A Layered SAW Gas Sensor Based on a Polyaniline/In_2O_3 Nanofiber Composite

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Abstract

A polyaniline/In_2O_3 nanofiber composite based layered surface acoustic wave (SAW) sensor has been developed and investigated towards different gases. Chemical oxidative polymerization of aniline in the presence of finely divided In_2O_3 was employed to synthesize a polyaniline nanofiber/In_2O_3 nanoparticle composite. The nanocomposite was deposited onto a layered ZnO/64° YX $LiNbO_3$ SAW transducer. The novel sensor was exposed to H_2, NO_2 and CO gases. Fast response and recovery times with good repeatability were observed at room temperature.

Keywords: Polyaniline Nanofiber, In_2O_3, Nanocomposite, Gas Sensor, SAW

Introduction

Metal oxide thin film gas sensors are widely used to detect gas species by changing conductivity. The sensing mechanism involves chemisorption of gas species on the metal oxide surface followed by charge transfer during the reaction with target gas molecules [1]. The adsorbed gas atoms inject electrons into or extract electrons from the metal oxide, depending on whether they are reducing or oxidizing agents, respectively [2]. Indium oxide is an n-type semiconductor, which has been extensively used for the sensing of H_2, NO_2, CO and O_3 gases [3-4]. However, sensors incorporating indium oxide require an elevated temperature (100-350°C) for optimum operation. The elevated temperature operation causes long-term instability due to a gradual change of the indium oxide crystal structure. Additionally, it requires extra power consumption for heating and an initial warm-up time, and reduces portability. As a result, it is highly desirable to develop sensors that operate at room temperature, and at the same time, keep the desirable properties of indium oxide for gas sensing.

An alternative to metal oxide materials for gas sensing applications are conducting polymers. They have received increasing interest for sensor design due to their room temperature operation, low fabrication costs, ease of deposition onto a wide variety of substrates [5] and their rich chemistry for structural modifications [6]. Polyaniline is unique among the family of conducting polymers as its conductivity can reversibly be controlled by the protonation of the imine sites and/or the oxidation of the main polymer chain [7]. It is well known that polyaniline in the emeraldine oxidation state can be reversibly switched between electrically insulating base and conducting salt forms [7].

The emeraldine base form transforms to an intermediate bipolaron lattice when protonated with a strong acid. The bipolaron form further undergoes dissociation to create a delocalized polaron lattice. A polaron can be considered as a type of electronic defect that occurs within the π orbitals of the polymer backbone, which produces the molecular asymmetry responsible for the high conductivity of doped polyaniline [8]. However, traditional polyaniline is not as sensitive as metal oxides towards gas species. There have been several reports on improving polyaniline's sensitivity and selectivity with methods such as synthesis of nanostructured forms [9-10], addition of metal catalysts [11-12] and combination with other polymers [13]. Among these options, the synthesis of nanostructured forms appears to be the most promising approach. The effects of sensitive layer morphology, such as grain size, structural formation, surface to volume ratio and film thickness on sensitivity are well recognized [14]. Gas sensors based on nanostructured materials have increased sensitivity due to high surface to volume ratios. Moreover, the whole sensitive thin film can be affected by the interactions with the gas species, rather than only the surface. Here we explore the idea of combining polyaniline nanofibers with metal oxide nano-structures for potential gas sensing applications.

There is a growing interest to combine both organic and inorganic materials for applications in electronics and optics [15]. The combination of nanosized metal oxides and polyaniline has the potential to increase the sensitivity and selectivity of the conducting polymer. Such composites can operate at room temperature and the selectivity towards different gas species can be controlled by the volume ratio of

nanosized metal oxides. In addition, the composite may have better long term stability. The nanocomposite organic/inorganic materials are considered as bi-phase materials where the organic and inorganic phases are mixed at the nanometer scale. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics [16].

