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Encapsulated Piezoresistor Cantilevers as Affinity Sensors: A Review

Kapil Sadani* and Pooja Nag*

Abstract : Current research on gas sensing is focused on developing specifically selective materials and systems for applications ranging from diagnostics, quality control to defense. a frontrunner in devisable technology is are pizeoresistive cantilevers. In this review is presented the commonly accepted design procedures, characterization and issues associated with encapsulated pizeoresistive cantilevers as affinity sensors.

Keywords : Microcantilever stack, piezoresistor, affinity sensor.

1. INTRODUCTION

Micro and nanofabrication technology today has opened up large avenues in micro-electromechanical (MEMS) based sensing systems[1] such as Quartz Crystal Microbalance (QCM) [2, 3], Surface Acoustic Wave (SAW) [4] and micro-cantilevers [5,6] for precision sensing odor, bio-molecules, volatile vapors, toxic trace elements etc. In this report is presented a review of the advancements of piezoresistive micro-cantilevers as bio/gas sensors.

The concept of cantilevers is age old as a beam anchored at only one end. Micro-cantilevers are miniaturized versions of the same (length ranging from 20 to 750 microns and width from 2 to 75 microns) and work on similar principles. Adsorption of the target molecules induces a small surface stress (0.5-5N/m) which strains the cantilever; transduction of which may be carried out in static mode or/and dynamic mode. A common static mode cantilever has within it a piezo element; deflection of the cantilever causes the change in resistance of a piezo-element which is suitably conditioned for electrical readout calibrated in terms of the analyte to be sensed. In the dynamic mode, the beam is resonated and transduction is observed by a reversible shift in the frequency. Optical transduction techniques yield higher accuracy but the system complexity and cost limits its extensive use in devices.

1.1. The Cantilever in Static Mode

Similar to surface tension in liquids, solids process surface free energy. Any system always tries to remain in a less excited state. Adsorption of molecules on a solid surface is known to reduce the surface energy of the surface. If it be possible to allow to make only one surface (preferably the upper) active, for adsorption; then during adsorption; a differential stress is generated resulting in deflection of the cantilever. Shuttleworths equation [7] clearly defines the aforesaid relationship between surface stress σ and surface free energy γ where $\partial\varepsilon$, the surface strain is change in surface area to the total area during adsorption.

$$\gamma = \gamma + \frac{d\gamma}{d\varepsilon} \tag{1}$$

Stoney's relation defines the relationship between the differential stress produced due to adsorption on one surface to the bending or displacement of the free end of the cantilever as [8]:

* Manipal Institute of Technology, Manipal University, Manipal-576104, Karnataka, India *E-mail: sadani.kapil@manipal.edu*

$$\delta h = \frac{4(1-\vartheta)L^2}{Et^2}(\Delta\sigma_1 - \Delta\sigma_2) \quad (2)$$

In practice, adsorption is a temporary phenomenon, the adsorbed molecules may be replaced by the target molecules or further adsorb more target molecules on themselves. Thus the theoretically calculated surface energy change causing defection may not always match the practically obtained deflection.

Static mode cantilevers fabricated for use as sensors are generally stack cantilevers comprising a structural layer at the bottom, an encapsulated piezoresistive layer and an immobilization layer on the top. Contact pads are brought out of the encapsulated piezoresistive layer and the transduction is conditioned in half or full bridge circuit. In such stacks there generally exists a neutral axis [9] where there is no effective stress. Design of cantilevers should take care that the piezo layer should not be a part of this axis. Mathematically, the position of the neutral axis may be determined by the following relation:

$$z_n = \frac{\sum_i E_i z_i h_i}{\sum_i z_i h_i} \quad (3)$$

where h_i is the thickness of i^{th} layer, z_i is the distance of the i^{th} layer from the neutral axis and E_i is the young's modulus of the i^{th} layer.

