Shear Horizontal Surface Acoustic Wave Resonators for Ammonia Detection

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Abstract: This Shear horizontal surface acoustic wave (SH-SAW) devices coated with L-glutamic acid hydrochloride have been fabricated and used as ammonia sensors in this work. The humidity effect on the ammonia sensors was also studied. The sensitivity of the ammonia sensor was 4.6 ppm/ppm and the frequency shift was negative at 50°C in dry air. As the humidity rose in the environment, the sensor exhibited a positively increasing frequency shift. It proved that the humidity in the environment interfered with the detection to ammonia. This work would focus on estimating the cross-sensitivity of the humidity interference.

Key-Words: Shear horizontal surface acoustic wave, L-glutamic acid hydrochloride, Ammonia, Sensitivity, humidity, Cross-sensitivity.

1 Introduction

The detection of ammonia gas is an important task in many circumstances such as food technology, industrial processes, environmental protection, and medical diagnosis, because ammonia presents in ambient polluting aerosols and may cause disease in humans. The chemical interfaces for ammonia detection have metal oxide, metal film, and polymer. SnO_2 and group-III-element-doped zinc-oxide were successfully used to detect ammonia at 350°C [1, 2]. Hohkawa et al. [3, 4] studied the characteristics of surface acoustic wave (SAW) sensors based on porous alumina with Pt or Co catalyst to ammonia. Palladium metal-oxide-semiconductor (Pd-MOS) structures were also proved to be useful for ammonia detection [5]. D'Amico et al. [6] employed a SAW delay line coated with selectively sorbent platinum (Pt) film to sensitively detect ammonia. Penza et al. [7-9] employed the polypyrrole film, prepared by the Langmuir-Blodgett (LB) technique, to selectively and sensitively detect ammonia gas from 46 ppm to 10000 ppm.

In this study, L-glutamic acid hydrochloride was as the chemical interface for detecting ammonia. The sensor was the shear horizontal surface acoustic wave (SH-SAW) resonator. We continuously studied the detection properties of SAW sensors based on L-glutamic acid hydrochloride to ammonia [10-15]. It was proved that the SAW delay line based on L-glutamic acid hydrochloride had high sensitivity, selectivity, reversibility, and repeatability to ammonia. The detection limit of L-glutamic acid

hydrochloride for ammonia has been found to be less than 0.90 ppm ammonia in dry air. In general, the humidity in the air seriously interferes with the detection of ammonia sensors. The previous report [11] showed the gas detecting properties of L-glutamic acid hydrochloride deposited on 128° YX-$LiNbO_3$ SAW delay lines were interfered with increasing humidity. All previous studies related to the humidity effect focused on the concentration of ammonia above 1 ppm. In fact, it is very important to realize the humidity effect on the detection of ppb concentration of ammonia for biosensor application. In this study, the SH-SAW sensors on 36°YX-$LiTaO_3$ resonators coated with L-glutamic acid hydrochloride were investigated to demonstrate the humidity effect on the detection of ppb ammonia.

2 Experimental

The SH-SAW resonators were fabricated on a 36°YX-$LiTaO_3$ substrate by lift-off methods, using aluminum 1200 Å metallization. The characteristics of the SH-SAW resonator were measured by network analyzer (E5071A, Agilent, USA). L-glutamic acid hydrochloride was the chemical interface. A known quantity of L-glutamic acid hydrochloride (Aldrich, USA) was weighed and dissolved in a known volume of deionized water at 75°C, to a concentration of 0.1 mg/ml. Prior to the coating layer being applied, the surface of the SH-SAW resonator had been cleaned in acetone, and dried in an oven (Rendah, Taiwan) at 80°C. Then, a coating of L-glutamic acid hydrochloride was deposited on the surface of the SH-SAW resonator by air brushing.

The SH-SAW resonators were introduced into a SH-SAW sensing system (Nenogram balance, ftech, Taiwan), which applied a dual-device configuration. The operating frequency was 148 MHz. The period of interdigital transducer (IDT) was 28 μm. Each IDT had eight finger-pairs and the acoustic aperture was 750 μm. The center-to-center spacing between the two IDTs was 1659 μm. The RF electronic oscillator circuit was employed to generate RF signals in SH-SAW sensing system. The improved circuit and precise temperature-controller were used to ensure temperature stability with ± 0.01°C. A gaseous ambience was controlled by the mass flow controller (Sierra, USA) on the flow rate of 110*ml/min*. All detections were preceded at 50°C. Before testing gas exposure, the sensor was exposed in dry air for 30 min to stabilize the initial SH-SAW signal. Lastly, a frequency counter monitored the frequency shifts in SH-SAW sensing system, which was connected to a computer system via a RS-232 interface board.

3 Results and Discussion

Most applications of the chemical sensor utilize a chemical interface, which acts as a selective sink, on the surface of the SH-SAW. The responses of the sensor respond to the changes of properties of the chemical interface due to the absorption of target. L-glutamic acid hydrochloride is a stiff and non-conductive material, so the perturbation for L-glutamic acid hydrochloride after absorption can be described as follows [16],

$$\Delta f = (k_1 + k_2) f_0^2 h \rho_f - k_2 f_0^2 h \left\{ \frac{4\mu'(\lambda' + \mu')}{v_0^2(\lambda' + 2\mu')} \right\}, \qquad (1)$$

where k_1 and k_2 are negative constants of the substrate material, h is the film thickness, ρ_f is film density, and λ', u' are the shear modulus and

Lame constants of the chemical interface. The two terms on the right of Eq. (1) indicate the contributions of change in mass loading and elastic effect, respectively, to total changes in the SH-SAW frequency shift. The frequency shift is negative when the mass loading dominates the perturbation, whereas the frequency shift is positive as the elastic effect is dominant. The responses of sensors at the various concentrations of ammonia in dry air at 50°C were measured and shown as Fig. 1. It shows that the frequency shift linearly increased as the ammonia concentration increased from 40 ppb to 400 ppb. The sensitivity of the sensor at 50°C in dry air was 4.6 ppm/ppm. Moreover, the negative frequency shift presents the mass loading is dominant during detecting ammonia in dry air at 50°C.

