

Research Article

Surface Acoustic Wave Sensors for Ammonia Detection at Room Temperature Based on $\text{SnO}_2/\text{Co}_3\text{O}_4$ Bilayers

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The selectivity of a SAW (surface acoustic wave) sensor, with a Co_3O_4 sensitive thin film for NH_3 (ammonia) and the influence of SnO_2 on its sensitivity, was studied. Thin films were deposited by pulsed laser deposition (PLD) on quartz SAW sensor substrates. Two sensors with different types of sensitive films were developed: a Co_3O_4 thin film sensor (S1) and a $\text{SnO}_2/\text{Co}_3\text{O}_4$ thin film sensor (S2). The sensitive films were deposited in conditions which ensured a porous structure. The sensors were tested in the presence of three gases: NH_3 , methanol, and toluene. The selectivity of Co_3O_4 for NH_3 was determined from the difference in the frequency shifts of the sensor for NH_3 and for VOCs (volatile organic compounds). The positive influence of SnO_2 on the sensitivity of sensor S2 was observed from the lower limit of detection (LOD) of this sensor and from the differences in frequency shifts between sensor S1 and sensor S2.

1. Introduction

Ammonia (NH_3) is a substance of interest in various domains (agriculture, cleaning products, refrigerants, etc.). It is being actively studied for a chemical energy storage, which is crucial for compensating the intermittent character of renewable energy [1]. However, the use of NH_3 requires strict safety precautions, due to the fact that it can lead to severe health problems, and is flammable in air at 50°C at concentrations over 160 000 ppm [2]. Since the maximum permissible exposure limit is 25 ppm, it is important to develop sensors capable of detecting the presence of NH_3 at such levels.

Volatile organic compounds (VOCs) also have a detrimental effect on the environment and on health [3]. They are released into the atmosphere by combustion of fuels such as gas, wood, coal, or natural gas but can also derive from paints, cigarettes, and other consumer products [4].

Resistance-based sensors, as well as optical devices or MOS-field effect transistors, have been used for detecting such hazardous substances [5, 6]. However, they have inherent disadvantages such as high working temperature, poor

selectivity, or relatively long recovery times. For instance, resistance-based sensors used for NH_3 detection give poor results at room temperature (RT) and therefore require operation at relatively high temperatures (over 140°C) [7].

SAW (surface acoustic wave) sensors present a series of important advantages such as high sensitivity, fast response, reliability, low cost, ease of fabrication, and possibility of wireless operation [8, 9]. The sensing mechanism for SAW sensors is based on the fact that the propagation of the acoustic wave at the surface of the sensor is affected by perturbations generated by mechanical and/or electrical effects in the presence of the analyte. Various materials are used for the sensing film in SAW sensors, such as polymers [10] p-type or n-type semiconducting oxides [11, 12]. Generally, for the SAW detection of VOCs, sensitive films are made of oxide or composite materials (polymers, nanoparticles) [13].

Co_3O_4 is a p-type semiconductor which has been used for NH_3 detection in various types of sensors [14], including SAWs [15]. However, Co_3O_4 alone does not give satisfactory response to NH_3 , especially at RT [15]. It is known that multilayer SAW sensing layers can improve the sensing

properties of SAW sensors compared to single layers, by ensuring a larger acoustoelectrical response to the gas, in addition to the mass loading effect [16, 17]. This leads to an increase of sensitivity and a decrease of the sensing limit, even at RT.

SnO₂ is an n-type semiconductor and one of the oxides most widely used in sensors. It is often used in the detection of reducing gases due to the active oxygen species present on its surface. The interaction between reducing gas molecules and oxygen species favors adsorption at the film level and leads to a change in conductivity [18]. One of the disadvantages of SnO₂ in gas detection is the lack of selectivity [19], which can be improved, depending on the gas which needs to be identified, by combining it with another material that offers selectivity for the specific analyte. We have therefore considered a bilayer Co₃O₄/SnO₂ sensing film in order to improve the response of the SAW sensor it is incorporated in, to NH₃ and VOCs. This also allows us to study the selectivity of the sensor, as was done before to determine the selectivity of other sensing layers (ZnO) to NH₃ [9].

