IMPROVED SURFACE ACOUSTIC WAVE SENSOR FOR LOW CONCENTRATION AMMONIA/METHANE MIXTURE GASES DETECTION

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ABSTRACT

In this research, we used the surface acoustic wave (SAW) sensor to detect chemical compounds such as ammonia, methane, and ammonia-methane mixture gases. Very low concentration of ammonia (～250 ppb) and methane (～9 ppm) can be detected by our SAW devices. And we used mesoporous carbon hollow nanosphere in Poly-N-vinylpyrrolidone (PNVP) film to increase the sensitivity to ammonia from 6.91 to 19.47 Hz/ppm. Besides, the signal loss is less than 6% after 17 detection cycles. Finally, we compared the response of ammonia and methane with ammonia/methane mixtures, finding synergy effect between these different gases by PNVP sensing film.

KEYWORDS: Surface acoustic wave, Ammonia-methane mixture gases, PNVP

INTRODUCTION

In traditional biomedical testing, ammonia concentration is an important biomarker for uremia and chronic liver disease. Breath ammonia level is significantly higher in chronic hepatitis patients (0.745 ppm) than that in normal person (0.278 ppm) [1,2]. Patients who have liver failure even exhale 4.8 ppm ammonia in their breath; in public safety issue, methane is an explosive gas and asphyxial to human. Therefore, we designed a high sensitivity SAW device for detecting low concentration of ammonia and methane. In the future, this gas sensor will be applied in liver disease detection and public security issue.Due to the threat of environmental pollution and human health, there is great demand for gas sensor with high sensitivity, fast response and low detection limit toward the NH_3 for real-time monitoring. Electronic nose has been wildly used for many applications, like indoor air measurement, food product quality control, environmental monitoring[3], military applications, even in national security to prevent. Therefore, it is useful and interesting to develop a portable electronic nose because of its size and convenience. Recent technological advances are certain to facilitate the application of SAW sensing devices[4, 5].

THEORY

The first work relating to the use of SAW devices as gas sensors appeared in 1979 and was due to Wohltjen and Dessy[6]. The basic principle of SAW sensors is that the materials are piezoelectric crystal or film with a constant frequency from the MHz to GHz range exhibits a decrease in frequency when molecules are adsorbed directly on the surface of the piezoelectric substrate or film coated with a thin film of polymer. The variation of oscillating frequency is proportional to the mass of foreign molecules deposited on the crystal surface and the center frequency of the piezoelectric crystal. Typical SAW-based sensors are coated with polymer films. One is the conducting polymer films exhibit reversible gas-elicited conductivity changes and provide a reasonable structure to immobility antibody and enzymes. In this paper, the piezoelectric substrate-$LiNbO_3$ with high electromechanical coupling coefficient, K^2, the ability of translation between electrical and mechanical potential was employed to fabricate SAW devices[7]. The value of K is determined by

$$K^2 = \frac{e^2}{c\varepsilon} \tag{1}$$

where e, c, ε are the piezoelectric coefficient, elastic coefficient, and dielectric coefficient of the substrate. We can calculate the value of K^2 by equation (1), depends on the properties of the piezoelectric substrate or on the experimental results due to the velocity shift under metallization. The frequency shift of a SAW delay line oscillator can be assumed to be governed by the following equation for acoustically thin, perfectly elastic thin film, derived using perturbation theory [8]:

$$\Delta f \cong (k_1 + k_2)\ f_0{}^2 m / A \tag{2}$$

where k_1 and k_2 are piezoelectric material constants, f_0 is the center frequency of the SAW device, m is the mass of adsorbed molecules by polymer.

Surface acoustic wave devices (SAW) consist of two major components: a transducer and a sensitive coating. Interdigital transducers (IDTs) are patterned on the $LiNbO_3$ substrate by MEMS technique, and the sensing polymer films like a smart skin of the sensor, it is responsible for generating the chemical reaction from the interactions between the target and the films[9]. IDTs have been widely used for electrical signal excitation and detection of surface acoustic wave (SAW). Each period of IDTs consists of multiple strips aligned and connected to the bus-bars periodically. The Different design parameters of IDTs will lead to different center frequency. It can be measured by network analyzer. The detail of IDTs design parameter will be reported in the following section.