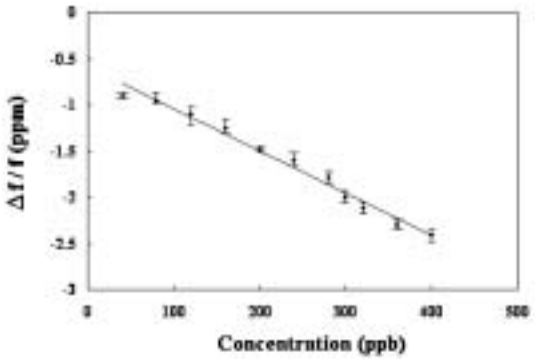

Fig.1 Responses of sensor coated with L-glutamic acid hydrochloride at the various concentration of ammonia in dry air at 50°C.

The frequency shift only due to the absorption of humidity was measured and shown as Fig. 2(a). The positive frequency shift rapidly increased as humidity increased until 40%RH. Then the frequency shift gradually increased and saturated at 60%RH. It can be found that the absorption of water molecules could change the modulus of L-glutamic acid hydrochloride and made the elastic effect to be the primary perturbation. The further increasing humidity above 60%RH did not significantly change the modulus and resulted in the saturation of the response. Fig. 2(b) shows the responses to 40 ppb ammonia gas as a function of humidity. It illustrates the similar results to Fig. 2(a) and means that the contribution resulted from humidity was evident.

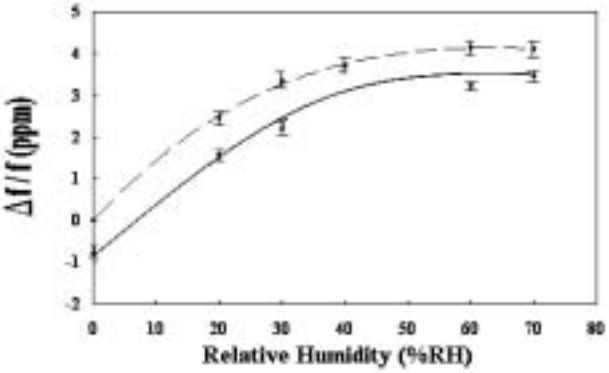

Fig. 2 Responses of sensor coated with L-glutamic acid hydrochloride at 50°C for (a) various relative humidity and (b) 40 ppb ammonia at the various relative humidity.

Therefore, the responses of the sensor can not be described by a simple linear combination of the individual sensitivities for dry ammonia and humidity. A mathematical relation of the response characteristics to dry ammonia and to humidity can be described as [17]

$$S_{(NH_3,H_2O)} = S_{(NH_3)} + S_{(H_2O)} + DS_{(NH_3)}S_{(H_2O)}, \quad (2)$$

where $S_{(NH_3,H_2O)}$ is the frequency shift to ammonia in humid air in Hz, $S_{(NH_3)}$ the frequency shift to ammonia in dry air in Hz, $S_{(H_2O)}$ the frequency shift to humidity in Hz, and D is the cross-sensitivity. The third term on the right of Eq. (2) is a cross-term that describes the mutual dependence of the response on ammonia and humidity. To explain the interference from humidity, $S_{(NH_3,H_2O)}$, $S_{(NH_3)}$, and

$S_{(H_2O)}$ were separately measured and substituted into Eq. (2).The cross-sensitivity is shown as Fig. 3. The cross-sensitivity slightly and positively increased as the humidity raised up to 30%RH, then it rapidly turned to negative value and gradually saturated at 60%RH. This saturation is consistent with the results of Fig. 2. The cross-sensitivity was zero when the humidity was 31.4%RH. It suggests that it can operate the SH-SAW ammonia sensor below 31.4%RH with negligible humidity interference.

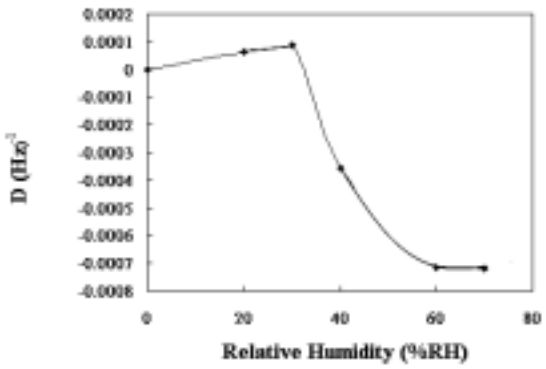

Fig. 3 Cross-sensitivity of ammonia sensor with various relative humidity at 50°C.

4 Conclusions

In this work, the humidity effect on the ammonia sensors coated with L-glutamic acid hydrochloride, which presented an excellent detection to ammonia in dry air, was studied. The sensitivity of the sensor was 4.6 ppm/ppm and the frequency shift was negative at 50°C in dry air. However, the sensor positively responded to the humidity in the environment. It suggests the operation below 31.4%RH is with negligible humidity interference for ammonia detection.

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