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Efficient detection of ammonia using SAW devices coated with oxide sensing layers

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Abstract:

Ammonia sensing response characteristics of the Surface Acoustic Wave (SAW) sensors having different oxide thin films (ZnO, TeO_2, SnO_2 and TiO_2) deposited by RF sputtering technique under the optimized parameters as sensing layer have been studied. SAW sensor with ZnO sensing layer is found to be exhibiting the maximum response towards liquor ammonia as compared to other oxides. The SAW sensor structure showed a peculiar bidirectional shift (increase or decrease) in frequency on exposure to liquor ammonia vapors, while other VOCs (volatile organic compounds) and gases in the presence and absence of water vapors showed poor response indicating the excellent selectivity of the prepared sensors towards ammonia. Further interaction of liquor ammonia is a one step process involving adsorption of ammonia and water vapors simultaneously.

Key words: *Zinc Oxide, NH_3 gas, Semiconductor, sensor, SAW*

Introduction

Recently, Surface Acoustic Wave (SAW) devices based chemical sensors are in demand because of their high sensitivity, fast speed, good reliability, high accuracy and low cost wireless detection capabilities. SAW sensors can be efficiently utilized for precise detection of hazardous gases, chemical warfare agents, explosive vapors, environmental pollutants etc. [1]. The adsorption of chemical vapor/gases by the sensitive layer on the SAW surface changes the SAW propagation characteristics such as attenuation and velocity, which in turn affects the amplitude, frequency and delay of the propagating surface acoustic wave.

Nowadays, air pollution caused by different pollutants is becoming an important environmental issue. Ammonia is one of the toxic and pollutant gases whose high concentrations lead to severe burns on our skin, eyes, throat, or lungs causing permanent blindness and lung disease. Further ammonia aerosols have a sun blocking function, and the smog produced results in temperature reduction. Also it is one of the industrial gases having multiple applications and hence chances of it being leaked are also very high. So its early and precise detection and monitoring of leakage in a wide range of industrial applications is desired.

Different polymers and metal oxides are employed in the literature as a gas sensitive layer for the detection of ammonia [2-5]. There are reports on detection of ammonia in ppm and ppb ranges using polymers including L Glutamic acid hydrochloride and PANI (polyaniline) as sensitive layer [2, 3]. However, the effect of interferants is not considered [2, 3]. Furthermore, there are few reports on using different metal oxides (TiO_2 and ZnO) as a gas sensitive layer [4, 5], but lack the study on the effect of humidity and common interfering gases and VOC besides high operating temperatures. CNTs have also been exploited for ammonia detection [6]. However, sensor was also sensitive to other gases. Hence, efforts are continuing towards the enhancement of sensitivity of ammonia sensors, which can operate at room temperature with good selectivity.

In the present work, SAW sensors having different oxide layers are used for the detection of ammonia. The effect of various interferants like VOCs, other gases and water vapors on sensing response characteristics is

studied. Sensing mechanism is explained in the light of different experimentations.

Experimental Procedure

One-port SAW resonators (RO2101) used in this work are obtained from RF Monolithics. The uncoated SAW resonator has a center frequency of 433.92 MHz and 2-dB insertion loss. The device package is cut open in order to have access to the SAW surface for the deposition of different oxide thin films as sensing layers. The ZnO, TeO_2, SnO_2 and TiO_2 thin films are deposited by RF sputtering technique using Zn, Te, Sn and Ti targets at 300, 150, 50 and 150 W power respectively. ZnO, TeO_2, and TiO_2 thin films were grown at 50 % Ar and 50 % O_2 whereas SnO_2 thin film was deposited under 100 % O_2 for higher stability of the SAW sensor. Crystallographic structure of the films has been investigated using X ray diffractometer (Bruker D8 Discover) and optical properties are investigated by UV-Visible spectroscopy (Perkin Elmer, Lambda 35). The SAW devices are placed as frequency determining element in Colpitt oscillator configuration as described in our earlier work [7]. A differential frequency ($\Delta f = f_0 - f_s$) SAW oscillator configuration is used in the present study to minimize the effect of various environmental fluctuations such as pressure, temperature and other disturbances. Here f_s and f_0 are the absolute frequency of the ZnO coated SAW sensor and the frequency of the reference SAW sensor respectively.

A laboratory-made vapor generation and delivery system is used for sensing vapors. Dry nitrogen is used as the carrier gas. A little quantity of liquid is placed at the bottom of a corrugated glass container, and carrier gas is continuously passed through its headspace to the sensor surface. Carrier gas from the source is bifurcated into two paths, controlled by individual gas flow controllers, one carrying the test gas and other the carrier. Flow rates along both the paths are maintained at 120 ml/min. Details of the vapor generator and delivery system are explained in our earlier work [7].

