Gas-detecting properties of surface acoustic wave ammonia sensors

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Abstract

The detecting properties of L-glutamic acid hydrochloride that is deposited on 128\(^\circ\) YX-LiNbO\(_3\) surface acoustic wave (SAW) delay lines are studied in this work. SAW gas sensors that were based on L-glutamic acid hydrochloride had good sensitivity, selectivity, reversibility, and repeatability to ammonia gas. A detection limit of 0.56 ppm for gaseous ammonia was observed when using L-glutamic acid hydrochloride for the sensing film at room temperature. The response degraded at a rate of \(-0.01\) ppm per day at room temperature, and it means that the long-term stability of L-glutamic acid hydrochloride is quite enough. The cross-sensitivity from humidity interference was approximately 0.011. Therefore, the interference from water molecules is slight in room ambient air, so the effect of humidity on SAW response is negligible.

Keywords: Ammonia; Surface acoustic wave; Sensitivity; Reversibility; Repeatability; Stability

1. Introduction

The continuous detection of ammonia is essential in personnel protection, industrial hygiene, and clinical diagnosis, because ammonia is present in ambient polluting aerosols and may cause disease in humans. Recently, ammonia gas sensors that are based on different chemical interfaces have been developed [1–7]. These chemical interfaces include metal, metal-oxide, and polymer films. Metal film is sensitive to target gases but its dynamic range is very narrow. Metal-oxide films must be used at an appropriately high temperature. Polymer films are superior to metal-oxide films, given their low detection limit and selective detection at room temperature.

Detecting ammonia involves real-time measurement, high sensitivity, good reliability, high accuracy, and low cost. Surface acoustic wave (SAW) gas sensors can satisfy these requirements. Moreover, SAW gas sensors are easily portable because of their compact size. The basic SAW gas sensor that is fabricated on a piezoelectric substrate is comprised of a SAW delay line or resonator coated with a chemical interface. The chemical interface is a chemical or biochemical compound over the SAW’s propagating path, and selectively and reversibly interacts with a specific gas. In fact, mechanical and electrical coupling between the substrate and chemical interface are possible due to the fact that the SAW generates mechanical deformation and electrical potential [4,8,9]. Interface interactions caused by mechanical coupling between the wave and chemical interface are attributed to mass loading and the elastic effect. However, the electrical coupling between the wave and chemical interface is described by acoustoelectric interactions. The adsorption and desorption of a specific gas by the chemical interface modulate wave propagation characteristics. Therefore, chemical interface modulates electrical signals that in turn alter the phase velocity and attenuation of the SAW sensors [10–13]. The shifts in phase velocity and attenuation are measured by recording the frequency and insertion loss of the SAW device, respectively.

L-Glutamic acid hydrochloride has been clearly demonstrated to act as a chemical interface for ammonia [1]. That work used a thickness-shear mode (TSM) sensor coated with L-glutamic acid hydrochloride. The measured sensitivity was 74 Hz/ppm. However, this experiment was the static measurement and completely neglected the environmental effects. Additionally, it only detected gas concentration to 10 ppm. Lately, highly sensitive SAW devices have attracted researchers’ interest. Most recently published chemical sensor applications involve dynamic measurement. Consequently, accurate detection mechanism of an SAW sensor...
based on L-glutamic acid hydrochloride is essentially realized by dynamic measurement. On the other hand, the water molecules in air easily interfere with the detection of an ammonia sensor. Commonly used chemical interfaces in ammonia sensors often show serious aging problems and humidity effect. Therefore, this work demonstrates the dynamic detection mechanism of ammonia by the SAW device based on L-glutamic acid hydrochloride under room temperature and different relative humidity. This work focuses on providing a chemical interface to better the performance of the previous SAW ammonia sensors. The frequency shift of the SAW clearly establishes sensitivity, reversibility, repeatability, selectivity, and long-term stability to a gas. The noise level, which directly affects the detection limit, is also measured.

2. Experimental

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 0.5 mg/ml. Before the coating was applied, the surface of the SAW delay line was cleaned in acetone, and dried in a drying oven (Rendah, Taiwan) at 80 °C. L-Glutamic acid hydrochloride was deposited on the surface of the SAW device by air brushed coating. The thickness of L-glutamic acid hydrochloride is about 2900 ± 2 Å measured by ellipsometry (ESM-1, UL VAC, Japan). The thickness of L-glutamic acid hydrochloride is less than 1% of the acoustic wavelength so that the chemical interface is acoustically thin.