The sensing bilayer was deposited using pulsed laser deposition (PLD). The advantage of this method is that it is more straightforward than chemical methods requiring many intermediate steps [20, 21]. PLD also has the great advantage of allowing a simple control of layer porosity, which is known to be important for improved gas sensor properties [22]. Nanoporous films facilitate rapid in/out diffusion of gas species in/out of the sensor (which shortens the sensor response and recovery times). Such films also lead to a larger film surface area, which considerably increases the sensor sensitivity. It is much more difficult to obtain such nanoporous films using chemical methods [23] than by PLD.

In the present paper, we present the sensing properties of SAW sensors based on SnO₂/Co₃O₄ bilayers, as well as for a single Co₃O₄ layer, obtained by PLD. The sensitivity, response, and recovery times of the sensors in the case of NH₃ detection and for VOCs (methanol and toluene) were determined. We have analyzed the sensitivity of Co₃O₄ for NH₃, the influence of SnO₂ thin film on sensor sensitivity, and its ability to detect NH₃ at RT.

2. Materials and Methods

The SAW sensors are based on a quartz substrate (ST cut, X propagation, 38 mm long, 10 mm wide, 0.5 mm thick), cut in a parallelogram geometry to reduce the effects of the unwanted SAW reflections. The SAW sensor is a “delay-line” type with an oscillating frequency of ~ 69 MHz [24]. The 150 nm thick gold interdigital transducers (IDT) were deposited using standard photolithographic techniques onto 10 nm thick chromium layers (which ensure gold adhesion to the quartz substrate). The IDT were made in a “double-comb” configuration, consisting in 50 straight finger pairs with a 2500 μm acoustic aperture and a 45.2 μm wavelength.

The bilayers were deposited by PLD using an Nd-YAG laser (EKSPLA NL301HT) having pulse durations of about 5 ns, at a repetition rate of 10 Hz. A UV wavelength of 355 nm was used with an energy per pulse of about 40 mJ.



FIGURE 1: SAW S2 sensor in a test chamber.

An energy density of about 25 J/cm² was obtained by focusing the laser beam onto the targets.

SnO₂ and Co targets were placed in a vacuum chamber on computer-controlled *x-y* tables which allow successive ablation of multiple targets as well as target movement during deposition in order to avoid target erosion. The vacuum chamber is equipped with a gas pressure and flow control system, which consists in a combination of mass flow controllers on the gas bottles and a throttle valve controlled by a pressure controller on a rotary vane vacuum pump. The ST-X cut quartz substrates are placed 40 mm from the target. Both Co₃O₄ layers and Co₃O₄/SnO₂ bilayers were deposited. The Co₃O₄ layers were deposited using 76000 pulses, leading to a thickness of about 250–300 nm, while the SnO₂ layer was deposited with 7200 pulses, leading to a thickness of 20–30 nm. All depositions were made at RT. An oxygen deposition pressure of 300 mTorr was used for both targets in order to ensure porosity of the thin film, as well as proper film stoichiometry.

The SAW sensors based on the Co₃O₄ layer (S1) and the SnO₂/Co₃O₄ bilayer (S2) were tested towards NH₃ and VOCs (methanol and toluene). The sensor operating scheme is presented in our previous works [11]. Figure 1 depicts the S2 SAW sensor in the test chamber. The frequency shift was measured with a CNT-91 Pendulum frequency counter connected to a computer with Time View 3 software. The circuit signal loss was compensated with a DHPVA-100 FEMTO amplifier (10–60 dB, 100 MHz). The response of the sensors to different concentrations of NH₃ and VOCs (methanol and toluene) was determined. Different quantities of analytes were injected in the mixer chamber. The flow rate of the VOC/air mixture was maintained constant at 150 cm³/s with a diaphragm pump (Pfeiffer MVP 035-2) for all the measurements. The temperature was maintained constant during the measurements, as well.