A number of researchers have already developed polyaniline/inorganic nanocomposite sensors. Conn, et al. [17] developed a polyaniline/PtO_2 based selective H_2 sensor and reported that the conductivity of polyaniline increases with H_2 exposure, due to the formation of water. It is known that water present in the polymer takes part in charge transfer leading to an increase in the conductivity of polyaniline which is reversible [18-19]. Wang, et al. [20] developed polyaniline intercalated MoO_3 thin film sensors and reported that the conductivity change is due to the reversible absorption of analyte. Parvatikar, et al. [21] developed polyaniline/WO_3 composite based sensors and reported that conductivity of the film increases with increasing humidity. Ram, et al. [22] developed conducting polymer/SnO_2 and TiO_2 nanocomposite thin film based sensors and found that conductivity of the film increases with NO_2 exposure. Geng, et al. [23] synthesized polyaniline/SnO_2 hybrid materials by a hydrothermal process for gas sensing applications. They found that hybrid materials are sensitive to ethanol and acetone vapor at 60 to 90°C.

In this paper, we report the development of polyaniline/In_2O_3 nanofiber composite based sensor. To the best of our knowledge, this is the first attempt to study this

nanocomposite for H_2, CO and NO_2 gas sensing applications. A layered surface acoustic wave (SAW) transducer is employed. In a SAW device, the change in electrical conductivity of the sensing layer perturbs the velocity of the propagating acoustic wave by causing a change in the electric field accompanying the mechanical wave. The variation in velocity can be monitored by measuring the change in resonant frequency of the SAW device placed in a closed loop circuit. This change in frequency is related to the concentration of analyte present in the environment.

Experimental

The gas sensor is made up of two important physical components: the sensitive polyaniline/In_2O_3 nanofiber composite layer, which interacts with the gas media by changing conductivity, and the SAW transducer, which changes its operating frequency with any conductivity change.

Transducer fabrication:

The SAW transducer pattern was formed on a 64° YX $LiNbO_3$ substrate with an intermediate ZnO protective layer. A shear-horizontal (SH) leaky surface acoustic wave is the dominant mode in this layered substrate. The transducer consists of a two-port resonator with 38 electrode pairs in input and output inter-digital transducers (IDTs), 160 electrodes in each reflective array, 700 μm aperture width and a periodicity of 40 μm. A two-port resonator structure was chosen over a delay line as its higher phase slope increases oscillation stability. The IDTs and reflectors were formed by patterning an 80 nm Au layer. The Au layer was deposited upon 20 nm Ti for improved adhesion to the

substrate. The ZnO layer was deposited by RF magnetron sputtering. The sputtering gas was 40% O_2 in Ar at 1×10^{-2} Torr, the substrate temperature was 220°C, giving a deposition rate of ~1.2 μm/hr. The ZnO thin film was deposited on the 64° YX $LiNbO_3$ substrate, with a thickness of 1.2 μm. A fabricated dual SAW transducer is shown in Fig. 1.

Sensitive thin film fabrication:

There are two major polymerization approaches to synthesize polyaniline nanofibers: electro-polymerization and chemical polymerization. In this paper, the chemical polymerization technique has been employed to synthesize polyaniline/In_2O_3 nanocomposites. At first, aniline monomer was rapidly added into the 1.0 M camphorsulfonic acid (CSA) solution of In_2O_3 nanoparticles. The concentration of aniline monomer to In_2O_3 is 5 to 1 in the solution. Next, ammonium persulfate was added to the mixture and allowed to further react overnight. The product was dedoped with 1.0 M NaOH and further purified by four cycles of washing with distilled water-centrifugation. Subsequently, the nanocomposite solution was drop cast onto the surface of the SAW transducer.

Experimental setup:

Using the layered SAW device as a positive feedback element in a closed loop circuit with an amplifier, an oscillator was formed. A frequency counter was used to measure the operational frequency of the transducer upon exposure to the gas. The operational frequency of the sensor was found to be approximately 107.2 MHz in dry synthetic air at

room temperature. The sensor cell and electronics were enclosed in a temperature controlled chamber and exposed to various concentrations of H_2, NO_2 and CO gases. A computerized mass flow controller (MFC) system was used to vary the concentration of gases in synthetic air. A Fluke high-resolution counter (PM66860B) was used to measure the operational frequency of the sensor. The gas mixture was delivered at a constant flow rate of 0.2 liters per minute. The sensor responses were displayed in real-time and saved for off-line processing and analysis. Gas exposure time was fixed for each pulse and the cell was purged with synthetic air between pulses to allow the surface of the sensor to recover. The sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% concentrations, a CO gas pulse sequence of 60, 125, 250, 500, 1000 and 125 ppm and a NO_2 gas pulse sequence of 0.51, 1.06, 2.12, 4.25, 8.5 and 0.51 ppm in synthetic air at room temperature.

