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MODELING AND SIMULATION OF NANOCANTILEVER BASED TOLUENE SENSOR

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ABSTRACT

This study deals with parametric optimization of cantilever based MEMS devices for the fabrication of toluene gas sensor. Silicon (Si), Silicon Nitride (Si_3N_4), Silicon Carbide (SiC) and Tungsten Carbide (WC) were compared to adjudge the best possible cantilever material. A known polymer coating which shows selectivity towards toluene was incorporated onto each of these cantilevers. Parameters such as deflection and resonant frequency shifts change as the concentration of analyte changes on the cantilever substrate. A comparative study was done keeping in mind the need for the best possible detection mechanism. Furthermore, FEM based simulations were carried out once the best cantilever material was known.

KEYWORDS: Parametric Optimization, Cantilever, Resonant Frequency

INTRODUCTION

In the midst of technological advancements, there has been an increasing need for better sensing mechanisms. Volatile organic compounds (VOCs) are widely used in industry where there is a strong demand for gas sensors detecting VOCs at trace level or ppm concentration. In recent years, gas sensors based on micro machined cantilevers have drawn a lot of attention. The small size and IC compatibility of the micro cantilevers can provide gas sensors with such advantages as miniaturization, high sensitivity and mass-production [1] Lavrik, N.V., (2004), which are favorable to the factory automation system. However, the commercial fabrication of precise cantilever devices on a large scale is expensive as it involves dexterity (raises production time) and the use of costly instrumentation and/or chemicals (ex. FIB, E Beam lithography, photo resists).Hence it becomes all the more important to understand all the parameters in relation to cantilevers before their fabrication is commenced.

THEORY

A sensor has essentially two parts - a detecting element, in which the presence of an external stimulus produces a change of some property (optical, mechanical, electrical), and a transducing element, which transforms this change into an electrical output signal. The sensor figures of merit, such as sensitivity, selectivity, linearity and drift, result from the combined performances of both the detecting and the transducing element. [2] Gopel W. et al., (1991). Sensors can be formed by a number of approaches. Of late, cantilever based sensors have gained popularity due to their superior detection qualities. Cantilevers became popular with the invention of the atomic force microscope (AFM) in 1986. A classical cantilever is viewed as a flat rectangular beam fixed at one end and free to move at the other. The length is moderately large than the width and significantly larger than the thickness of the beam. For small amplitudes, a vibrating cantilever is equivalent to a spring-mass system, in which a spring of spring constant k applies a force,

$$F = -kx$$

on a mass M when this is displaced a distance x from its equilibrium position. For a cantilever of rectangular cross section, the equivalent spring constant k is

$$k = \frac{Ewh^3}{4L^3}$$

Consequently, the deflection (δ) caused by any added force is obtained as:

$$\delta = F\frac{4L^3}{Ewh^3}$$

MEMS Gas Sensor

To construct a gas sensor, the micro/nano cantilever must be functionalized through depositing a gas sensitive layer. Quite a number of polymers have been employed as sensitive material for the detection of VOCs vapor [3] M. Maute, et al., (1999) & [4] F.M. Battiston, et al., (2001). The sorption of gas molecules from the ambient air by the polymer layer can bring two kinds of modifications: one is the resonant frequency shift resulting from the mass change of the device; the other is the bending variation due to the surface stress difference between the cantilever and the polymer layer. Micro cantilever gas sensors based on the measurement of resonant frequency are more attractive than those based on the measurement of surface stress because of their good linearity and high accuracy [5] G. Stemme, (1991).

Role of Conducting Polymers in Gas Sensors

Many important organic analyte, such as benzene, toluene and some other volatile organic compounds (VOCs) are not reactive at room temperature and under mild conditions. Therefore, it is difficult to detect them by their chemical reactions. However, when interacting with conducting polymers, they may have weak physical interactions involving absorbing or swelling the polymer matrixes, etc. These interactions do not change the oxidation levels of conducting polymers, but can also influence the properties of the sensing materials and make these gases detectable.

Absorbing of the analyte molecules on the surface of sensing film is widely used in gas sensing. In fact, absorption is the first step in all the sensing techniques, especially in some quartz crystal microbalance sensors. The absorption of organic gases on conducting polymers has been experimentally studied. It is assumed that the absorption process is described by the Langmuir adsorption isotherm, that is:

$$A + < site > \underset{Kb}{\overset{Kf}{\Leftrightarrow}} < A >$$

where kf and kb are the forward and backward reaction rate, respectively, *A* is the analyte

Conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980s [6] Nylabder, C., et al., (1983). In comparison with most of the commercially available sensors, based usually on metal oxides and operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time; especially, these features are ensured at room temperature.Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers, and a lot of related articles were published.There are several reviews emphasize different aspects of gas sensors [7] Dubbe, A., (2003) and some others discussed sensing performance of certain conducting polymers [8] Nicolas-Debarnot, D.; et al., (2003) & [9]Maksymiuk, K., (2006).