Alternatively, the bending of stack cantilevers may be derived by using stokes law which establishes a direct linear relationship between applied force (F) and displacement (z) with a constant of proportionality called spring constant as:

$$F = kz \quad (4)$$

For a rectangular cantilever, the spring constant (k) is related to the youngs modulus (E), cross sectional moment of inertia (I) and length (l) as:

$$K = \frac{3EI}{l^3} \quad (5)$$

For a composite cantilever, EI [9-11] is given by

$$EI = W\sum_i \left(E_i \left(\frac{h_i^3}{12} + h_i\,(z_i - z_n)^2 \right) \right) \quad (6)$$

Substitution of the parameters obtained in (6) in (5) can be used to determine the deflection easily.

1.2. The Cantilever in Dynamic mode

In dynamic mode, the cantilever is made to vibrate at its natural frequency. Adsorption of mass causes the frequency to decrease which is calibrated in terms of the concentration of the target molecule in that particular environment. The natural frequency (f) of a vibrating cantilever of mass m and spring constant k is given by

$$f = \frac{1}{2\pi}\frac{k}{m} \quad (7)$$

The mass sensitivity [12, 13] of this cantilever of young's modulus Edensity P, width w and length l is given by:

$$\left|\frac{df}{dm}\right| = \frac{f}{2m} = 0.08\,\frac{1}{l^3 w}\sqrt{\frac{E}{\rho^3}} \quad (8)$$

It is evident that smaller the cantilever, greater will be its mass sensitivity. The use of cantilevers in dynamic mode is generally limited to gaseous medium as liquid causes viscous damping which would adversely affect the sensitivity. However, in [14] authors have demonstrated photolithographic design and fabrication of thermally excited in plane micro-cantilevers which overcomes the viscous damping forces significantly.

2. DESIGN CONSIDERATIONS

2.1. Stiffness

An affinity cantilever has to undergo several wet processes for surface modification and receptor immobilization post fabrication. If the upper surface of the cantilever be a polymer generally, it is required to have one of the groups –CHO, -NH_2, SH etc [15]. It involves the use of strong hydrolyzing/oxidizing agents (acids/bases). Thus the design and simulation study should take into consideration all of these issues to make the cantilever stiff enough to withstand forces at the air-liquid interface post fabrication. However, the cantilever should also be compliant enough to bend as a response to target molecules' adsorption.This is the critical tradeoff that determines the stability of a cantilever.

