Study of toxic gas adsorption on silicon substrate integrated with piezoelectric material for sensing application using COMSOL Multiphysics

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Abstract. This paper aims to study the analytical response of micro cantilever based gas sensor for the quantification of NO\textsubscript{x} gas molecules, simultaneously discussing the possibility of a different measurement technique. Numerous packed and digital gas sensors are available in the market, but each with its own limits. MEMS sensors provide smart working, portable, save space, and reusable. Hence the micro cantilever beam deposited with an active material such as palladium, reduced graphene oxide to monitor and obtain the concentration of NO\textsubscript{x} was identified in terms of deflection for deposited mass. The physics and study provided by COMSOL Multiphysics will be exploited for the current usage. Various materials such as silicon and diamond as a substrate were simulated and compared. This paper discussed about the different micro cantilever beam structures for the gas sensing mechanism and selects the better structure based on their deformation in structure due to applied mass. The excellent trapping substrate material for NO\textsubscript{x} is chosen. A new measurement technique using piezoelectric material will be discussed. The proposed method will be discussed based on their pros and cons by compared with other sensors. The drawbacks of the proposed technique are also highlighted. Overcoming the drawback of conventional measurement methodology and devising a novel sensor to make it compatible for gas sensing.

Keywords: Micro cantilever, Gas adsorption, Displacement study, MEMS, Silicon, Diamond and Piezoelectric material.

1. Introduction

Air pollutant is a primary danger to environment. It is the due to combination of pollutant gases and foreign particles which completely changes the quality of natural air [1]. This pollutant air usually starts affecting the all living beings including human being that causes many health related problems like eye irritation, bronchitis, cancer, asthma emphysema, breathing issues, muscular paralysis etc. Not only does it affect humans health but also green lifes by eradicating its chlorophyll and disrupting the process of photosynthesis due to ozone layer. One of the major contributors to air pollution is...
transport system which spews toxic gases into the atmosphere by burning fuels. There are four major toxic gases operating for corrupting the air quality level are CO, CO$_2$, NO$_2$ and HC. To keep a tab on the exhaust gases, government has imposed a certain set of standards known as the emission standards. It is mandatory for every vehicle to undergo the emission test to maintain the gases under acceptable limits [2]. Although, the gases emitted do not always remain constant between two test periods. Emission depends on many factors such as the maintenance of the vehicle, type of vehicle, type of road driven on, load variations etc. Hence the need of portable device to monitor the level of pollutant, it has to be suitable to place a device within minimum space. The microcantilever based sensor designed and analysed the concentration of target gas as a electrical readout. The IC technology has improved a lot for making innovations with advantages to saving space. MEMS has introduced methods of fabricating smaller and more compatible devices with its high accuracy. It also deals with continuous monitoring periodically. The microcantilever designed and to measure the target analyte by reacting with an active layer. This causes a shift in the equilibrium position of the beam as well as its natural resonant frequency. Gas analyte deposited can be measured in static and dynamic way. The static method obtains as the mass deposited as a function of deformed of the microcantilever. The dynamic mode obtains the analyte results in terms of resonant frequency [3]. In this work, integrated microcantilever with a piezoelectric material were used in the static mode of operation wherein the deformation induces a stress on the microcantilever on the piezoelectric. A voltage is generated by the piezoelectric crystal which can be measured using external circuitry. Simulation were performed and response was recorded on different microstructures [4] by maintaining their length, breadth and thickness constant. The main aim is to sense the target gas molecules for applied load by deforming its structure. This work totally differs from conventional micro gas sensors. It measures the target gas molecules and deforms its microstructure directly using piezoelectric crystal instead of a Wheatstone bridge.