The Sensing Mechanism

This is another integral part of a gas sensor. Two basic detection methods are used: static and dynamic. The static method is based on the fact that a cantilever structure will bend when its mechanical stress is not uniform along its thickness. Specifically, static molecular detection is based on an asymmetric coating of the cantilever surfaces, which is typically achieved by coating a single surface. If a coating on the upper surface has a compressive stress, it will tend to expand and the cantilever will bend downwards. The coating layer stress may change by physical adsorption or chemical bonding of the analyte molecules [10] Berger R., et al., (1997) or by permeation of the analyte molecules leading to coating swelling. A related technique is based on detecting intermolecular forces by approaching and retracting a functionalized cantilever tip to a functionalized surface [11] Rief M., et al. (1997). If specific molecules are present on the surface so that a ligand receptor interaction between the tip and surface exists, the cantilever will bend during the retraction. This technique is called molecular force spectroscopy.

The dynamic method is based on modifying the resonance properties of a vibrating cantilever. A number of transducing principles have been used over the years to convert mechanical displacements into electrical signals [12] Göpel W., et al., (1994). We briefly discuss here the most relevant and their applicability to cantilever-based sensors. The most widely used method to detect the (static or dynamic) deflection of cantilevers is based on an optical principle, as this is the method used in commercial AFM instruments. The cantilever deflection is monitored by measuring the position of a laser beam deflected by the cantilever [13] Meyer G. et al., (1988). This measurement method is extremely sensitive, but it requires a light reflecting surface on the cantilever and a minimum reflecting area, and thus it cannot be used for nanocantilevers (specifically, it loses efficiency for cantilevers narrower than about 5 µm). The need for a laser source and a detector separated a minimum distance from the cantilever makes it difficult to miniaturize the system, which would be a problem for the development of portable sensor systems.The capacitive principle has been extensively used to detect the movement of micromechanical structures in MEMS sensors such as accelerometers. It is based in detecting the variation of the capacitance on a two-electrode capacitor, where one electrode is fixed and the other is in the mobile structure.As discussed earlier, the cantilever system behaves like a spring for small amplitudes. Hence, it is viable to calculate the resonant frequency of the system and monitor its change with increase in mass of analyte on cantilever tip. A study of resonant frequency shifts is thus an easy detection mechanism.

METHODOLOGY

For efficient sensing of toluene, we have evaluated different materials which could act as possible substrates for the cantilever. Silicon, Silicon Nitride, Silicon Carbide, and Tungsten Carbide are compared in this study. The next course of order was to experiment with different thickness of the selective coating and study its effect.Variation in resonant frequency shift and deflection is measured against increase in concentration of analyte. The subsequent selection of substrate will depend upon easy detection, low concentration and measurable resolution from the analysis of graphs.

STUDY

The quality of such a sensor completely relies on the cantilever dimensions. The geometric shape, size as well as the material used to build the cantilever determines the cantilever's stiffness. The choice of dimensions depends extensively on the fact that Toluene needs to be detected on a ppb level or even lower.

Molecular detection requires the ability to perceive forces of about 10 pN. It can be seen however from [1] (Lavrik, N.V., 2004) that for a given thickness, longer and narrower cantilevers i.e. $L \gg w$ & $L \gg\gg$ t would compensate to detect even the tiniest of forces and produce a readable deflection. Many would argue about the feasibility of fabrication of cantilevers at such small scale but it is well supported in literature. One of the cantilevers has the “minimum” dimensions that can be achieved by the standard nanofabrication techniques (1 μm length, 100 nm width and 10 nm thickness). [11] Rief M., et al. (1997)Various nanofabrication methods are available to define nano mechanical structures with lateral dimensions of the order of 10 nm. These include electron beam lithography [14] Matsui S. (1997), scanning probe lithography [15] Snow E.S. et al., (1997) nano imprint lithography [16] Chou S.Y., et al., (1996) and focused ion beam [17] Ishitani, T., et al., (1991). These are complemented with accurate reactive ion etching processes. Precisely defined nanomechanical structures have been fabricated by using a combination of these processes [18] Cleland A.N., et al., (1996), [19] Cleland A.N., et al., (1998), and [20] Carr D.W., et al., (1999)