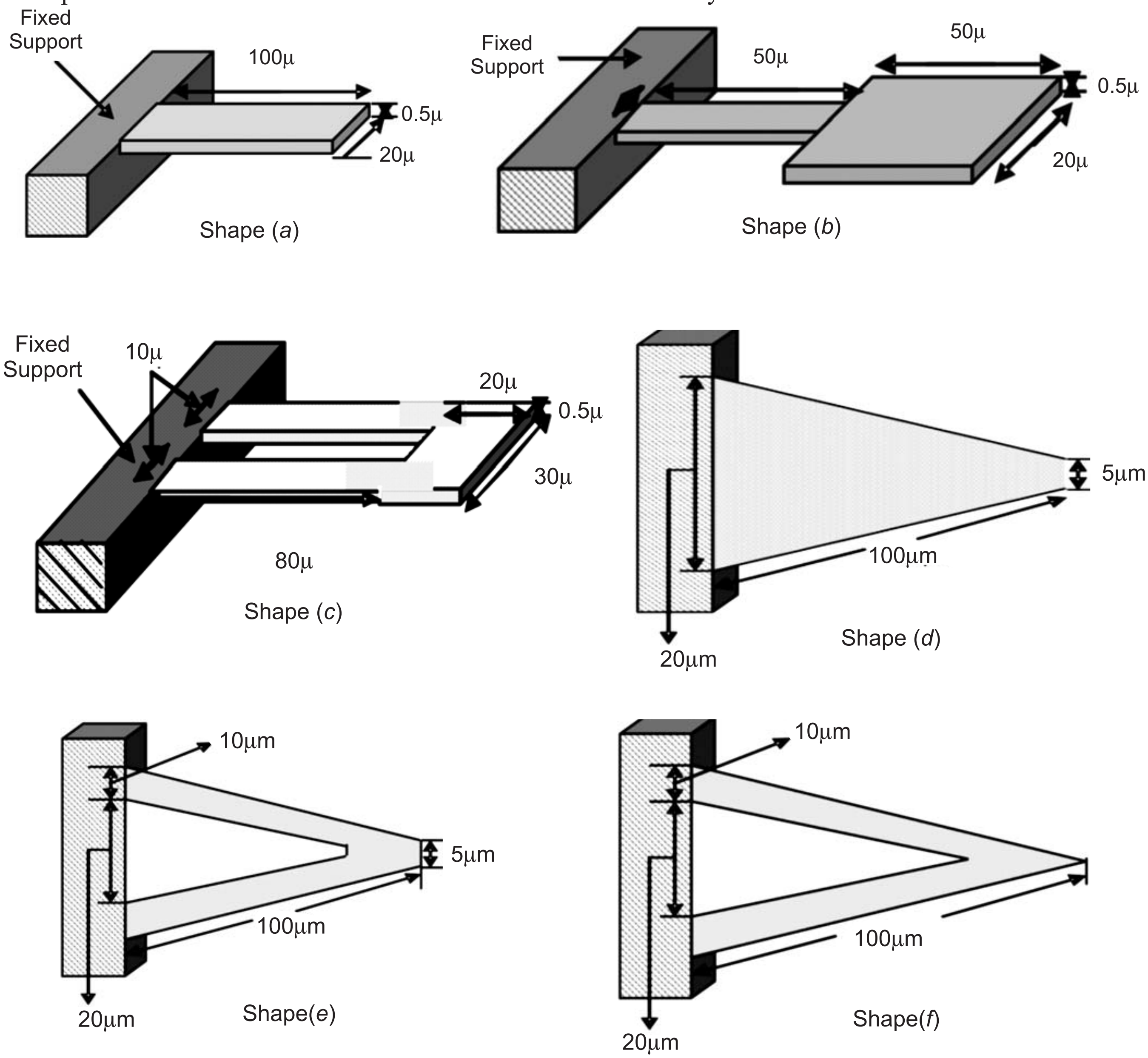

Figure 1: Cantilever geometries [17]

2.2. Resonant Frequency

Electro-static and electromagnetic interference (from nearby devices such as a pump or an inductive circuit) may affect the performance of cantilevers adversely. To make affinity microcantilevers immune to noise, theyshould be designed to have resonant frequency higher than at least 5 kHz [16]. This would also reduce the burden on signal conditioning circuitry for filtering and noise rejection.

2.3. Cantilever Shape

Shape plays a critical role in determining the sensitivity of a cantilever. In [17] a comparative analysis of the sensitivity to different shapes (figure 1) has been carried out using ANSYS and it has been proven that a hollow V- type of cantilever is most sensitive as an affinity cantilever. The dynamic behavior of the different shapes has been summarized in Table 1.

Table 1

Mass sensitivity and natural frequency for different shapes

Geometry of Microcantilever	*Natural Frequency (KHz)*	*Mass sensitivity (Hz /pg)*
Shape-*a*	67.74	43
Shape-*b*	40.19	52
Shape-*c*	59.12	86
Shape-*d*	98.94	186
Shape-*e*	117.49	344
Shape-*f*	99.89	228

However, to enable easy characterization, the dimensions of the cantilever should be so chosen that it may easily fit in the cantilever holder of a standard atomic force microscope (AFM) [18]. The resonant frequency can be easily determined by using the piezo stage, laser position sensor and feedback electronics of a conventional AFM. Also this consideration of design would facilitate its use with the liquid cell of the AFM to perform immobilization related experiments.

2.4. Simulation

Simulation of the cantilever parameters (for equations 1-13) is essential to predict the performance of the cantilever. Also, detailed mesh analysis helps optimize the individual heights of the constituent layers of the stack. It is thus a mandate to compute the stiffness of the overall cantilever stack before proceeding to fabrication.