1.1. Principle of operation

The principle of operation is finding the lump of the target gas adsorbed on the sensing material that creates the deformation of the microcantilever. When the microcantilever is exposed to the exhaust gases, the target gas molecules only reacts with the active layer, it causes accumulation of particles on the sensing area. This makes the microcantilever to deform its structure from equilibrium position to new and its clearly shown in figure (1). Better structure is selected based on the maximum deflection response for a applied pressure. Piezoelectric characteristic to generate a output voltage, when the sensor is undergoing stress/strain. The deformation of the structure because of the stress created on the faces of the piezoelectric crystal integrated with the microstructure directing to create of EMF on its contradictory faces. The relationship between stress induced in the micro cantilever structure after the adsorption of particular gas analytes, this induces the deflection in the beam structure. Such displacement can be found from the stoney’s equation [5].

$$d = \frac{3\sigma(1-\nu)}{E} \left( \frac{L}{t} \right)^2$$  

(1)

Where, $\sigma$ is the stress created due to applied mass on the trapping area of the cantilever beam. $\nu$ is poisson’s ratio of the material chosen for sensing. L is micro cantilever beam length, t is the total thickness of the micro cantilever beam and E is the young’s modulus of the material chosen for sensing. The output voltage from the beam structure after adsorption of target molecules can be given by

$$V_{output} = MxSxT$$  

(2)
By solving the equation 2 the output voltage of the piezoelectric material due to the continuous deposition of gas molecules can found. Where M is the applied mass, S is the deflection sensitivity from the simulation for the applied load & t is the density of the substrate material. Solving the above equations can define the displacement and output voltage generated due to mass deposition.

SnO$_2$ and coated with palladium and reduced graphene oxide is the sensing material for NO$_x$. A thin layer of this sensing material is deposited on microcantilever. When the microcantilever is exposed to pollutant gases, the target gas get adsorbed over the sensing material which increases the mass of the beam at free end to deform its structure. Due to this increased mass, the cantilever beam bends resulting in generation on voltage which can be measured using external circuitry.

**2. Materials and methods**

It is crucial for this application that the sensing material detect selectively only NO$_x$ and no other gases. Metal oxides are the most suitable materials to sense oxidizing or reducing gases. SnO$_2$ is one such material suitable to sense different gases. Based on temperature and doping of external agents, the selectivity to gases of SnO$_2$ varies. SnO$_2$ can sense various gases such as CH$_4$, NO, CO etc. at different temperatures [6-7]. But it specifically senses NO$_x$. It is observed that by adding external impurities, such as palladium, its selectivity to NO$_x$ can be increased [8]. But the temperature at which it sense will be drastically reduced. Also coating it with polymers such as porphyrin and polyaniline can also increase the selectivity to other gases while increasing its working temperature [9]. SnO$_2$ can also sense CO at high temperature[10-11]. The temperature and additional impurities
are different from that of NOx. Sensitivity of the material to gases increases as its thickness reduces. Hence thin film SnO$\textsubscript{2}$ is used where thickness of the film is maintained below 100μm. NO$x$ can also be sensed using Yttrium stabilized zirconia [12]. This material is found to be most suitable to sense the gas even at 500°C. YSZ is used as the sensing material in the designed sensor. The main consideration for selecting appropriate material is temperature. Temperature from the commercial and other sources like industries, automobile can go up to 1000°C [13]. It is necessary for the sensor performance to remain intact even at such high temperatures. Also the material should be sensitive only to a particular gas among the various gases in the exhaust. It should sustain the rugged environment of the exhaust system. Keeping these considerations in mind the above materials are chosen. For piezoelectric crystal vast material are available [5,14]. Lead zirconate titanate (PZT) is selected for its high energy density, better piezoelectric properties and electromechanical coupling. It is observed that among all the available materials, PZT crystals are best suited for higher energy harvesting. Silicon is the substrate material that is used in the fabrication of almost all the MEMS sensors. The drawback of silicon is that it cannot withstand temperature higher than 300°C. Extensive search of temperature compatible materials is performed [15-18]. It is deduced that thin film diamonds can be used for gas sensing applications. They can work without any variation in their properties even at 900°C. Silicon and diamond are both compared for best results.