Results and Discussions

For structural and optical studies, the ZnO, SnO_2, TeO_2 and TiO_2 thin films were deposited on the glass substrate under the similar optimized deposition conditions. The XRD pattern of ZnO thin film shows only reflection corresponding to (002) plane of wurtzite ZnO structure, indicating growth of highly oriented films with c axis normal to the surface of quartz substrate. XRD spectra of SnO_2 thin films show that films are polycrystalline with well defined peaks at $2\theta = 33.83^o$ and 51.61^o corresponding to (101) and (211) planes of the rutile structure of SnO_2 respectively. However TiO_2 and TeO_2 thin films are found to be amorphous. Optical properties of all the prepared oxide thin films deposited on glass substrates were studied in the wavelength range of 190 to 1100 nm and the variation in optical transmission with wavelength is shown in figure 1. All the films (ZnO, TeO_2, SnO_2 and TiO_2) are found to be highly transparent with transmission greater than 75 %, in the visible region (figure 1). The value of optical bandgap, E_g as estimated from the Tauc plot for the ZnO, TeO_2, SnO_2 and TiO_2 films are found to be 3.1, 4.0, 4.1 and 3.0 eV respectively.

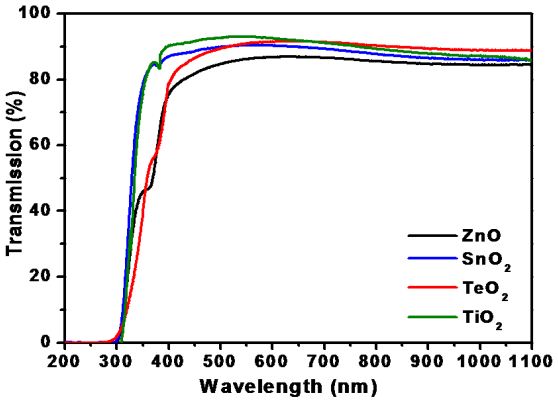

Figure 1: UV-Visible Transmission Spectra of different oxide films (ZnO, TeO_2, SnO_2, TiO_2)

The sensing response characteristics of SAW sensor having ZnO thin film (ZnO/SAW) as a function of time for the headspace vapors of liquor ammonia (25% NH_3) is shown in figure 2. As can be seen from figure 2, during interaction of liquor ammonia vapors with ZnO/SAW sensor, an initial decrease in differential frequency (Δf) followed by a significant increase has been observed. The magnitude of positive shift is about 380 kHz.

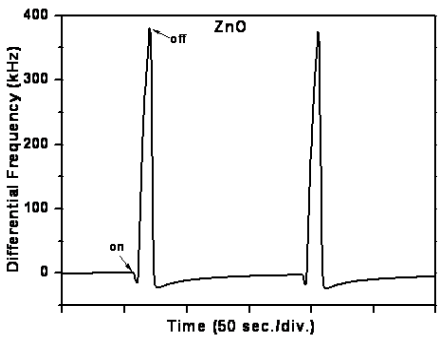

Figure 2: Response of ZnO coated SAW sensor on exposure to headspace vapors of liquor ammonia

The response of TeO_2 coated SAW sensor (TeO_2/SAW) on exposure to liquor ammonia vapors (25%) is shown in figure 3. No negative shift in the differential frequency was observed in figure 3 during adsorption or desorption of liquor ammonia vapors with TeO_2 sensing layer. Maximum positive differential frequency shift of about 8 kHz is obtained for TeO_2/SAW sensor. Figures 4 and 5 are the response of SnO_2 and TiO_2 coated SAW sensors respectively on exposure to 25% liquor ammonia vapors. It may be seen that the SnO_2/SAW sensor is giving both positive and negative frequency shifts similar to the one obtained for ZnO/SAW sensor. However, for TiO_2 coated SAW sensor, negative frequency shift was found only during the adsorption cycle of target gas whereas during desorption cycle no negative shift was obtained (Fig. 5). Maximum positive frequency shift of 10 and 2.5 kHz was obtained for SnO_2 and TiO_2 coated SAW sensors respectively on exposure to liquor ammonia (25%) vapors.