3. Results and Discussions

In X-ray diffraction, no peaks other than those of the substrate were visible, indicating that the sensitive layers are amorphous.

The film morphology was analyzed using scanning electron microscopy (SEM, Thermo Scientific Apreo S). SEM images indicate nanoporosity of the layers (Figures 2(a) and 2(b)), especially SnO₂. This nanoporosity favors gas diffusion into the layers. The thicknesses of the thin films are about

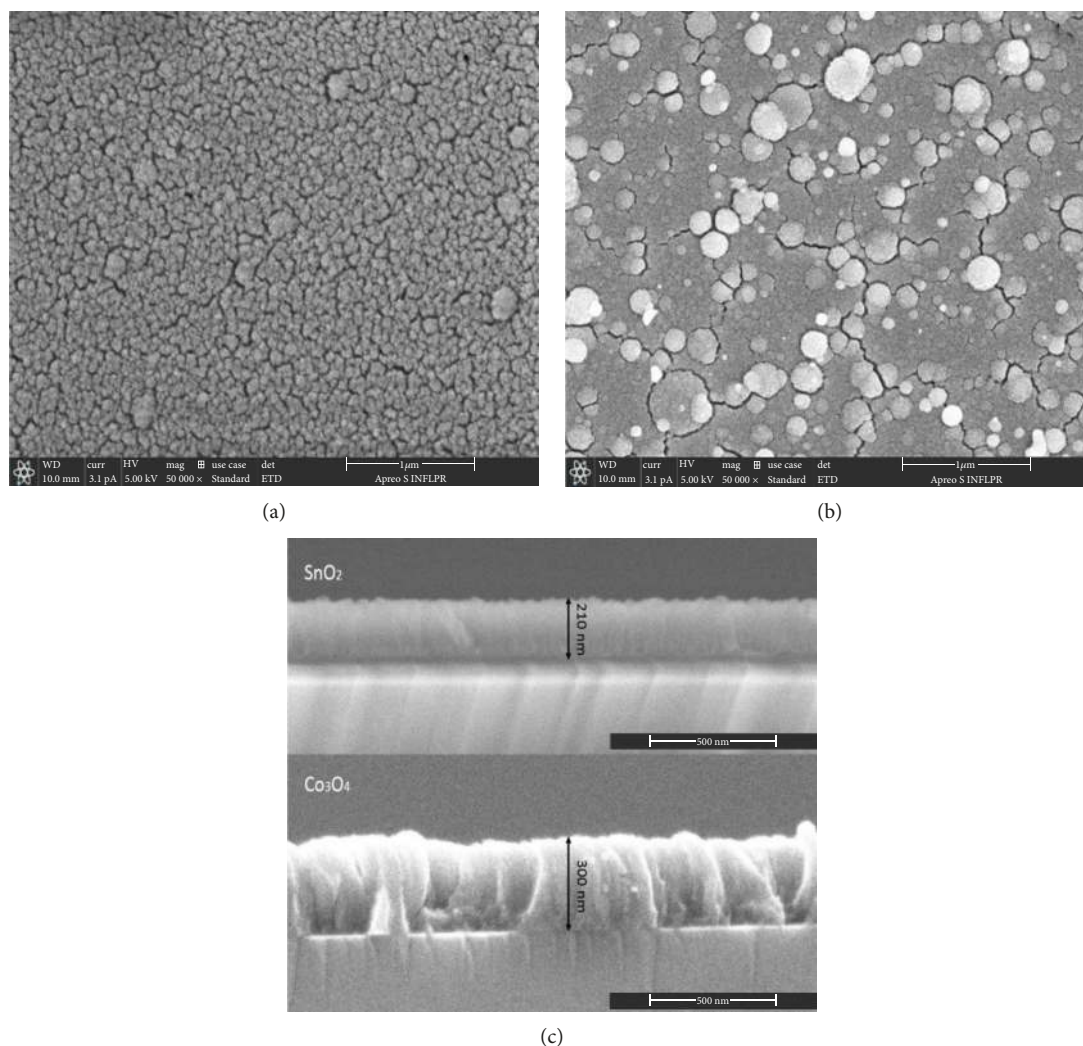


FIGURE 2: SEM images of (a) SnO_2 layer, (b) Co_3O_4 layer, and (c) SnO_2 and Co_3O_4 layer cross section.

TABLE 1: Sensitivity and limit of detection.

SAW sensor	NH_3		Methanol		Toluene	
	Sensitivity $\Delta f/c$ (Hz/ppm)	LOD (ppm)	Sensitivity $\Delta f/c$ (Hz/ppm)	LOD (ppm)	Sensitivity $\Delta f/c$ (Hz/ppm)	LOD (ppm)
S1	2.00	15	0.83	36	0.50	60
S2	3.33	9	1.33	23	0.60	50

Δf : frequency change and c : analyte gas concentration for the two sensitive films.

210 nm for SnO_2 and 300 nm for Co_3O_4 as it can be seen in Figure 2(c).

The frequency shifts of sensors S1 and S2 in the presence of NH_3 , methanol, and toluene were measured. Figure 2 presents the dependence of these frequency shifts on the concentration of the analyte introduced in the test chamber. A remarkable difference between the frequency shifts in the presence of NH_3 for the two sensors is evident. Sensor S2 presents a larger frequency shift than S1 at the same analyte concentration. In the case of methanol and toluene, although there are differences in the frequency shifts of S1 and S2 at the same analyte concentrations, these are noticeably lower than that for NH_3 . Repeating 10 measurements of the

frequency deviation for each of the 2 sensor films yielded errors below $\pm 3.5\%$.

Table 1 presents the sensitivity and limit of detection for the two sensitive films. The sensitivity, defined as the frequency shift in Hz per unit analyte concentration in ppm, was determined from the data shown in Figure 3. The limit of detection (LOD) is defined as three times the noise level per sensitivity. The noise level was around 10 Hz for all sensors and was determined by measuring the resonance frequency for 10 min as a maximum frequency deviation from the trend line. The results in the table indicate that there is a sensitivity difference between the two sensors for the same analyte. This is true for all three gas types studied, and S2