2.1 Improvement over existing technology
Conventional method of measurement involved with gas sensors uses the Wheatstone bridge. This increases the device complexity. This paper presents a novel method using the piezoelectric crystal wherein voltage is directly obtained without the use of any external components. The Wheatstone bridge has 4 arms with balanced resistances made of piezoresistive material. One of the arms contains the sensor. When sensor produces deflection, its resistance changes causing an imbalance in the bridge which creates a voltage. This voltage is measured using electronic circuitry. The similar technique were implemented using piezoelectric crystal. When deformation occurs, it induces stress on the crystal which generates a voltage. This is detected using sensitive electronic circuitry which filters noise and amplifies the signal for further processing. The amplifier must have wide band gap along with high gain to amplify small signals. Also a high frequency operation is expected for fast sensing and smaller time delay. This application calls for high signal to noise ratio which filters the noise from the signal and gives an undistorted output.

3. Results and discussion
Eigen frequency and stationary study were performed on all the structures making the selected design suitable for both static and dynamic measurements. A maximum deflection was the main consideration for varying mass loading. A comparison is shown in figure (2).
Figure 2. Three different shapes are compared by varying the mass loading. Maximum displacement is obtained for T shape structure.

The T shaped cantilever beam was the best structure considering its simple design and maximum deflection. Placement of PZT is based on the area of the beam where stress is maximum. This can be observed in figure (3).

Figure 3. Mass applied to the sensing area induces a stress on the fixed end of the cantilever beam.
As a result, the PZT is placed at the fixed end of the beam. The T shape is then integrated with selected piezoelectric material and compared with the second best design, i.e. Rectangle based on the structure feasibility and withstand. Displacement and voltage generated is compared for the two structures in figure (4) and (5).

**Figure 4.** Mass is applied to the two best shapes, and the respective displacement is compared.

**Figure 5.** Mass applied to the two better shapes is varied, and voltage generated is plotted.
Figure 6. Trapping area Vs. Displacement for varying mass deposition.

Trapping area is varied and the results are plotted in figure (6) and (7). It is observed that lower the trapping area higher the displacement and hence the voltage generated. Although a low area of sensing is preferred, for efficient sensing 25% of the sensing area is coated with sensing material.

Figure 7. Trapping area VS. Voltage for varying mass deposition.
3.1 Material optimization

Wheatstone bridge is the most opted measuring technique. But the piezoelectric method comparatively provides ease of design and integration within the sensor beam. PZT is the best material that can give a measurable voltage even for small deflections. Also it is suitable for temperature of up to 500°C. Although vast number of materials are available for sensing gases, SnO\textsubscript{2} is found to be most suitable. It can sense both NO\textsubscript{x} and CO with the doping of external impurities. The sensor, in general, has to be made compatible to very high temperature. Silicon can be used only up to 300°C. Thin film diamonds show best results when it comes to high temperature gas sensing.

![Figure 8. Displacement comparison for Silicon and Diamond](image)

![Figure 9. Voltage comparison for Silicon and Diamond](image)
Figure (8) and (9) show the difference between measurements done using silicon and diamond as a substrate materials. It shows that silicon has higher deflection compared to diamond. This is because diamond has lower elasticity. This also causes larger stress on PZT material which causes higher generation of voltage compared to silicon substrate.

4. Summary and Conclusions

Results obtained from the simulation work confirms the working of gas sensing. The relation between the applied load and adsorption were extracted into displacement and output voltage. Structure optimization performed by comparing the total displacement and output voltage of all the three structure i.e., T-shape were chosen as a best structure for gas sensing mechanism with its high deflection $4.52 \times 10^{-3}$ nm and output voltage 2.6 mV. From the observed results, optimized structure taken to the practical application in future work. Measured displacement and output voltage of the cantilever is shown almost linear and simulation were done for nitrogen oxides active materials in the trapping area. Hence designed gas sensor with its active materials has a wide application range. Not only nitrogen oxides but also one can implement this same technique by simply changing the trapping material, then it can be made selective to different gases based on the requirement. The uses of piezoelectric crystal simplifies the measurement but yields unreliable results which can be regulated by electronics. Also due to the simpler design, size of the overall sensor is miniaturized. Substrate and active materials were selected based on high temperature sustainability. Their sensitivity is believed to be very slightly hampered with increase in temperature.

5. References

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