Highly Sensitive Surface Acoustic Wave NH$_3$ Gas Sensor Based on TiO$_2$ Film

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(Received October 8, 2020; accepted November 16, 2020)

Keywords: surface acoustic wave, NH$_3$, gas sensor, hydroxyl group

We fabricated a surface acoustic wave (SAW) NH$_3$ gas sensor based on a TiO$_2$ sensitive film. The TiO$_2$ film was deposited using a combined sol-gel and spin-coating technology. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results indicate that the film was porous and had good crystallinity. Fourier Transform infrared spectroscopy (FTIR) analysis revealed that there was a large amount of hydroxyl groups on the film, which can capture H$_2$O molecules from the ambient environment. The sensor showed a positive response to NH$_3$ gas and the response increased significantly with increasing relative humidity. The positive response was found to be caused by the change in the elastic modulus of the sensitive film, which was induced by the condensation of the hydroxyl groups on the film catalyzed by NH$_3$. The sensor also had a low detection limit of 1 ppm and excellent selectivity and stability to NH$_3$ gas.

1. Introduction

NH$_3$, an important industrial gas, is widely used in some traditional industrial fields such as fertilizers, rubber, and refrigeration.$^{(1–4)}$ In addition, NH$_3$ plays a critical role in some advanced areas of semiconductor technology, such as the LED and solar cell manufacturing industries.$^{(5–7)}$ It is also a source of atmospheric pollution and can cause various respiratory diseases even at low concentrations.$^{(8–10)}$ Furthermore, when the concentration of NH$_3$ is higher than 500 ppm, it can even cause death.$^{(11)}$ Therefore, continuous monitoring of the concentration of NH$_3$ gas in factories and living spaces is extremely important.

Sensors based on various techniques have been used for NH$_3$ monitoring, such as electrochemical sensors,$^{(12)}$ semiconductor sensors,$^{(13,14)}$ and surface acoustic wave (SAW) sensors.$^{(15)}$ Among these sensors, SAW sensors have the advantages of high sensitivity, reliability, and accuracy. These advantages are due to the fact that any physical and chemical changes on the surface of the SAW device can induce a perturbation of the velocity of a SAW, which leads to changes in the working frequency of the SAW sensor.$^{(16)}$ To further enhance the sensitivity of SAW gas sensors, sensitive films are usually deposited on the devices. Upon
exposure to tested gases, the films may react with the gases. As a result, the conductivity, weight, and elastic modulus of the sensitive film may change, resulting in the response of the sensor.\cite{17-21}

Different materials have been used as the sensitive films of SAW NH$_3$ sensors. For example, Chen et al.\cite{22} reported a sensitive SAW NH$_3$ gas sensor based on a Pt-doped polypyrrole sensitive film and Su et al.\cite{23} reported a NH$_3$ gas sensor based on a Pd/SnO$_2$/RGO ternary composite that operated at room temperature. Among the materials used for sensitive films, TiO$_2$ has been widely used and studied because of its chemical sensitivity, high thermal and chemical stabilities, amenability to doping, nontoxicity, and low cost.\cite{24-26} Nevertheless, the sensing mechanism of a SAW sensor with a TiO$_2$ sensitive film has not been revealed yet.

In this study, we fabricated a SAW NH$_3$ gas sensor based on a TiO$_2$ sensitive film. This sensor had a detection limit of 1 ppm, as well as excellent selectivity and stability. The sensing mechanism of the sensor was investigated. It was found that the positive responses of the sensor were caused by the change in the elastic modulus of the sensitive film, which was induced by the condensation of the hydroxyl groups on the film catalyzed by NH$_3$.

2. Experimental Details

The SAW device used in this work was a two-port resonator based on a ST-cut quartz substrate. Interdigital transducers (IDTs) and reflecting gratings were deposited on both ends of the quartz substrate. The period of the IDTs and gratings was 16 µm, as shown in Fig. 1, and the velocity of a SAW propagating on the resonator was 3158 m/s. Thus, the working frequency of the uncoated resonator was \approx 200.102 MHz. The insertion loss and the Q factor of the resonator measured by a vector network analyzer (VNA) were \approx 9.45 dB and \approx 7000, respectively, as shown in Table 1.

