Nonlinear Analysis of Transient Response in Thin Film based Ammonia Detector

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Abstract

The nonlinear analysis of the transient response of a $\beta - Ga_2O_3$ thin film based ammonia detector is performed using standard techniques such as Wavelet Analysis and Lyapunov Exponents, all of these targeted towards the resistance transient response as a function of ammonia concentration in ppm. While the distance plots reveal maximum asymmetry in the vicinity of 5ppm, positive Lyapunov Exponents obtained confirm the presence of chaos, while exhibiting a very prominent peak at 5ppm concentration levels. This trend is attributed to the moderate response and recovery times seen for the 5ppm concentration level, making it an 'optimum' level of sensitivity. It is opined that the results of nonlinear analysis presented in this work will serve as a stepping stone in the systematic benchmarking of various sensing mechanisms taking into account the nonlinearity in the underlying mechanisms.

Keywords: Chemical Sensor, Ammonia, $\beta - Ga_2O_3$, Nonlinear Analysis, Lyapunov Exponents

1. Introduction

In recent times, the toxicity and strong reducing nature of ammonia has been the impetus for research efforts targeted at its detection, partially owing to the diverse applications ranging from agriculture and food industry, automobiles, fertilisers and fuels [1]. However, the first analytical techniques to detect ammonia involved electrochemical methods, laser technology and mass spectrometry, all of which are time consuming and expensive [1, 2, 3, 4, 5]. Fortunately, methods have been developed to detect ammonia using $\beta - Ga_2O_3$ thin films, where various techniques such as spray pyrolysis, sol-gel, sputtering and pulsed laser and chemical vapor deposition have been used for deposition of $\beta - Ga_2O_3$ thin films [6, 7, 8, 9, 10]. Consequently, the transient response is seen to exhibit an almost instantaneous change of the film electrical resistance in response to various concentrations of ammonia ranging from 0.5 ppm to 100 ppm [12].

Based on these results, the present work is targeted towards a nonlinear analysis and chaotic characterization of the transient response, the key motivation for such a study being the fact that nonlinear analysis enables the understanding of key information such as sensitivity using standard and established measures such as Lyapunov Exponents. The presence of chaos is indeed ascertained from these studies, and it is seen that the nature of chaos is most sensitive to initial conditions for an ammonia concentration of around 5ppm.

It is opined that the results of the present work will serve as a curtain riser to a whole new paradigm of benchmarking of sensors, based on nonlinear analysis and chaotic characterization.

2. An overview of Ammonia Sensing using $\beta - Ga_2O_3$

Owing to its simplicity and various optimization options, spray pyrolysis is used to deposit the Gallium Oxide thin films. Gallium acetylacetonate is used as precursor, where thermal decomposition is used to form a non-stoichiometric coordinate compound $[Ga(OH)CHOO]^+$, further decomposes into acetic acid CH_3COOH and Gallium, which at 350 degrees Centigrade readily oxidises to form Gallium Oxide film [13]. X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM) along with Energy Dispersive Spectroscopy (EDS) are the key tools used to characterize the formed thin film [13].

In order to conduct vapor sensing studies, ohmic contacts are made on the film, and by introducing calibrated volume of liquid ammonia into the test chamber maintained at constant pressure, the electrical resistance R_g of the film is measured. Using the value R_0, denoting the electrical resistance of the film in absence of ammonia, the sensing response is given as follows:

$$S(percentage) = \frac{R_0 - R_g}{R_g} \times 100 \tag{1}$$

The concentration dependent resistance behavior is studied from the transient response and then plotted for ammonia concentrations ranging from 0.5ppm to 100ppm [12]. It is seen that when the thin film is exposed to ammonia, the resistance changes almost instantaneously, with an interesting observation: recovery times increase with increasing concentrations of ammonia. As the ammonia concentration is increased, the lowering of response times is attributed to increase in the number of ammonia molecules striking per second on the surface, whereas increase in recovery times is attributed to increased strength of chemisorbed oxygen bonding on the nanocrystallites [12].