3. CANTILEVER STACK FABRICATION PROCEDURES

A piezo encapsulated cantilever has minimum three structural components in the stack namely the structural layer at the base, the piezo layer and the encapsulating layer on top. Generally, the structural layer and the encapsulating layer are made of the same material with the former being the thickest and latter being the thinnest. Commonly used materials for structure and encapsulation are silicon dioxide (SiO_2) [19, 20], silicon nitride (SiN) [21-23] and Su8 [24, 25]. While the latter offers a cost effective low thermal budget process and very sensitive device fabrication process, SiN is a more stable and rugged device suited for harsh environments. The cantilever is designed such that the neutral axis is embedded in the structural layer itself. The fabrication procedure generally followed is described below:

3.1. Substrate Cleansing

In any nanofabrication process, the first step is cleansing of the substrate wafers [26]. Generally silicon is used when fabrication processes need to be carried out at temperatures > 170˚C. The wafer is first cleaned with piranha (1:3H_2O) which is followed by standard RCA procedure where the wafer is cleansed off organic particulate matter, grown oxides followed by cleansing off ions from the surface. Finally the wafer is rinsed and dried.

3.2. Selection of sacrificial layer

Generally an oxide layer of around 200-1000 nm is grown thermally on the silicon by wet oxidation process. In [27] is reported 200nm of sputtered SiO_2 as the sacrificial layer. The use of Cr-Au has also been reported as the sacrificial layer. The essential requirements of the sacrificial layer are that it should be perfectly smooth as observed from spectroscopic ellipsometry and should be etchable selectively by a readily available etchants.

3.3. Structural Layer

In polymer cantilevers, Su8 2002 is generally used as the structural layer [27-29]. It is spun on the substrate using a spin coater to a thickness from 500 to 1800 nm as per the design simulation studies. This is followed by photolithography and stripping off the photoresist as per the mask of cantilever design. Alternatively, in [23] is reported formation of a 650nm thick layer of SiN by hot wire chemical vapor deposition process (Weismann 1979). Here the substrate is first spun with positive photoresist (PPR) which is masked, exposed and developed as per the design. Nitride is deposited by keeping a ratio of 1:20 sccm (standard cubic centimeters per minute) of silane and ammonia for an hour. During the process, substrate was kept at a temperature of 160˚C and filament at 1900˚C while the chamber was maintained at 0.11mbar. Later the PPR is stripped off and film thickness is measured using profilometer.