EXPERIMENTAL

The SAW devices of 117.4 MHz were fabricated by MEMS techniques, and Cr/Au (20/100 nm) interdigital transducers (IDTs) were deposited on the piezoelectric substrate ($LiNbO_3$). Then a PNVP film with high selectivity for ammonia detection was spin-coated on the sensing area. Besides, we used mesoporous carbon hollow nanosphere in PNVP to enhance mixture gas adsorption ability. The property and adsorbing mechanism of the film are shown in fig. 1.

Here we used the same system and techniques for ammonia, methane, and ammonia/methane mixtures detection, analyzation and comparison. In the sensing gas system, fig. 2 & 3 show the dynamic experiments and the schematic about sensing chamber. Gas sensing process contains three steps. In the beginning, zero order air was injected into sensing chamber for 6 minute to stabilize the system. Then the ammonia/methane mixtures were injected for detection. Finally, air flow was used to clean the chamber.

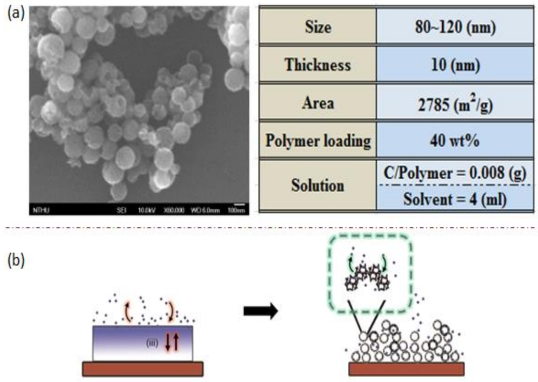

Figure 1: (a) The information about PNVP with mesoporous carbon hollow nanosphere film (800nm). (b) The schematic diagram about adsorbing mechanism of polymer film.

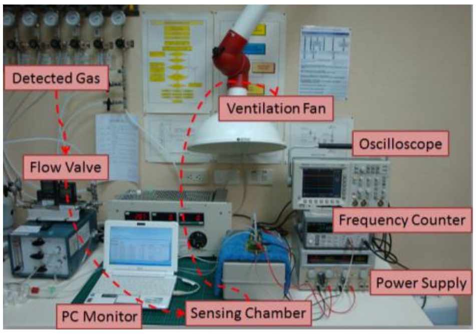

Figure 2: The complete system and gas flow path.

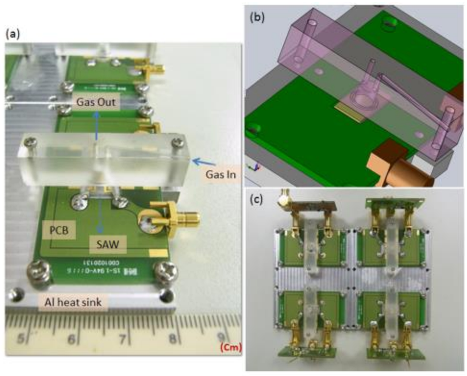

Figure 3: (a) The complete system and gas flow path. (b) The schematic about sensing chamber ad fluidic channel. (c) The gas sensor array.

RESULTS AND DISCUSSION

It took about 4 minutes to finish single detection process. The ammonia concentrations of 150~0.25 ppm and methane concentration of 150~9 ppm could be detected by the polymer-coated SAW sensor device as shown in table 1. When mesoporous carbon hollow nanosphere is used in PNVP sensitive film, ammonia sensitivity was highly increased from 6.91 to 19.47 Hz/ppm. The gas sensor also demonstrated great sensitivity and response to ammonia/methane mixtures. As shown in fig. 4, detection result of 150 ppm and 75 ppm ammonia/methane mixtures shows great sensitivity and repeatability. From fig. 5, we can find that the frequency shift of ammonia/methane mixtures equal to the sum of frequency shift of ammonia and methane.