The SAW delay lines were fabricated on a 128° YX-LiNbO3 substrate by standard photolithographic techniques, using aluminum (1500 Å) metalization. The center frequency of the SAW delay line was 100 MHz and the period of interdigital transducer (IDT) was 40 μm. Each IDT had ten finger-pairs and the acoustic aperture was 1600 μm. The center-to-center spacing between the two IDTs was 8400 μm. The device was characterized using a network analyzer (HP8753C, Agilent, USA). The insertion loss of the uncoated and untuned delay line was about 15 dB. The insertion loss was increased by around 0.5 dB after L-glutamic acid hydrochloride was deposited. A dual delay line configuration was used, and two electronic oscillator circuits were used to generate RF signals.

The SAW devices were introduced into a temperature-controlled test chamber (Zaoyi, Taiwan), ensuring temperature stability within ±0.5 °C for 5 h, and a gaseous ambient was controlled by the mass flow controller (Sierra, USA). The flow rate was 110 ml/min, and the reference and carrier gas was dry air. The ammonia gas was diluted with dry/humid air to monitor SAW responses toward various concentrations of ammonia gas. The relative humidity of the ambient air under test was varied in the range 0–90%, by mixing the calibrated flows of dry air and wet air, produced by a bubbler, according to known ratios. Before test gas exposure, the sensor was exposed to dry air for 40 min to stabilize the initial SAW signal. The frequency shifts were monitored by a frequency counter (HP53132A, Agilent, USA), which was connected to a computer system via a GPIB interface board. Noise measurements were taken from frequency data collected for 10 min at 20 points/min when there is no analyte present. The noise was the standard deviation of the residuals of the linear least squares fit through the data [14].

The signal-to-noise (S/N) ratio is defined as (frequency shift when analyte is present)/(noise level when there is no analyte present) [4].

![Fig. 1. The time response of SAW gas sensor for a 0.90 ppm ammonia concentration in dry air at room temperature.](image-url)
3. Results and discussion

L-Glutamic acid hydrochloride is not conductive so the acoustoelectric interaction is neglected. Considering the perturbation mechanism, the propagation characteristics of the acoustic wave are influenced as follows:

\[
\frac{\Delta f}{f_0} = \frac{v_0 \Delta v}{v_0} \approx - \frac{v_0 \rho_s h}{4 P_a} \left( v_{y0}^2 + v_{z0}^2 \right) \]

where \( f \) is an unperturbed frequency, \( \Delta f \) is a shift in frequency, \( v_0 \) is an unperturbed phase velocity, \( v_g \) is an unperturbed group velocity, \( \Delta v \) is a shift in phase velocity, \( v_{y0} \) and \( v_{z0} \) are the surface particle velocity, \( h \) is the coating thickness, \( \rho_s \) is the coating density, \( P_a \) is the SAW power density, and \( K \) and \( G \) are the elastic moduli of the coating. The terms on the right of Eq. (1) represents the contribution of the mass loading which the elastic effect is included.

If the mass loading does not include the elastic effect, then Eq. (1) can be presented as follows:

\[
\frac{\Delta f}{f_0} = \frac{-v_0 \rho_s h}{4 P_a} \left[ v_{y0}^2 + v_{z0}^2 \right] = -K(\sigma),
\]

and the elasticity of mass loading layer can be given in

\[
\frac{\Delta f}{f_0} = \frac{h}{P_a v_0^2} \left[ \frac{3K + G}{3K + 4G} \right] = K(\sigma)C_R.
\]

Fig. 2. (a and b) The curve of frequency shift vs. the concentration of ammonia in dry air at room temperature.
where
\[ C_R = \frac{4G^3K + G^2}{\rho \beta_0^3K + 4G \beta_0^3 + \nu_0^3} \]

Fig. 1 shows the real-time responses of the SAW sensor in dry air at room temperature. The response time is in seconds of exposure to ammonia in dry air and the response quickly returns to the base line when ammonia turns off. The period of the gas turning on/off is about 5 min. Three gas on/off cycles produce similar responses, revealing repeatable detection properties. The time responses are almost the same. It means that the l-glutamic acid hydrochloride film is reversible. The noise level in the figure is 0.04 ppm.

Fig. 2 presents the ammonia concentration dependence of the SAW response in dry air at room temperature. It is shown that at the beginning the frequency increases with the concentration sharply up to about 4 ppm where the frequency shift suddenly turns to decrease, and it decreases significantly up to around 10 ppm, and then decreases slowly and further saturates. The sensitivity that is derived from the slope of curve in Fig. 1 is 0.476 ppm/ppm in the range of ammonia concentration not more than 4.0 ppm. It is better than that of the Langmuir–Blodgett (LB) polypyrrole film coated SAW ammonia sensors (≈ 0.125 ppm/ppm) [6]. The noise of our system is around 0.04 ppm, and so the minimum detectable level (MDL) is 0.56 ppm by taking the S/N ratio of 2. Prior investigators [6] reported the detection limit of Langmuir–Blodgett (LB) polypyrrole film coated SAW ammonia sensors to be 20 ppm. Our result of the MDL is greatly improved.