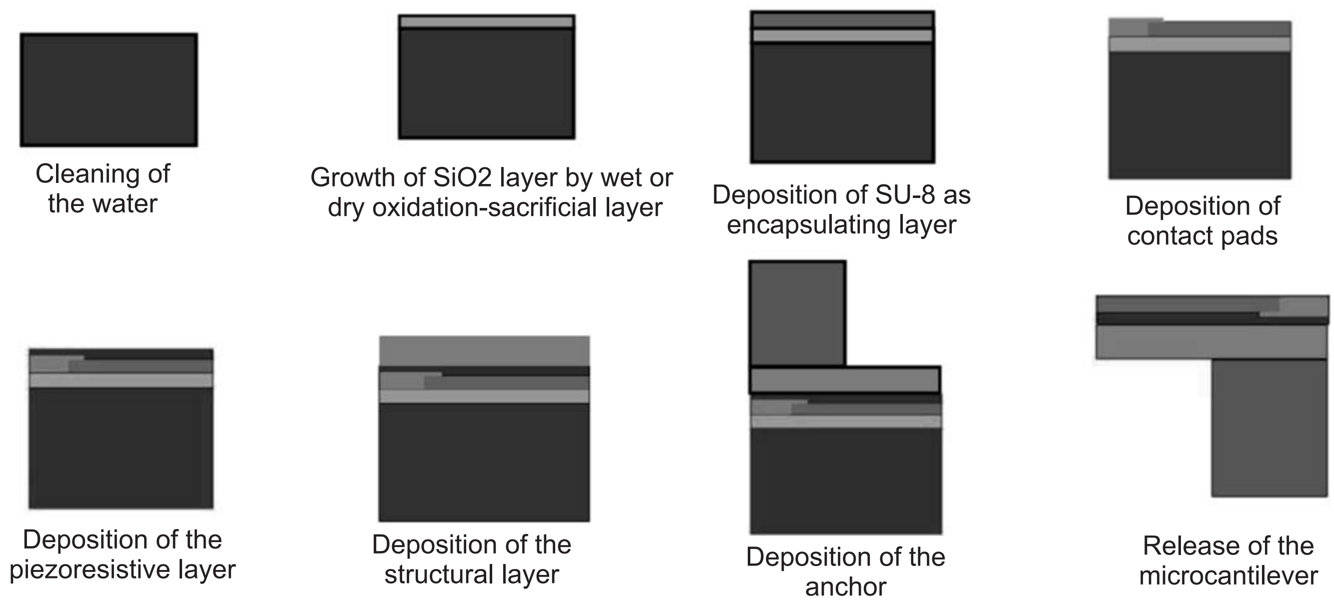

Figure 2: Steps for the fabrication of polymer microcantilever stack

3.4. Piezoresistive Layer

The piezo layer is actually the layer which responds with a change in resistance to a change in bending of the cantilever. A PPR is spun, exposed and developed followed by vacuum deposition/sputtering/ HWCVD/LPCVD of the piezo-element followed by its lift off. Metals like Au [30], Cu [31], Mn [32], Ni-Cu [33], Ni-Cr [34, 35], Ti [36], Pd-Cr [37] have long been used as strain sensors. They suffer from self-heating and large losses due to high conductivity. In [37], it has been reported that to avoid self-heating, base resistance of the piezo element should be in excess of 500 ohms. Polysilicon [23, 27], B doped Polysilicon, monocrystalline Si [40] are more widely used because of this reason, also because of their higher gauge factors. CarbonBlack-Su8 [29, 38], Graphene-Su8 [39] have also been reported of as encapsulated piezoresistors. These are directly spun over the structural layer, exposed to UV with a suitable mask and developed. The most commonly used piezo element is polysilicon because it can be grown in-situ on the structural layer in a sputtering system, LPCVD or HWCVD. Substrate being kept at 170˚C and silane, diborane and H_2 being passed in the ratio 1:7:10 in the HWCVD process[23].Of the piezo elements mentioned graphene nanoplatelet has been reported to have the highest gauge factor (144) [39]. The thickness of this layer varies from 100nm to 450nm. Special care must be taken during design to ensure that the piezo layer is not a part of the neutral axis.

3.5. Contact Pads

Chrome Gold is generally used to take out electrical contacts from the piezo layer. Generally Cr is sputtered first to improve the adhesive property of the piezo layer followed by gold. A third layer of photolithography defines the contact pads. Gold is etched out using KI and iodine in water while chrome is etched out usingceric ammonium nitrate and acetic acid in water. Pt [41, 42] and Ti-Au [23] are other commonly used metals for making the contact pads. The thickness of the contact pads ranges from 150nm-250nm.

3.6. Encapsulating/Immobilization Layer

Piezo encapsulation is essential so that the immobilized adsorbent biochemicals do not short the piezo layer. The Encapsulating layer of SiN or SiO_2 is patterned and deposited using HWCVD or Sputtering in a process similar to the structural layer. Su8 is spun on the piezo layer and patterned, exposed and developed using a designed mask in the fourth lithographic step. The thickness of this layer varies from 150 to 900 nm so as to keep the axis of the piezoresistive layer away from the neutral axis of the cantilever stack [11]. CHO, NH_2 or SH groups [15] are grafted on this layer to facilitate bio-receptor immobilization.

3.7. Die Base/Anchor formation and Cantilever Release

Bulk micromachining is the preferred technique for affinity cantilevers as these need to be used in liquid environments where stiction related issues are significant. The substrate may be back etched using HNA for Su8 cantilevers and using KOH and TMAH for SiN cantilevers. However there are some severe problems with pad undercut and cantilever release. Hence lately [11, 27, 29], a die is spun using Su8 2100 a negative tone, highly viscous photoresist up to a thickness of 80 to 100 microns using standard photolithographic process. However during design of such cantilevers the encapsulating layer is spun first then the piezo layer and then the substrate followed by the die. Finally the sacrificial layer is stripped off to release the cantilever. Pores may be defined throughout all masks to facilitate quick etching.