Ammonia concentration	***AVG. Frequency shift (Hz)***	***C.V(%)***
0.25 ppm	*62.33*	*14.01*
75 ppm	*1437.25*	*20.97*
150 ppm	*3132.29*	*6.73*
methane concentration	***AVG. Frequency shift (Hz)***	***C.V(%)***
75 ppm	*218.29*	*13.11*
150 ppm	*547.18*	*14.59*

Table 1. The frequency shift and C.V of the ammonia and methane.

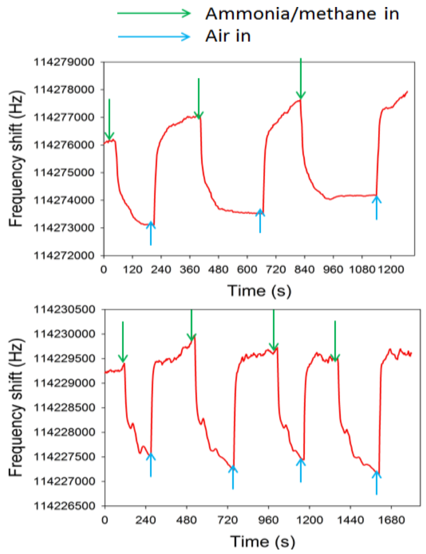

Figure 4: (a) The response of 150 ppm ammonia/methane gas. (b) The response of 75 ppm ammonia/methane gas.

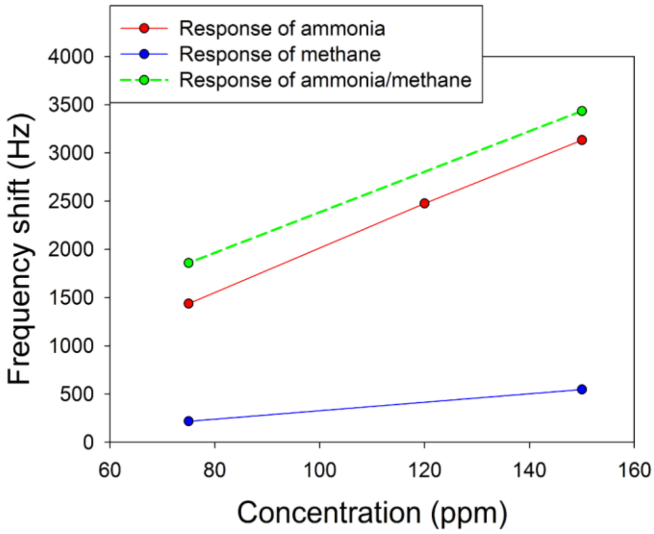

Figure 5: The difference of ammonia, methane and ammonia-methane gas.

CONCLUSION

A surface acoustic wave (SAW) sensor and recovery was developed for ammonia-methane mixtured gas sensing, in which, as a sensitive interface material toward NH_3, a Poly-N-vinylpyrrolidone (PNVP) composite film was deposited onto a 117.4 MHz SAW delay line on 128° YX-$LiNbO_3$ substrate by the spin coating technique. Moreover we have developed an improved portable electronic noise based on a 2x1 continuously working oscillators equipped with differently coated SAW sensors. We used the surface acoustic wave (SAW) sensor to detect chemical compounds such as ammonia, methane, and ammonia-methane mixture gases. Very low concentration of ammonia and methane can be detected by our SAW devices. And we used mesoporous carbon hollow nanosphere in PNVP film to increase the sensitivity to ammonia from 6.91 to 19.47 Hz/ppm. The first focus of this paper is using the improved gas sensor array to detect gas rapidly and replace SAW chip easily. The second focus is to detect ammonia-methane mixtured gas.

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