3. Nonlinear Analysis of Transient Response

The key motivation behind performing nonlinear analysis of the transient sensing response is to understand in more detail, the signal-oriented dynamics of the transient, revealing details such as optimal sensitivity, which would not be possible with conventional linear analysis techniques. The fundamental premise here is that sensitivity, seen as the key aspect of interest in a thin film based ammonia detector, is also the bedrock of chaos theory, the flagship of nonlinear science [14, 15, 16, 17, 18, 19]. In essence, a chaotic system is characterized by determinism and an extreme sensitivity to initial conditions, with very small differences in initial conditions often leading to drastic changes in the outcome [14, 15, 16]. The nonlinear analysis of the transient response uses two well established techniques, briefly outlined as follows:

3.1. Solitary Wavelet Analysis

It is well known that wavelets occupy a crucial niche in signal processing applications. [20, 21, 22, 23, 24].

In the present work the solitary wavelet, with the scaling function defined as a hyperbolic secant is used, owing to the fact that hyperbolic secant solitons are known to be very smooth, compact functions, making them ideal choices for a wavelet. This fact is verified by plotting the moments of the various existing wavelets along with the solitary from the third order onwards in a logarithmic scale in Fig. (2). It is clearly seen that while all the other wavelet moments including those of the Daubechies and Meyer show an increasing trend, the chaotic solitary wavelet moments show a decreasing trend with a negative logarithmic slope. This indicates that the moments of the solitary wavelet rapidly decay and vanish toward zero. This gives the solitary wavelet the exclusive advantages of smoothness, compactness, thus detecting bursts and discontinuities with minimal filtering.

3.2. Lyapunov Exponent

Largest Lyapunov Exponent (LLE) is a quantitative measure of a system's sensitive dependence on initial conditions. Rosenstein's algorithm is used to compute the Lyapunov Exponents λ_i from the voltage waveform, where the sensitive dependence is characterized by the divergence samples $d_j(i)$ between nearest trajectories represented by j given as follows, C_j being a normalization constant [25, 26]:

$$d_j(i) = C_j e^{\lambda_i (i\delta t)} \tag{2}$$

3.3. Results and Discussion

The Wavelet Analysis for three concentrations of ammonia, namely 0.5ppm, 5ppm and 50ppm are illustrated using the 'jet' colormap in Fig. (3) - (5).

The wavelet analysis plots for each of the three concentrations exhibit a different behavior. For the low concentration case, a rather symmetrical pattern, with the fall and rise transitions seen as shifts from red to blue and vice versa. For the 5ppm case, the sharp transitions characterize the plot, with a fractal nature observed in the bunching seen at higher scale levels. However, for the 50ppm case, the recovery time has a drag significant enough to delay the final blue to red transition gradient. Moreover, a significant lack of fractal features is seen.

The LLE values of all the ammonia concentration responses from 0.5ppm to 100ppm are computed and plotted in Fig. (1).

The graph indicates that the sensitive dependence on initial conditions, quantified by the LLE, reaches a peak at a 5ppm concentration, to a hitherto unseen high value, close to 100, with significantly lower LLE values on either side of this peak. It is also seen that higher concentrations, close to 100ppm exhibit a higher LLE, albeit slightly than low concentrations such as 0.1ppm and 1ppm. The presence of the prominent peak at 5ppm is an indicator of maximum sensitivity, which can be attributed to both fast response as well as fast recovery. Given that response times decrease and recovery times increase with increase in ammonia concentration, it is only appropriate that an 'optimum' point is reached midway, at around 5ppm. Thus, this concentration could also be viewed as the optimal condition of the thin film based ammonia sensor.

