAW resonator, resonant frequency was designed at 40 MHz, and the pitch, duty, pair number of the interdigital transducer (IDT), and number of the reflector were set to 100 μm, 50%, 20 and 40, respectively.

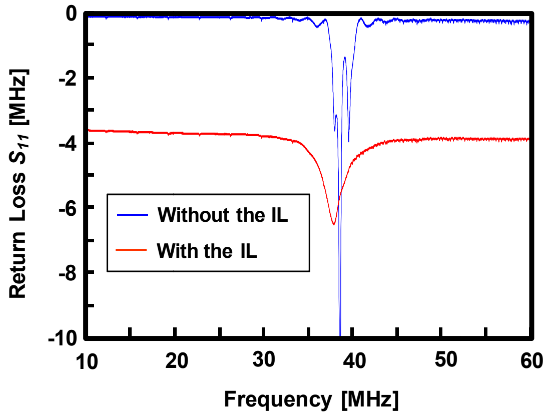

Fig. 4. Resonant characteristics of the H_2S gas sensors.

Figure 2 shows a fabrication flow of the H_2S gas sensor. At first, 128°Y-X cut $LiNbO_3$ substrate was cleaned by organic solvent in the ultrasonic bath. And then, aluminum (Al) was sputtered on the substrate to the thickness of 200 nm, and patterned using the etchant, which is a diluted compound liquid of H_3PO_4, HNO_3 and CH_3COOH. Using the epoxy-based photoresist (MICRO CHEM: SU-8 3050), the reservoir was fabricated on the resonator. The depth of the reservoir was about 170 μm. Finally, the IL [BMIM]-[BF_4] was delivered by drops into the reservoir.

Figure 3 shows optical micrographs of the sensor. The sensor was mounted on the print board and was wired from the pads on the sensor to a RF connector with Cu wires. Figure 3(b) shows an enlargement of the IDT. It was confirmed that the IDT pattern was fabricated successfully.

Experimental results

Figure 4 shows resonant characteristics measured from the sensor with and without the [BMIM]-[BF_4] using the network analyzer (Rohde & Schwarz: ZVB8). The resonant frequency was decreased from 38.6 MHz to 37.9 MHz by coating the [BMIM]-[BF_4]. It was also confirmed from Fig. 4 that spurious responses were suppressed though the Q factor was dissipated by the coating.

Figure 5 shows a block diagram of an experimental setup to evaluate the H_2S gas detection. The following steps were executed for the evaluation: 1) Evacuating the chamber to the pressure of 1.0 Pa: 2) Stopping the evacuation and introducing nitrogen (N_2) gas to the pressure of 1.2×10^4 Pa: 3) Introducing the H_2S gas, and adjusting the pressure to the 4.1×10^4 Pa (partial pressure of H_2S and N_2 were 0.028×10^4 Pa and 4.07×10^4 Pa,

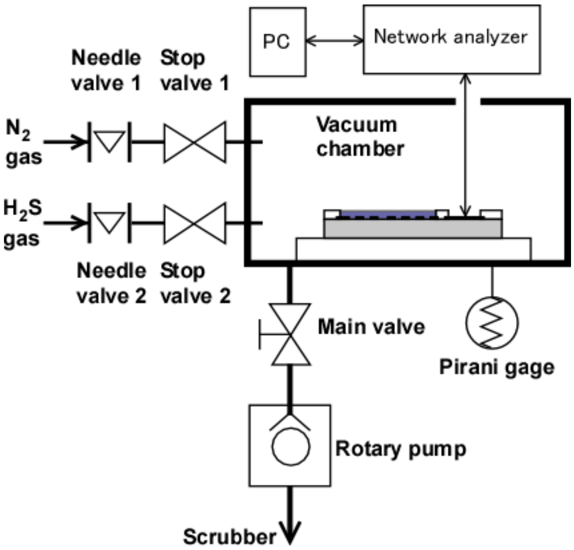

Fig. 5 Experimental setup for evaluation of the H_2S gas sensor.

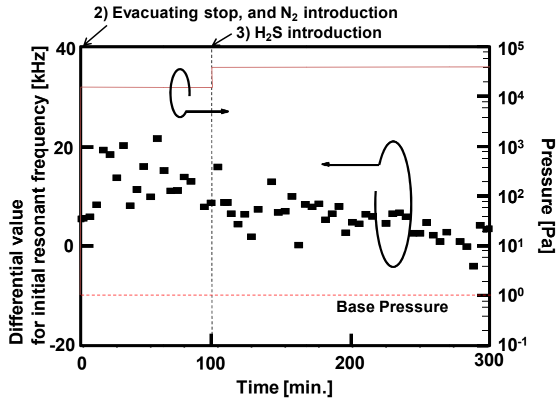

Fig. 6. Variation of the resonant frequency due to the exposing the sensor into the H_2S gas.

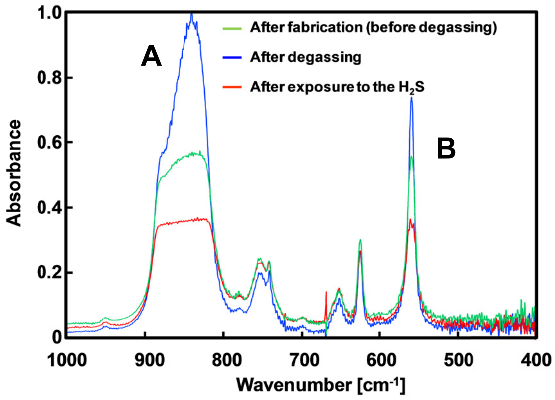

Fig. 7. FT-IR spectra for the [BMIM]-[BF_4].

respectively).

Figure 6 shows a variation of the resonant frequency by exposing the sensor to the gasses.When the N_2 gas was introduced to the chamber, essential change of the resonant frequency could not be observed. However, it could be observed after the introduction of the H_2S gas that the resonant frequency of the sensor was downshifted for the exposure time.

After the above experiments, the resonant frequency could be recovered to the initial frequency by baking in vacuum (degassing). Thus, the sensor can be used repeatedly.

Fourier transform infrared (FT-IR) spectra for the [BMIM]-[BF_4] were shown in Fig. 7. Two strong peaks were observed, which were named to A and B in Fig. 7. The peaks indicate a bonding between the cation $[BMIM]^+$ and the anion $[BF_4]^-$ [11]. These were increased by degassing in vacuum and were decreased by exposing to the H_2S gas. From this result, it was grasped that the [BMIM]-[BF_4] could trap the H_2S gas, and the bonding of ions in the [BMIM]-[BF_4] was disturbed due to the H_2S absorption.

Conclusion

Hydrogen sulfide (H_2S) gas is one of the common toxic gases in our life today. To construct the safety and comfortable society, we developed a new type H_2S gas sensor based on a surface acoustic wave (SAW) resonator.

In this sensor, a reservoir for the IL was integrated above a surface acoustic wave (SAW) resonator. The IL serves as an absorber for H_2S gas. Mass change due to this absorption is detected as a frequency-shift of the resonance. In this study, we fabricated and demonstrated the sensor using the $LiNbO_3$ based SAW resonator with the resonant frequency of 38 MHz. The integrated reservoir was filled by the IL 1-butyl-3-methlimidazlium tetrafluoroborate ([BMIM]- [BF4]).

Exposing the fabricated sensor into the H_2S gas, we could observe experimentally the linear correlation between the amount of the frequency-shift and the exposure time. From the FT-IR spectra of the [BMIM]-[BF_4], it was confirmed that the frequency-shift was induced by trapping the H_2S gas to the [BMIM]- [BF_4].

Acknowledgements

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