![Fig. 1. Structure of the IDTs on the quartz substrate.](image)
The TiO\textsubscript{2} film was deposited onto the SAW resonator using a combined sol-gel and spin-coating technology. Tetrabutyl titanate was first added to a beaker containing ethanol under magnetic stirring for 30 min, and then ammonia (25–28 wt\%) was added to the beaker dropwise under vigorous stirring. The obtained solution was then aged for 1 day to obtain the colloidal TiO\textsubscript{2} sol. The TiO\textsubscript{2} sol was coated onto the SAW resonator using a spin-coating technique with a speed of 3000 rev/min for 30 s. The coated quartz resonator was annealed at 300 °C for about 1 h in air.

Compared with the pristine resonator, the annealed resonator had a decreased working frequency of 199.325 MHz, which was caused by the mass of the TiO\textsubscript{2} film loaded on the resonator. The coated resonator also had a higher insertion loss of ~19.46 dB and a lower Q factor of ~2300, as shown in Table 1.

The coated resonator was used as a frequency selector to build a SAW oscillator with a cascaded amplifier having a gain of 40 dB and a phase shift network consisting of capacitors and inductors, as shown in Fig. 2. The oscillating frequency was recorded as the output signal of the SAW sensor using a frequency counter (HP5385A), and the response of the sensor was defined as the frequency shift, $\Delta f = f_s - f_0$, where $f_s$ is the oscillating frequency of the sensor in the tested gas and $f_0$ is the frequency in pure air.

The responses of the sensor to different gases were measured using the experimental setup shown in Fig. 2. The sensor was placed in a chamber with a volume of 20 L. The tested gases (NH\textsubscript{3}, H\textsubscript{2}, CH\textsubscript{4}, CO, ethanol, and SO\textsubscript{2}) were injected into the chamber with a syringe to investigate the response of the sensor. The concentration of the tested gases in the chamber was controlled by adjusting the amount of the tested gases injected. When the response of the sensor reached a stable value, the chamber was opened to expose it to pure air to allow the recovery of the sensor.

The crystallinity of the prepared films was characterized by an X-ray diffractometer (XRD, Rigaku D/max-2400). The morphology and thickness of the as-prepared films were characterized by a field-emission scanning electron microscope (SEM, FEI Inspect F). An FTIR spectrometer (Nicolet 6700) was used to collect the infrared transmission spectra of prepared films. A VNA (Agilent Technologies, E8363B) was used to characterize the transmission properties of the pristine and coated SAW resonators.

3. Results and Discussion

The XRD pattern of the prepared TiO\textsubscript{2} is shown in Fig. 3. Peaks located at $2\theta = 25.4, 38, 47.9, 54.4,$ and $63^\circ$ were observed. These peaks were assigned to the diffraction signals of (101), (004), (200), (105), and (204) planes of rutile TiO\textsubscript{2}, respectively. This result indicates that the film had high crystallinity.
SEM images of the TiO$_2$ film are shown in Fig. 4. The film consisted of TiO$_2$ nanoparticles with a diameter of ~15 nm. In addition, it was found that there are some open pores in the film, which provide paths for gas to diffuse in and out from the films. These pores are beneficial for the gas sensor application.

The FTIR result of the TiO$_2$ film is shown in Fig. 5. Two broad bands at 3490 and 1640 cm$^{-1}$ were observed, which are the stretching and bending modes of absorbed water, respectively. The broad and intense band in the range of 400–800 cm$^{-1}$ was assigned to Ti–O and Ti–O–Ti groups. The band at 3737 cm$^{-1}$ was ascribed to surface Ti–OH groups and the band ranging from 1300 to 1500 cm$^{-1}$ was assigned to the residual carbon. This FTIR result indicates that there were abundant hydroxyl groups that absorbed water on the film.

Figure 6 shows the sensing performances of the sensor to 10 ppm NH$_3$ at room temperature and RH = 10, 50, and 80%. The response of the sensor was significantly enhanced with
increasing RH value and reached 4200 Hz at RH = 80%. It has been established that the response of a SAW gas sensor is derived from three effects occurring on the film, i.e., those of mass loading, elastic loading, and conductivity loading, which refer to the changes in weight, elastic modulus, and conductivity of the sensing film, respectively.\(^{16-21}\) Previous research has revealed that the conductivity loading effect contributes little to the response of a SAW sensor based on an insulating sensitive layer.\(^{18}\) Therefore, in this work, the mass loading and elastic loading effects are the two possible mechanisms dominating the responses of the sensor.