After tedious calculations and multiple considerations, the cantilever dimensions were set as: $L = 250\ \mu m\ w = 2\ \mu m\ t = 0.2\ \mu m$. Henceforth, the dimensions shall remain unchanged unless mentioned otherwise. Polythiophene (PTh) is known to show affinity towards toluene [21] Li, B., et al., (2006) and the sensor detection limits were upto 20ppm. The polymer coating on top of the cantilever is envisaged as 20 nm. We tweaked with the coating thickness by varying it from 20nm to 70nm (incrementing 10nm each time) and studied its effect. There was however, no significant change in the behavior of the cantilever. Nevertheless, keeping consistency and feasibility in mind, we settled for a standard 20nm coating. Henceforth, the analysis of all materials has been carried with a fixed absorbent layer coating of 20 nm. This makes the effective thickness of the cantilever as $0.22\ \mu m$. The tests and simulations carried out on the cantilevers involved exposure to gas molecules in the Nanolitre domain. It was found that, the minimum detection limit of the cantilever was found to be 3 pL(12.34 pg) of toluene gas which corresponds to measurable deflection and frequency shift. This is the lowest ever reported detection level for any theoretical analysis of toluene.

RESULTS AND DISSCUSSIONS

The change in deflection of the cantilever is recorded against a change in force applied (by the absorbent molecules). This is a comparative study of all materials and it enlightens us about one of the most important features of a sensor, i.e. Resolution. The resolution of a sensor is slightest change it can detect and be able to reproduce it. Figure 1. contrasts the deflection of the various materials. It is easily understandable that the slope of the curve in this graph measures change in deflection / change in Force. This essentially is proportional to and forms the physical basis of resolution.

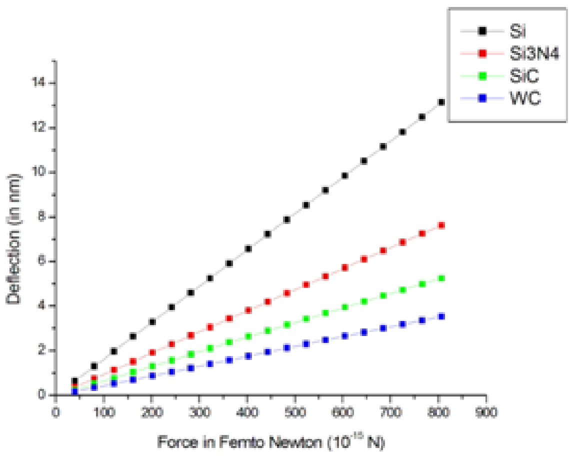

Figure 1: Deflection Vs. Change in Force

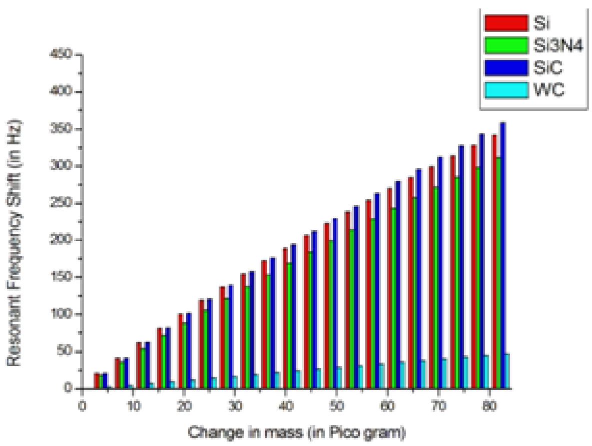

Figure 2: Resonant Frequency Shift Vs. Change in Mass

We see that the greatest slope is observed in case of Silicon. This makes Silicon most suited for the detection of Toluene. Figure 2 measures the Resonance Frequency Shift against Change in mass on the cantilever. This is the most important parameter in this paper because this forms the basis of the detection mechanism.

We now know that a Silicon cantilever is most responsive with greatest resolution amongst all contenders. So, by selecting Silicon as our cantilever material coated with the polymer (PTh), we have carried out FEM based COMSOL simulations to conclusively record the bending of the cantilever as projected by theoretical outcomes. Now, we have simulations to back our conjectural claims.

Simulations

Materials: Cantilever: Silicon **Coating:** 20nm of Polythiophene

The cantilever model was first designed and rendered in AutoCAD 2011. The model was then exported to COMSOL in a compatible format. The appropriate physics was defined and simulation was carried out.

The simulation was carried out by adding a fixed constraint to one end of the cantilever so that it does not move. A boundary load was added along the top surface of the cantilever to simulate the adsorption of gas molecules. A parametric sweep was performed in which the force due the molecules was varied from 0N to maximum value and the corresponding displacement was simulated by COMSOL.