Results

Characterization:

Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the nanocomposite are shown in Fig. 2 and Fig. 3, respectively. The layer of 0.4 μm thickness consists of polyaniline/In_2O_3 nanofibers with average diameters of 90 nm. The nanofibers are connected together in a network. An X-ray diffraction (XRD) pattern is shown in Fig. 4, in which the sharp peaks are due to In_2O_3 and the broader peaks at 2θ~26° are due to polyaniline [24]. The diffraction peaks from the nanocomposite sample are well matched to the sharp lines from the pure standard

In_2O_3 (shown below the polyaniline/In_2O_3 diffraction pattern) indicating that the sample contains In_2O_3 particles.

Test Results:

The dynamic response to a sequence of different H_2, CO and NO_2 gas concentrations in synthetic air is shown in Figs. 5, 6 and 7, respectively. The sensor response is defined as the variation in operating frequency of oscillation due to the interaction with the target gas. Measured sensor responses were approximately 11.0, 2.0 and 2.5 kHz towards 1% of H_2, 500 ppm CO and 2.12 ppm NO_2 in synthetic air, respectively. The 90% response times were 30, 24 and 30 s for H_2, CO and NO_2, respectively. The corresponding 90% recovery times were 40, 36 and 65 s. It was also observed that for all three gases response was slower at low concentration compared to high concentration. As a result, at low concentration, high gas exposure time is required for stable response (frequency shift).

Reproducibility was observed as indicated when a second pulse of 0.12% H_2, 125 ppm CO and 510 ppb NO_2 were introduced into the sensor chamber. It was found that the polyaniline/In_2O_3 nanofiber based sensor produce repeatable responses of the same magnitude with good baseline stability for H_2 and CO gases, but not for NO_2. Repeatability was confirmed by testing the sensor continuously over a 5 day period. It is inferred from the dynamic response curve of the 3 gases that the frequency shift increases almost linearly for the increase of H_2 concentration but for CO and NO_2, the frequency shift vs gas concentration are non linear. For NO_2 gas, the sensor response

was not repeatable and baseline seems to drift down ward. It was found that the sensor could not recover to baseline and at 4.25 and 8.5 ppm NO_2 concentration; the sensor response magnitude is lower than that of at 2.12 ppm. It is believed high concentration of NO_2 gas is poisoning the nanocomposite film. This was confirmed by exposing the sensor to a single pulse of 8.5 ppm NO_2, where a response of 4.5 kHz was observed. The result proves that the sensor is useful to detect low concentration range of NO_2.

The sensor was tested in dry air. The results reported by other authors [17-19, 21] would suggest that humidity has a significant effect on the operation of the sensor presented here. This effect could be due to a combination of the conductivity change of the polyaniline layer or the adsorbed water on the surface of nanofibers. High temperature operation of the sensor results in less susceptibility to humidity than room temperature operation, and the application will generally determine which is preferred.

Although the developed gas sensor is promising, low selectivity and lack of long term stability are of concern. There are several approaches to reduce these limitations, such as the use of catalysts and promoters, multi-sensor array systems and intelligent signal processing.

The gas sensing mechanisms of polyaniline/In_2O_3 are not yet understood, however we propose several possible mechanisms here. There two possible mechanisms for the H_2 gas interaction. The first one is activation of the hydrogen by In_2O_3 due to formation of indium-dihydrogen complexes. The second one is an interaction with the polyaniline

backbone, possibly facilitated by In_2O_3 which may induce dissociation of the hydrogen leading to either a doping type response or chain alignment.

The increase of the nanocomposite conductivity upon exposure to CO can be similarly described as a conductivity increase due to interaction of polyaniline with CO [25-26]. A plausible sensing mechanism involves activation of CO, which is helped by In_2O_3 nanoparticles, to form $C^+{\equiv}O^-$. This facilitates C^+ conjugation with the amine nitrogens ($–HN^{\bullet\bullet}–$) of polyaniline. The conjugation results in polaronic forms ($–HN^{\bullet+}–$) in amine sites which increases the charge mobility on the polyaniline. The formation of a polaron could then be responsible for the increase in conductivity observed after exposure to CO.