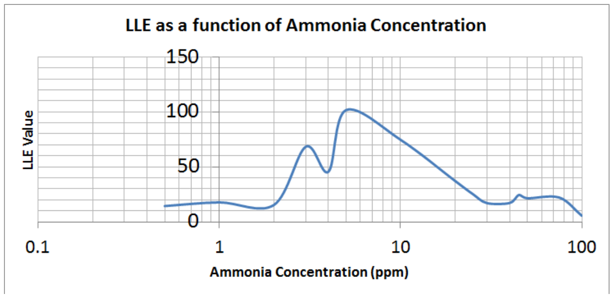

Figure 1: Largest Lyapunov Exponents of the Transient Response as a function of Concentration

4. Conclusion

After a brief overview of ammonia sensing $\beta - Ga_2O_3$ thin films, a nonlinear analysis of the transient resistance response is performed. The techniques used involve the Wavelet Analysis, Lyapunov Exponents (LLE). The Wavelet Analysis indicated an increase in asymmetry as concentration is increased to the vicinity of 5ppm, followed by a decrease in asymmetry. The analysis of LLE as a function of concentration clearly ascertained the presence of chaos also establishing the highly sensitive behavior seen at 5ppm concentrations, a level deemed 'optimum' considering its moderate response and recovery times. The results discussed is the present work offers a fresh perspective using nonlinear analysis techniques on the sensing capabilities and interactions of nanostructured thin films with various chemicals and gases, and such a perspective will surely aid in the benchmarking of sensing devices for various applications.

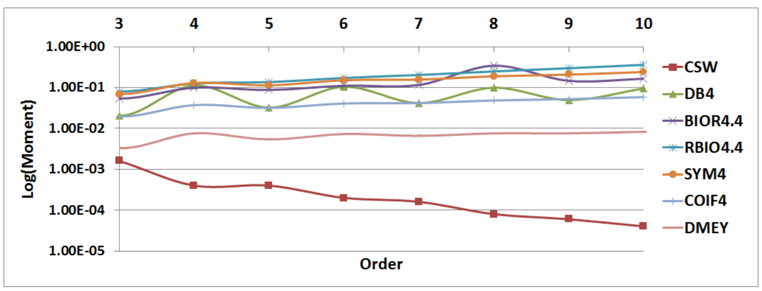

Figure 2: The Moments (upto Tenth Order) of Chaotic Solitary Wavelets compared with contemporary wavelets on a logarithmic scale. The negative slope vanishing fast towards zero clearly sets apart the chaotic solitary wavelet

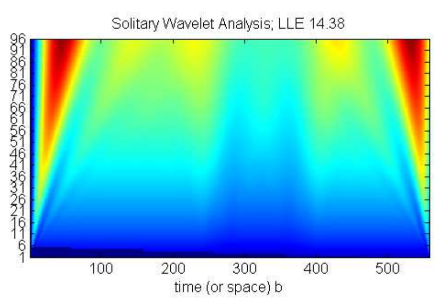

Figure 3: Wavelet Analysis for 0.5ppm Ammonia Transient Response

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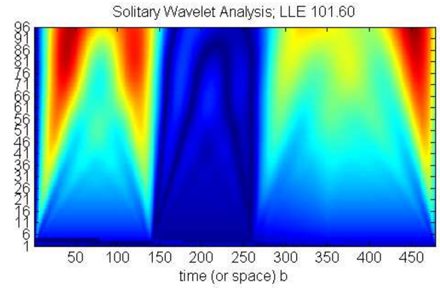

Figure 4: Wavelet Analysis for 5ppm Ammonia Transient Response

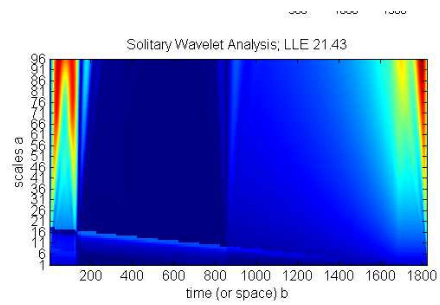

Figure 5: Wavelet Analysis for 50ppm Ammonia Transient Response

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