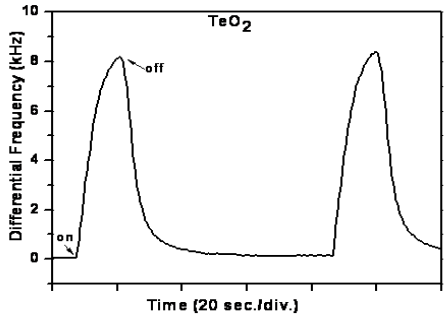

Figure 3: Response of TeO_2 coated SAW sensor on exposure to headspace vapors of liquor ammonia

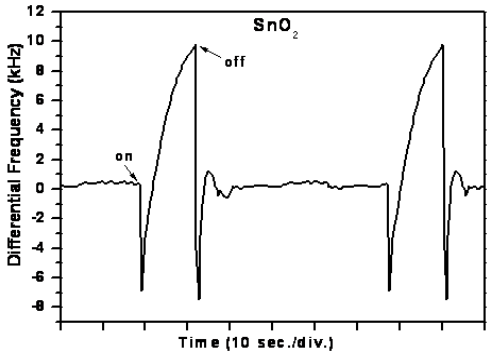

Figure 4: Response of SnO_2 coated SAW sensor on exposure to headspace vapors of liquor ammonia

It may be inferred that only ZnO coated SAW sensor is giving maximum frequency shift (380 kHz) amongst all the prepared SAW sensors in the present work. Hence, further studies were performed only on ZnO/SAW sensor structure. In order study the sensing mechanism, independently dry ammonia (500 ppm) and water vapors (headspace vapors) are allowed to pass over the surface of ZnO coated SAW sensor. In this case, no positive differential frequency shifts were observed, and only negative differential frequency shifts of 2.1 kHz (dry ammonia) and 4.6 kHz (water vapours) were obtained respectively. Hence it may be concluded that the observed positive differential frequency shift in figure 2 is due to the interaction of ZnO layer with the combination of both dry ammonia and water vapors. Further, the response of ZnO/SAW sensor for different VOCs (methanol, ethanol, acetone) and gases (N_2O, H_2) in the presence and absence of water vapors were also studied and found to be giving only negative differential frequency shift. Hence, if proper amount of water vapors are present, ammonia can be selectively detected in the presence of various interferants (VOCs and gases).

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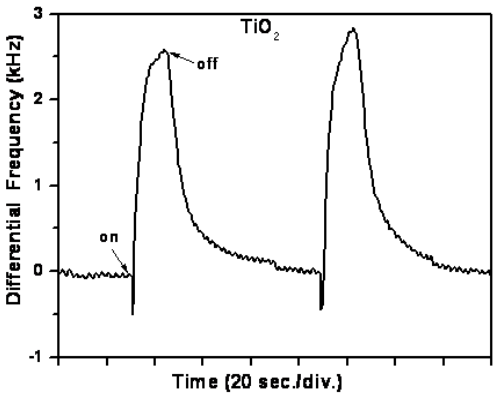

Figure 5: Response of TiO_2 coated SAW sensor with exposure to headspace vapors of liquor ammonia

Further in order to elaborate the sensing mechanism, it is noted that during the adsorption of liquor ammonia vapors there may be two cases:

1. The surface of ZnO thin films adsorb water vapors because of it being hygroscopic and subsequently these adsorbed water molecules attract the ammonia vapors due to the presence of lone pair of electrons. Hence, adsorption adsorption of liquor ammonia in this case will be two step process.
2. It might be possible that ammonia and water vapors are simultaneously getting adsorbed on the surface of ZnO/SAW sensor giving the peculiar response.

To confirm the adsorption behaviour, dry ammonia and water vapors are passed over the surface of ZnO/SAW sensor sequentially as shown in figure 6. Initially the base line of

ZnO/SAW sensor was stabilized in the presence of carrier N_2 gas. Water vapors were passed over the sensor surface for different time intervals and subsequently dry ammonia was passed. As can be seen from figure 6 that after passing water vapors to the sensor surface, differential frequency (Δf) decreases. Then with the passage of dry ammonia vapors (400 ppm), differential frequency slightly increases (Fig. 6). However, no positive shifts in the differential frequency were found with respect to the baseline. The observed results clearly indicate that the adsorption of ammonia and water molecules is a single step adsorption process on the surface of ZnO/SAW sensor that leads to both the negative as well as positive shifts in differential frequency.

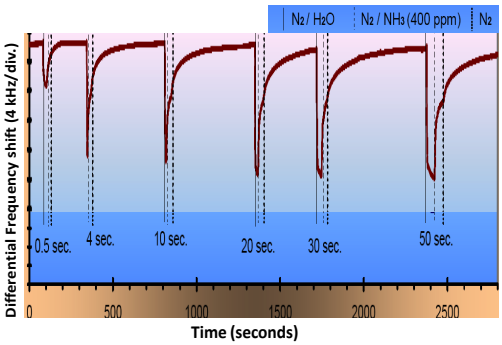

Figure 6: Response of ZnO coated SAW sensor with sequential exposure to water vapors and dry ammonia

Conclusions

SAW sensors coated with different oxide thin films (ZnO, TeO_2, SnO_2 and TiO_2) are shown to detect ammonia selectively in the presence of water vapors. ZnO coated SAW sensor is giving maximum response to liquor ammonia vapors. Controlled experiments suggest that the adsorption of liquor ammonia vapors on the sensor surface is a single step phenomenon.

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