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High-Performance Ammonia Sensor at Room Temperature Based on a Love-Wave Device with $Fe_2O_3@WO_{3-x}$ Nanoneedles †

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Abstract: An innovative, simple and inexpensive Love-wave gas sensor based on $Fe_2O_3@WO_{3-x}$ nanoneedles to detect the variation of ammonia at room temperature was developed. The nanoneedles were successfully formed on Love-wave device via aerosol-assisted chemical vapor deposition (AACVD). The nanoneedles worked as guiding and sensitive layers detecting the changes of the elastic properties presented by ammonia interaction. The sensor was tested to ammonia concentrations between 25 to 90 ppm and showed large frequency shifts, high sensibility, short response time and good reproducibility.

Keywords: Love-wave; Ammonia Sensor; nanoneedles; tungsten oxide; ferric oxide; AACVD

1. Introduction

Pollutants released into the atmosphere cause global environmental issues and harm to human health. For instance, ammonia is a colorless and toxic gas that irritates the skin, eyes, and throat and damages the lungs. Monitoring of ammonia is of great interest for the industry because ammonia affects health and performance of workers and causes corrosion of equipment. Therefore, an efficient detection of ammonia in real time and in situ is required.

Chemical-resistive sensors with metal oxides as a sensitive layer have been commonly used for the detection of toxic agents due to their high sensitivity and stability [1]. Tungsten oxide has been extensively studied as sensitive layer for gases due to its high capacity to detect different analytes, such as NO_2 [2]. In recent years tungsten oxide has been nanostructured as nanoneedles and functionalized with second-phase nanoparticles (e.g., Fe_2O_3) to increase the gas sensitivity and selectivity to gases such as toluene, hydrogen or ethanol [3]. Our previous works, recently, have also showed the possibility to Love-wave sensors to detect gaseous molecules by elastic properties [4]. Therefore, in this work, Love-wave devices have been combined with $Fe_2O_3@WO_{3-x}$ nanoneedles for first time to detect ammonia by using the elastic properties of these gas sensitive nanostructured layers.

2. Materials and Methods

2.1. Love-Wave Device

A Love-wave device is a type of micro-electromechanical system (MEMS) that consists of a piezoelectric material with inlet and outlet aluminium interdigital transducers (IDT) on its surface, and an over-layer of a low shear acoustic velocity material to guide the surface acoustic waves that propagate transversely at the interface between the substrate and the guiding layer (Figure 1). The IDTs enable electrical excitation and reception of the wave and any change in the delay time is used to detect a physical phenomenon. In this work, we used quartz as piezoelectric substrate and plasma enhanced chemical vapour deposited SiO_2 as guiding layer (3.5 µm think). The wavelength used was 28 µm and the separation between IDTs 2100 µm.

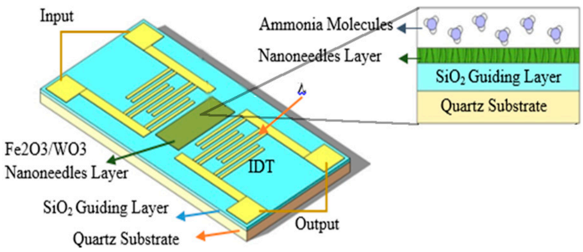


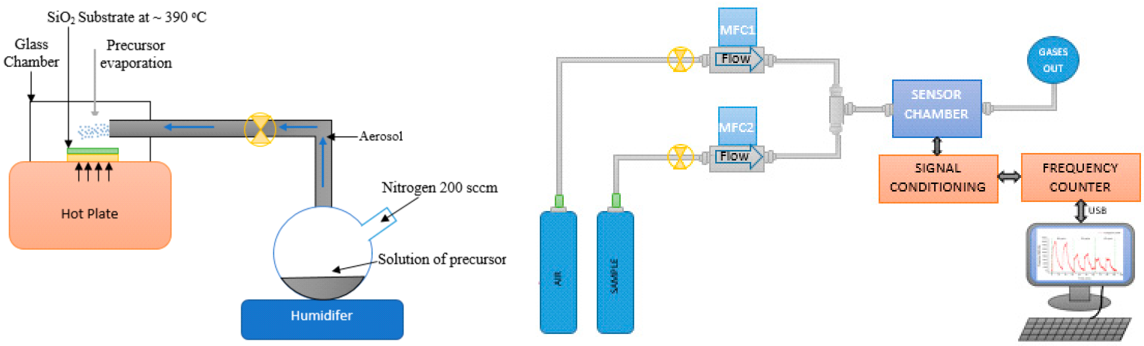
Figure 1. Scheme representing a Love-wave sensor, layer composition.