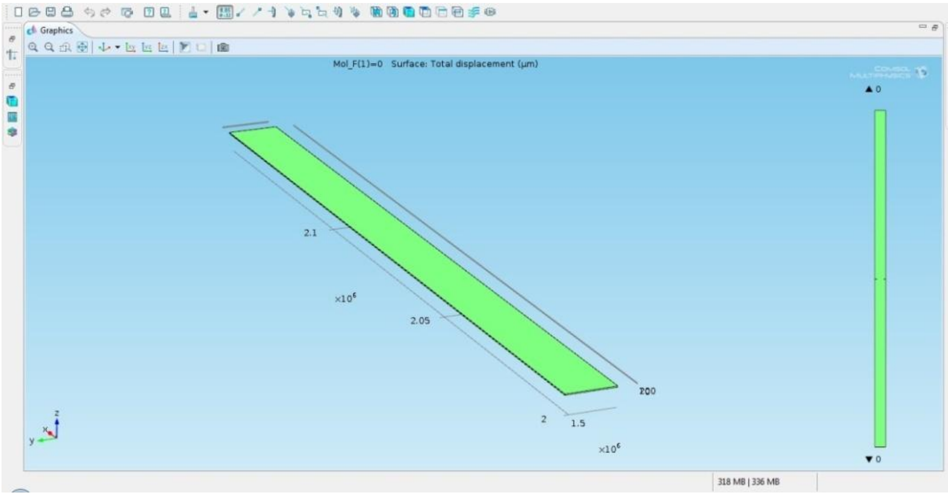

Figure 3: Polymer Coated Silicon Cantilever with No Load (Before Interaction)

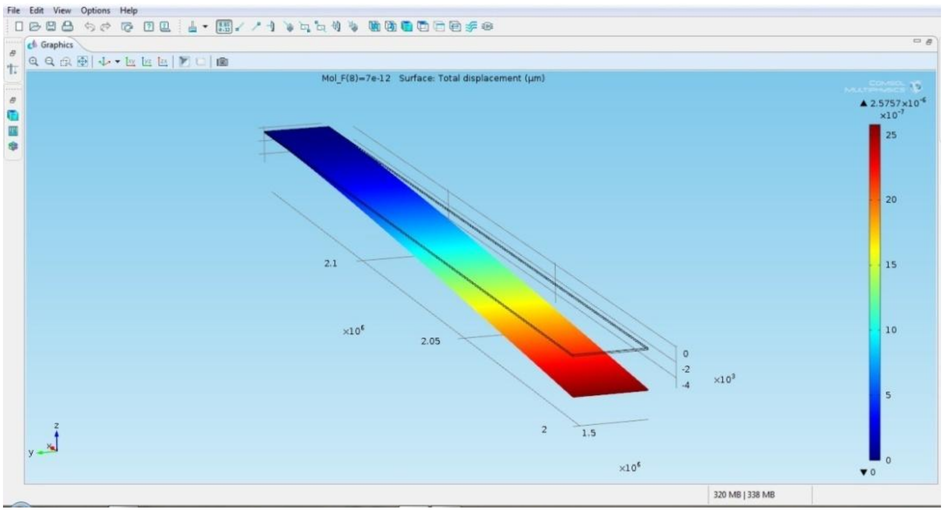

Figure 4: Polymer Coated Silicon Cantilever with Analyte Molecules (After Interaction)

CONCLUSIONS

It has been found that Silicon has emerged to be the best candidate for substrate material. Silicon shows excellent deflection and reasonable resonant frequency shifts even at low analyte concentrations.

Silicon has very good mechanical properties [22] Petersen K.E. (1982). It's yield strength (7 GPa) is about twice that of steel, with a density (2300 kg/m^3) that is about one third. In its crystalline form is completely elastic until the breaking point is reached, with no plastic deformation. Very precise micromechanical structures can be defined from the bulk material using wet etching or plasma etching (bulk micromachining, [23] Kovacs G.T.A., (1998)), or by structuring thin films combined with sacrificial layers (surface micromachining, [24] Bustillo J.M., (1998)). Micromechanical structures based on simple elements were used from the very beginning to obtain sensors for the measurement of mechanical quantities [22] Petersen K.E. (1982).

In our findings, we see that compared to the other candidates, Silicon was ideal as a cantilever material for the detection of toluene. Other than the attributes discussed above, one important feature is crucial for choosing Silicon. It's Young's Modulus of 180 GPa happens to be the most optimum in regard to detection of toluene. Consequently, even heavier gases would require a cantilever material with an even higher value of Young's Modulus.

It should be mentioned here that Silicon may not necessarily be an appropriate substrate as far as detection of other gases are concerned. The choice of Silicon here was strongly influenced by molecular weight of the gas and the sensing mechanism. Other detection mechanisms may require a more gradual change in the way a cantilever reacts. For such cases, gases with steep slopes (refer Fig I) will not hold good.

By analysis of the graphs and the simulations, we conclude that; Polythiophene (Pth) coated Silicon Nanocantilever based gas sensor would be excellent for the detection of toluene.

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