The conductivity of a polyaniline/In_2O_3 film also increases with NO_2 exposure, which indicates that this gas acts as a dopant for the composite. Polyaniline and In_2O_3 may form a p-n junction with a depletion region. Exposure to NO_2 may cause reduction of the depletion region and hence increase the nanocomposite conductivity [22].

Conclusions

SAW gas sensor has been fabricated based on polyaniline/In_2O_3 nanocomposites synthesized by chemical oxidative polymerization of aniline in the presence of finely divided In_2O_3. The sensor has been investigated for its response to the gases H_2, NO_2 and CO. The sensor shows a repeatable and large response towards H_2 and also responds well towards CO. Future work will be devoted to improve NO_2 sensitivity and

improve selectivity. Due to room temperature operation, these composite gas sensors may prove to be useful for environmental and industrial applications after further development.

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Figures:

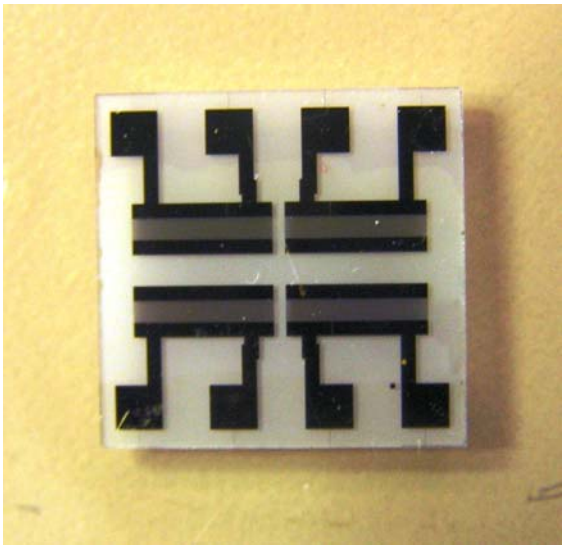


Figure 1: A typical sensor showing two sets of identical resonators.

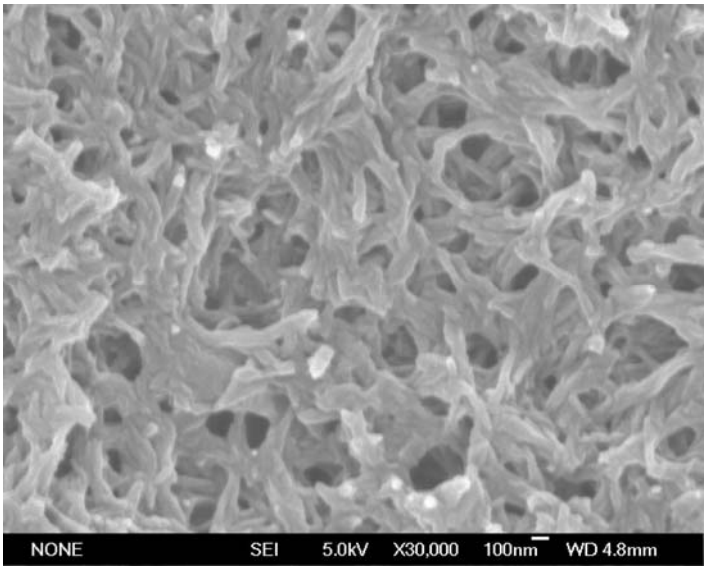


Figure 2: Close-up SEM image of a polyaniline/In_2O_3 nanofiber matt.