When the sensor is exposed to NH\(_3\) gas, NH\(_3\) may absorb on the surface and in the pores of the TiO\(_2\) film. The adsorbed NH\(_3\) can first lead to an increase in the weight (mass loading effect) of the film. Furthermore, the NH\(_3\) can also lead to condensation between the hydroxyl groups on the film by acting as a catalyst, as shown in Fig. 7.\(^{26,27}\) This condensation may enhance the stiffness of the film, finally resulting in an increase in the elastic modulus (elastic modulus effect) of the film. According to previous reports,\(^{16-21}\) the mass loading effect leads...
to a negative response while the elastic loading effect leads to a positive response in this case. Hence, it was concluded that the positive responses of the sensor at different RH values were dominated by the elastic loading effect.

The reason for the different responses at different RH values was further investigated. The FTIR result revealed that there were abundant hydroxyl groups on the TiO$_2$ film. These hydroxyl groups can effectively capture H$_2$O molecules from the ambient environment by the formation of hydrogen bonds, as shown in Fig. 7, and the amount of H$_2$O captured by the film is dependent on the ambient humidity; with increasing humidity, the amount of H$_2$O increases. NH$_3$ has a good affinity to H$_2$O; therefore, when the film is exposed to NH$_3$ gas, NH$_3$ molecules can be captured by H$_2$O, as shown in Fig. 7. Thus, the amount of NH$_3$ captured is related to the RH value. At a low RH (10%), the amount of NH$_3$ captured by hydroxyl groups is relatively small, while at a high RH (80%), a large amount of NH$_3$ is captured. As a result, more NH$_3$ acts as the catalyst for the condensation reaction between the hydroxyl groups at a higher RH, leading to a stiffer film and a stronger positive response of the sensor.

Although the sensor had the best performance at RH = 80%, such a sensor would normally be used in an ambient environment with an RH value around 50%. Thus, all the following tests related to the sensitivity, selectivity, and stability of the sensor were conducted at RH = 50%.

Figure 8 shows the dynamic response of the sensor to 1–100 ppm NH$_3$ gas. The sensor had a response frequency of 500 Hz to 1 ppm NH$_3$, and the response frequency increased with the concentration of NH$_3$, reaching 3200 Hz when the concentration was 100 ppm. The selectivity of the sensor was also investigated by exposing it to different gases. As shown in Fig. 9(a), the sensor showed no response to H$_2$, CO, CH$_4$, and ethanol gases with a concentration of 100 ppm. When exposed to SO$_2$ gas, the sensor exhibited a slight positive response. This positive response may also have originated from the condensation of hydroxyl groups since SO$_2$ can also
act as a catalyst for the condensation reaction. However, the positive response to SO$_2$ was much weaker than that to NH$_3$. Thus, the sensor had excellent selectivity to NH$_3$ gas. The stability of the sensor was further investigated by conducting five tests over 30 days. As shown in Fig. 9(b), this sensor had similar responses to 1 and 10 ppm NH$_3$ gases throughout the 30 days, indicating its good stability.

4. Conclusion

A SAW NH$_3$ sensor based on a TiO$_2$ sensitive film was fabricated. Its response to NH$_3$ gas was enhanced significantly with increasing RH value and reached 4200 Hz (10 ppm NH$_3$) at
RH = 80%. This enhancement is due to the fact that more NH$_3$ molecules are captured by H$_2$O absorbed on the film at a higher RH. The sensing mechanism of the sensor was found to be dominated by the change in the elastic modulus of the sensitive film, which was caused by the NH$_3$-catalyzed condensation between the hydroxyl groups on the film. The sensor also showed excellent selectivity and stability to NH$_3$ gas, indicating its potentially practical application.

Acknowledgments

The authors acknowledge the Jiangsu Intelligent Sensor Network Open Fund (ZK16-02-04). This study is supported by Jiangsu Government Scholarship.

Declaration of Interest

The author(s) declare that they have no competing interests.

References