2.2. Sensitive Layer Deposition

$Fe_2O_3@WO_{3-x}$ nanoneedles were directly deposited on the SiO_2 guiding layer using a single-step deposition process via aerosol-assisted chemical vapor deposition (AACVD) (Figure 2a). Briefly, the functionalized structures were co-deposited using a solution containing tungsten hexacarbonyl (20 mg, $W(CO)_6$), Sigma-Aldrich, ≥97%) and ferric chloride hexahydrate (3 mg, $FeCl_3{\cdot}6H_2O$, Sigma-Aldrich, ≥99.6%) dissolved in methanol (5 mL, Sigma-Aldrich, ≥99.9%). The aerosol droplets of the solution were transported to the heated substrate (390 °C) using a nitrogen gas flow (200 sscm). The total time taken to transport the entire volume of solution was typically 45 min. The $Fe_2O_3@WO_{3-x}$ nanoneedles were examined using scanning electron microscopy (SEM–Carl Zeiss, Auriga Series) and scanning transmission electron microscopy (STEM–STEM FEI Tecnai F20, 200 k) equipped with EDX (Energy-dispersive X-ray spectroscopy).

2.3. Setup of Gas Sensor and Data Acquisition

The sensor was tested to different concentrations (25 ppm–90 ppm) of ammonia diluted in synthetic dry air. Mass flow controllers were used to obtain the desired concentrations with a constant flow of 100 sccm. The responses were displayed and saved in real time with an own program developed for this study. The sensing system consisted of a test chamber that contained the Love-wave sensor connected to a feedback circuit with gain of 1 and a coupler to obtain the characteristic oscillation frequency of the sensor. The signal was acquired using a frequency counter (Keysight 53220A). The scheme of the experimental configuration is shown in the Figure 2b.



(**a**) (**b**)

Figure2. (**a**) Basic scheme of aerosol assisted chemical vapour deposition technique; (**b**) Diagram of instrumentation and experimental setup for the gas sensing tests of the Love-wave sensors.

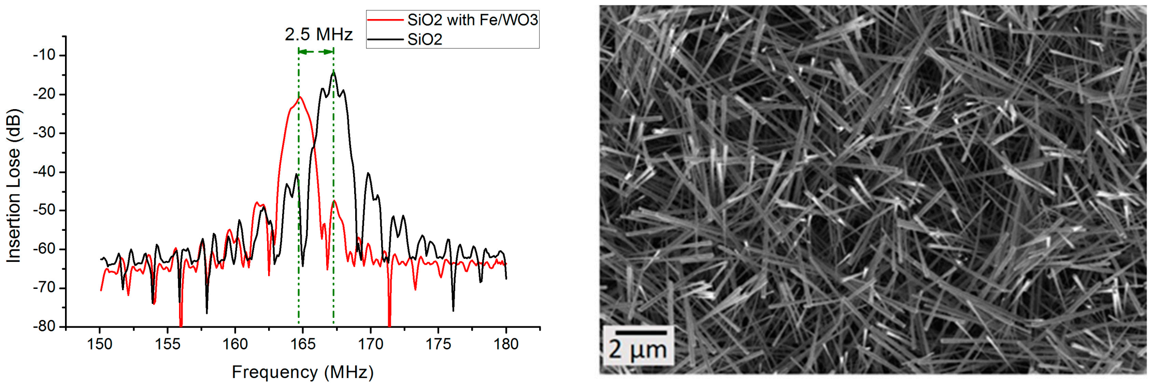
3. Results

3.1. Electrical Characterization of Love-Wave Sensor

The Love-wave device was characterized before and after the integration of $Fe_2O_3@WO_{3-x}$ nanoneedles using RF transmission parameter S_{21}. The frequency response variation was examined using an Agilent Automatic Network Analyzer (ANA E5070B). To control the frequency shift and attenuate the acoustic wave of the gas sensitive structures the length and density of the nanoneedles were diminished using sonication. Insertion losses of sensor were studied with and without nanoneedles, resulting in 23 dB and 14 dB respectively. A frequency shift of 2.5 MHz was observed for the final sensor with the $Fe_2O_3@WO_3-x$ nanoneedles (Figure 3a).