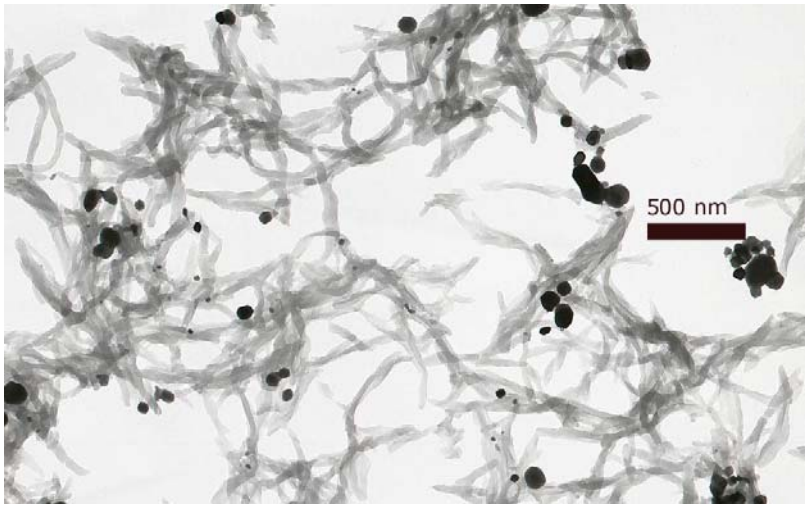


Figure 3: TEM image of a polyaniline/In_2O_3 nanofiber matt.

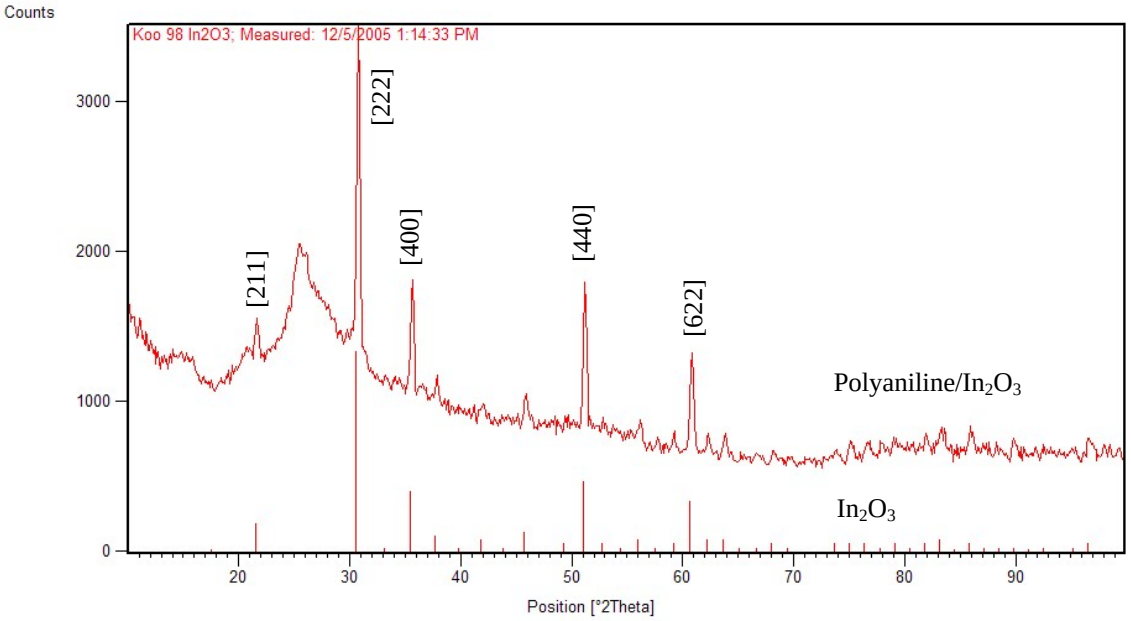


Figure 4: Powder X-ray diffraction pattern of a polyaniline/In_2O_3 nanofiber composite (top) and a bar graph for pure In_2O_3 from the JC-PDS database (bottom).