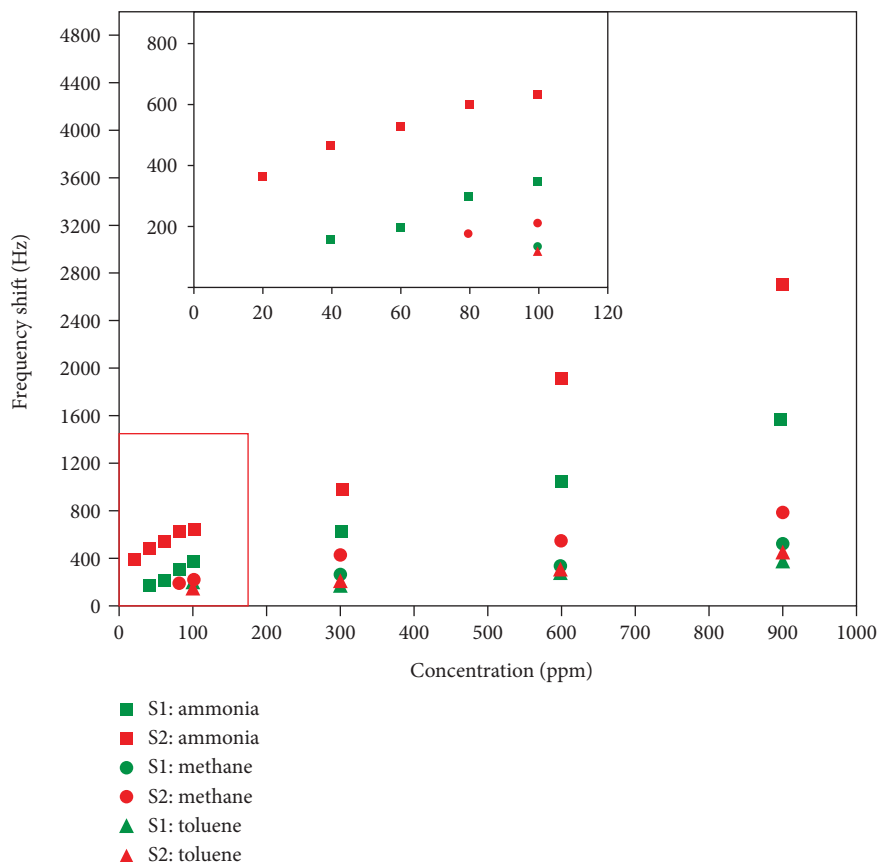


FIGURE 3: Response of sensor S2 as a function of NH_3 , methanol, and toluene concentration.

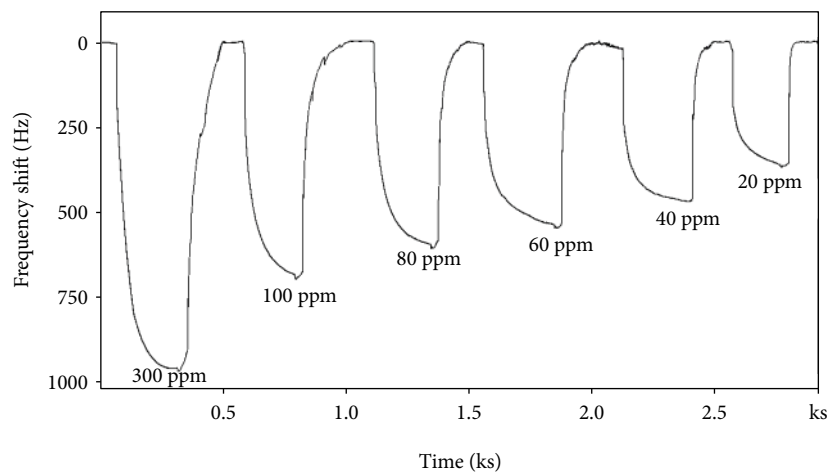


FIGURE 4: Dynamic response of sensor S2 to NH_3 for various concentrations.

gives better results in all cases. For example, the sensitivity of S1 in the presence of NH_3 is 2.00 while for S2 it is 3.33. It is also clear from Table 1 that the LOD of S2 is improved in comparison to that of S1, as well. The smallest LOD of 9 ppm was registered by sensor S2 in the presence of NH_3 .

Considering these results, it can be stated that Co_3O_4 shows selectivity for NH_3 , while SnO_2 significantly improves sensitivity of the sensor.

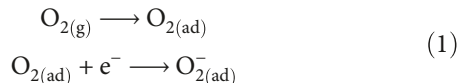
Figure 4 shows the variation of the frequency shift, response, and recovery times of sensor S2 for NH_3 , at different concentrations. It can be seen that the sensor has reversibility and that with the decrease of the analyte concentration, the frequency shift decreases. The response and the recovery times were measured between 10% and 90% of the maximum signal. The response time was about 100-120 s, and the recovery time was between

30 and 50 s for a concentration of NH₃ between 40 and 80 ppm.