It can be concluded that the SAW gas sensor based on l-glutamic acid hydrochloride is suitable for applications at very low concentration of ammonia.

The frequency shift shown in Fig. 2 is positive when the absorbed ammonia is in a few ppm, because it may be a modification of the elastic effect of l-glutamic acid hydrochloride can compensate for the negative frequency shift caused by Eq. (2). Therefore, a modification of the elastic effect positively changes the oscillation frequency. The elasticity of l-glutamic acid hydrochloride is obvious when ammonia concentration is less than 4 ppm, so that the positive frequency shift increases with ammonia concentration. Because the mass loading gradually increases and offset the elastic effect above 4 ppm ammonia, the positive frequency shift decreases with ammonia concentration. The turn point of frequency shift from positive to negative appears approximately at 195 ppm ammonia.

Selectivity refers to the ability of a chemical interface to discriminate between the analyte of interest and possible interferences. Fig. 3 plots the response of the l-glutamic acid hydrochloride coated SAW sensor to CO. No effect of this interference gas is observed. The other interference gases that are NO\(_2\) and CO\(_2\) give similar results. Because l-glutamic acid hydrochloride presents high sensitivity to ammonia and no obvious response to others, l-glutamic acid hydrochloride is highly selectivity to ammonia.

Fig. 4 displays the response of SAW to 3.04% ammonia over 34 days at room temperature. The drift of response at room temperature is attributable to the degradation of l-glutamic acid hydrochloride, and the response degrades at a rate of \(-0.01\) ppm per day, as shown in Fig. 4. The previous report [7] presented the degradation of response of LB polypyrrole film coated SAW ammonia sensors to be \(-0.025\) ppm per day. Thus, SAW sensor based on l-glutamic acid hydrochloride exhibits adequate stability at room temperature.

Fig. 3. The frequency variation of SAW gas sensor in 1% CO mixed in dry air at room temperature.
Fig. 4. The long-term stability of the SAW ammonia gas sensor in dry air at room temperature.

Fig. 5 shows the SAW response to ammonia in relation to humidity. Increasing humidity induces a slight increase in the frequency shift of SAW sensors. Therefore, SAW gas sensors based on L-glutamic acid hydrochloride are also sensitive to water molecules, as stated in Fig. 6. Therefore, the effect of the relative humidity on the detection to ammonia must be evaluated. The response of SAW sensors to ammonia at different degrees of humidity can be described as

$$S_{\text{NH}_3, \text{H}_2\text{O}} = S_{\text{NH}_3} + S_{\text{H}_2\text{O}} + D S_{\text{NH}_3} S_{\text{H}_2\text{O}},$$

(4)

where $S_{\text{NH}_3, \text{H}_2\text{O}}$ is the frequency shift to ammonia in humid air in Hz, $S_{\text{NH}_3}$ the frequency shift to ammonia in dry air in Hz, $S_{\text{H}_2\text{O}}$ the frequency shift to water molecules in Hz, and $D$ is the cross-sensitivity. The third term on the right of Eq. (4) is a cross-term that describes the mutual dependence of the response on ammonia and humidity. $S_{\text{NH}_3, \text{H}_2\text{O}}$, $S_{\text{NH}_3}$, and $S_{\text{H}_2\text{O}}$ were measured and substituted into Eq. (4) to determine $D$ value. Fig. 7 plots the dependence of $D$ on relative humidity. For typical values of relative humidity in room ambient air (35–50%), $D$ is approximately...
0.011 in this work and is smaller than that (=0.018) of 4,4′,4″-[benzene-1,3,5-triyl-tri(ethin-2,1-diyl)]tribenzoic acid (SPCA) coated TSM ammonia sensors [15]. It demonstrates that l-glutamic acid hydrochloride takes less humidity effect than SPCA. Consequently, the presence of water molecules in air can be neglected for the ammonia response of SAW gas sensors based on l-glutamic acid hydrochloride.

4. Conclusions

Highly sensitive SAW ammonia gas sensors based on l-glutamic acid hydrochloride were developed in this work. l-Glutamic acid hydrochloride has fairly sensitive, reversible, repeatable, and selective detection of gaseous ammonia. The minimum detectable level of l-glutamic acid hydrochloride to ammonia at room temperature was under 0.56 ppm. The response degraded at a rate of −0.01 ppm per day, therefore the long-term stability of l-glutamic acid hydrochloride is quite enough at room temperature. The relative humidity slightly interferes with the absorption of ammonia, but this interference can be ignored in room ambient air. The performance of SAW ammonia sensors based on l-glutamic acid hydrochloride is better than others published in the past. Hence, SAW ammonia sensors based on l-glutamic acid hydrochloride hold considerable promise for practical application.
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References


Biographies

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