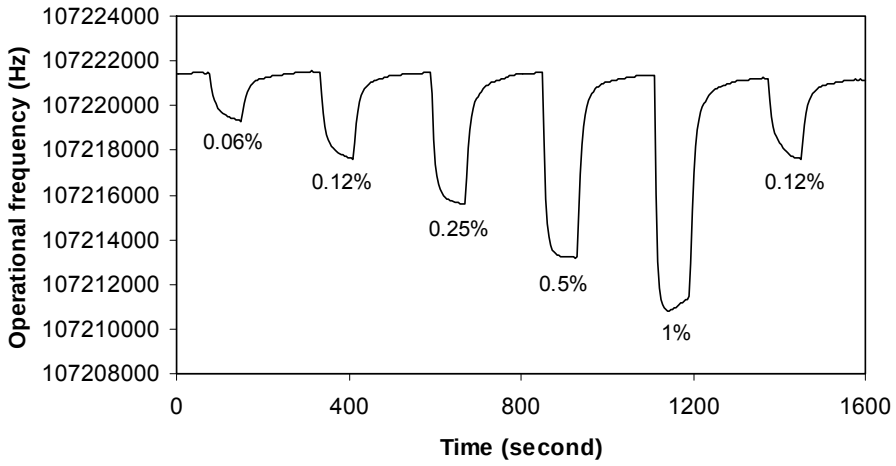


Figure 5: Dynamic response of the SAW sensor towards different concentrations of H_2 at room temperature.

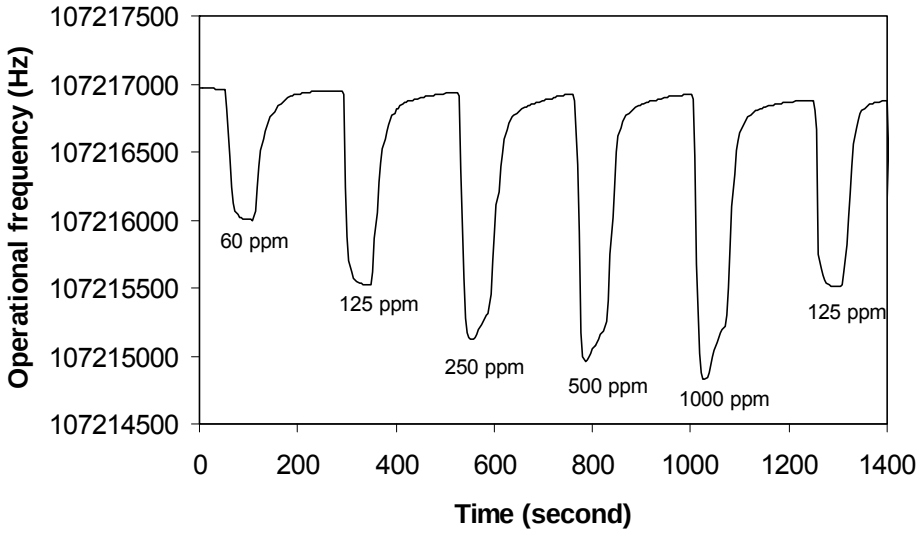


Figure 6: Dynamic response of the SAW sensor towards different concentrations of CO at room temperature.

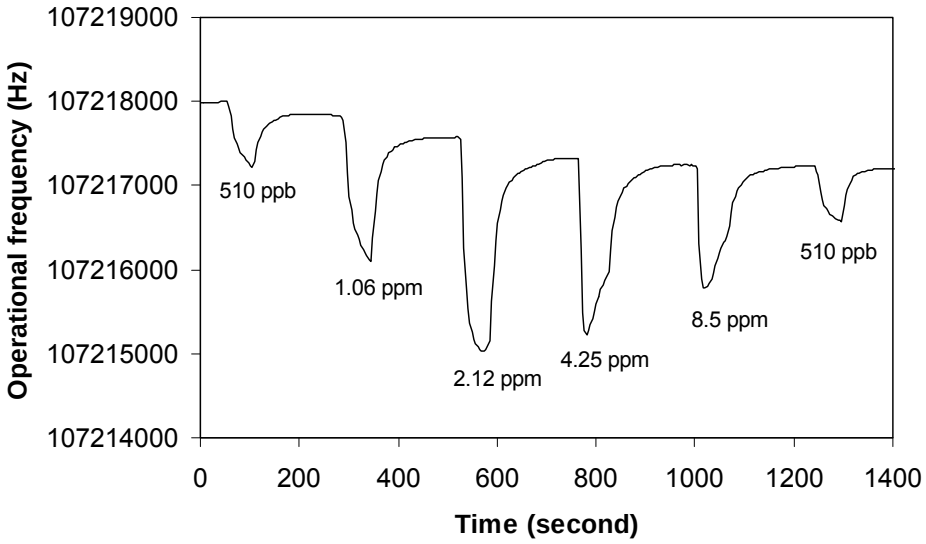


Figure 7: Dynamic response of the SAW sensor towards different concentrations of NO_2 at room temperature.