The best results in the presence of NH₃ are obtained for sensor S2, which has the highest frequency shift, for all NH₃ concentrations. It was possible to detect NH₃ for concentrations down to 20 ppm (see the inset of Figure 2), with a LOD of 9 ppm. In addition, S2 has good selectivity for NH₃, as a comparison between results for VOCs and NH₃ shown in Table 1. Since good selectivity to NH₃ also appears in the case of sensor S1, we can attribute it to the Co₃O₄-sensitive layer common to S2 and S1. Therefore, the improved sensitivity and LOD of S2 can be attributed to the SnO₂ layer.

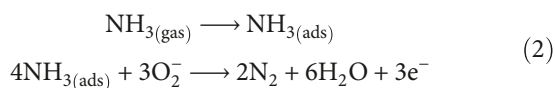
A significant increase in film conductance was observed in [15] when a Co₃O₄-sensitive film is exposed to NH₃. The authors of [15] therefore concluded that the response of the SAW sensor based on such a film is due both to this shift in film conductance and to a mass effect. The NH₃ sensing mechanism based on the shift in film conductance, involved in Co₃O₄-based sensors, has been attributed to resistance changes due to surface conductivity modulation by the adsorption and desorption of gas molecules [7].

In the case of our SnO₂/Co₃O₄ bilayers, the oxygen species in the surrounding air which are adsorbed on the surface of the porous-sensitive SnO₂ layer diffuse to the Co₃O₄ surface. At RT, the free electrons are then captured by the adsorbed oxygen species, forming reactive oxygen ion species at the surface, as in equation (1) [25].



Thus, at the surface of the Co₃O₄ p-type semiconductor, a hole accumulation layer is formed. When Co₃O₄ has a porous structure, the accumulation layer is correspondingly formed over a larger surface.

When exposed to NH₃, there is a reaction with the highly reactive oxygen ions on the surface of the Co₃O₄ and a release of the trapped electrons [25].



This generates a resistance variation and a variation of the surface conductivity, which in turn leads to a shift in the central frequency [15, 16].

In addition, the use of two different types of oxides, p-type (Co₃O₄) and n-type (SnO₂), in their interaction area, leads to the formation of heterojunctions. These are active areas that favor the adsorption of oxygen species, thus increasing sensitivity of the sensor [26].

A great influence on the results obtained was that the sensitive films were porous. This type of morphology confers a large contact surface between the sensing material and gas and also favors the diffusion of the gas on its volume [27].

4. Conclusions

In conclusion, porous thin films were deposited by PLD onto the quartz substrates of SAW sensors. Sensor S1 was coated with a single layer of Co₃O₄, while sensor S2 had a SnO₂/Co₃O₄ bilayer. Sensors were tested at RT in the presence of NH₃, methanol, and toluene, at various concentrations, at RT. The best responses were obtained for sensor S2, especially in the presence of NH₃. The sensitivity of S2 in the presence of NH₃ was 3.33 Hz/ppm, with a LOD of 9 ppm. The response and the recovery times for S2 to NH₃ were 100–120 s and 30–50 s, respectively. Thus, it could be stated that at RT, Co₃O₄ is selective for NH₃, while SnO₂ has the ability to improve sensitivity of the sensor.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

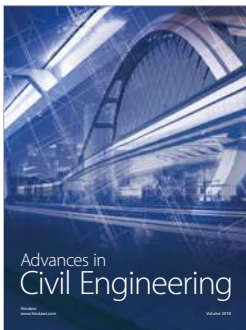
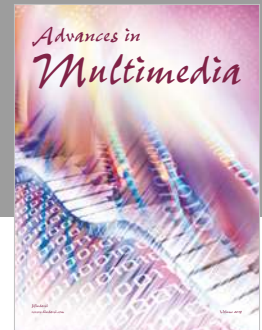
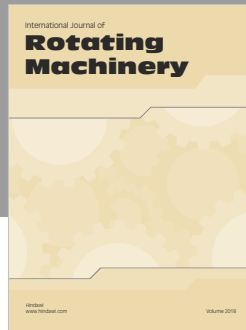
Acknowledgments

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