3.2. Morphology of the Gas Sensitive Layer

SEM of the sensitive layer (Figure 3b) displayed non-aligned structures in the form of nanoneedles with diameters of approximately 100 nm and lengths of 10 μm. Further, analysis of these structures by EDX and HRTEM confirmed the presence of ferric oxide nanoparticles (4–15 nm) dispersed along the tungsten oxide nanoneedles, which is consistent with our previous results for the deposition of $Fe_2O_3@WO_3-x$ nanoneedles on polymer substrates [3].



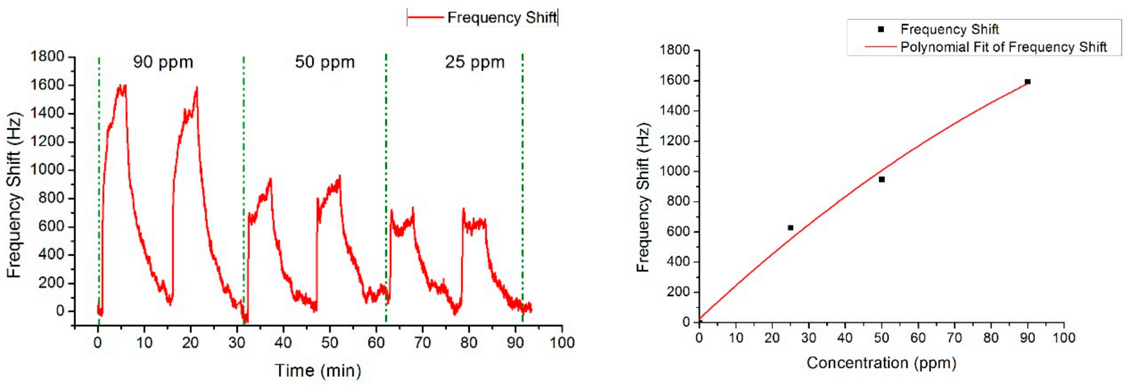
(**a**) (**b**)

Figure 3. (**a**) Frequency response of the sensor before and after $Fe_2O_3@WO_3-x$ deposition; (**b**) SEM image top view of $Fe_2O_3@WO_3-x$ nanoneedles.

3.3. Sensor Characterization

The Love-wave sensor was tested to different concentrations of ammonia (90, 50 and 25 ppm) showing variations of 1600, 850 and 627 Hz respectively, with an average response time of 90% is 2 min (Figure 4b). After exposition of the sensors to each concentration of ammonia for 5 min the system was purged with synthetic dry air for 10 min and a fast recover of the response in frequency was observed. The $Fe_2O_3@WO_3-x$ nanoneedles based sensor response to different concentrations of ammonia is shown in Figure 4a.

Two measurements were realized for each gas concentration to confirm the reproducibility of the response. The sensor responses showed a high variation of frequency versus the concentration of ammonia. These variations were represented by a second-order polynomial fit, which showed a direct relation of the sensor response with the gas concentration (Figure 4b) as reported previously for similar gas sensing systems having behaviors similar to these concentrations [4]. The signal to noise ratio (SNR) for the lowest concentration measured (i.e., 25 ppm) was 62.7, with a frequency shift of 627 Hz as the measured signal and with a noise about of 10 Hz. The estimated limit of detection is about 1 ppm considering that the minimum signal measurement is 3 times higher than noise.



(**a**) (**b**)

Figure 4. Ammonia characterization. (**a**) Dynamic response of sensor to different concentrations of ammonia; (**b**) Response of sensor as a function of ammonia concentration.

4. Conclusions

Love-wave sensors with Fe_2O_3@WO_{3-x} nanoneedles as sensitive material showed high responses to low concentrations of ammonia in the span of 25 ppm to 90 ppm, with the losses of the Love wave propagation set up to 23 dB. Gas sensing results showed variations of 627 Hz for 25 ppm of ammonia with a noise level of 10 Hz and an estimated limit of detection of 1 ppm. The high response of the nanoneedles to ammonia in Love-wave operation is attributed not only to the high surface to volume ratio of these structures, but also to its chemical and electronic sensitization due to the functionalization of the WO_{3-x} nanoneedles with Fe_2O_3 nanoparticles.

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Conflicts of Interest: The authors declare no conflict of interest.

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