The cantilever release is the most crucial step in any cantilever fabrication process and the process parameters for the same need to be monitored and controlled very precisely.

4. SURFACE FUNCTIONALIZATION

For bio and gas sensing applications the encapsulating layer should be functionalized with the receptor of the target molecule. For polymers, generally co-valent bio-molecule immobilization requires surface modification by grafting amine (NH_2) group, or-CHO or –SH or -OH group which bonds to the biological molecule. Immobilization on silicon dioxide or silicon nitride surface by organosilane [41, 42] methods is well studied. Also a thin layer of gold is sputtered on to the top surface and the surface is functionalized using thiol derivatization [43, 44, 45]. In [28] is demonstrated a dry method of polymer surface modification whereby amine groups were grafted on the encapsulating surface by pyrolytic dissociation of ammonia in a HWCVD setup. Followed by surface modification, the VOC receptor or the antibody specific to the target analyte is functionalized. Care needs to be taken so that the immobilization takes on the upper surface only (while the lower surface remains inert) so as to be able to create the differential stress required for the bending of the cantilever.

5. CANTILEVER CHARACTERIZATION

All fabricated cantilevers need to undergo mechanical and electromechanical characterization for determining its stiffness, gauge factor and resonant frequency. After each fabrication step a profilometry has to be done to ensure smoothness of the surface for the next fabrication step in the stack.

5.1. Mechanical Characterization

One of the most important device parameters that has to be characterized is the spring constant of the device. Generally for a polymeric cantilever, this is measured by beam bending technique using AFM.

The AFM has a standard microcantilever the motion of which can be monitored to atomic precision by a photodetector and regulated to the same resolution using a precision piezoelectric stage. The AFM cantilever gradually approaches the cantilever to be tested exerts a small force on it and retracts back. During this phenomenon, the two cantilevers (*i.e*, the one under test and the standard AFM cantilever) can be thought of as two springs in series with spring contants K_{afm} and K_{sample} respectvely. The net spring constant is given by:

$$K_{total} = \frac{K_{afm} K_{sample}}{K_{afm} + K_{sample}} \tag{9}$$

If the alignment be made such that the torsional component of the force is zero, from [*z*] we have

$$K_{total} . z = K_{afm} . d \tag{10}$$

where *z* and *d* are displacements of the AFM and sample cantilevers respectively. From the slope of the approach curve obtained after, the AFM cantilever establishes contact with the sample cantilever, K_{total} can be calculated. Thereafter K_{sample} may be calculated as

$$K_{sample} = \frac{K_{total} . K_{afm}}{(1 - K_{total})} \tag{11}$$

Alternatively, the spring constant may be computed using a berkovich nanoindentor. The nanoindentor has a sharp conical tip which is placed at the apex of the cantilever and the force versus deflection curve is obtained. It is practically impossible to place the tip of the nanointendor exactly at the apex of the cantilever. If the length of the cantilever be L and the tip be placed at a distance l from the apex and the slope of the force versus deflection curve be noted, then spring constant (*k*) of the cantilever is given by equation (10):

$$k = \text{slope}\left(\frac{L - l}{L}\right)^3 \tag{12}$$

In practice the stiffness of a nitride stack varies from 0.6 to 1 N/m [23] whereas that of polymer cantilevers is less than 0.6N/m [27] primarily because it is difficult to perform precision nanoscale spinning of layers in contrast to a HWCVD or LPCVD. A correlative study between the simulated model and actual device stiffness needs to be established and deviations need to be justified.

5.2. Electromechanical Characterization

5.2.1. Determination of Resonant Frequency

The measurement of resonant frequency is of utmost importance even when it is to be used as an affinity cantilever in static mode. The resonant frequency of the microcatilever determines the thermos-mechanical or power line noise that it may pick up. Higher the resonant frequency (>5kHz), greater is the immunity of the device and relatively simple signal conditioning may be used. Laser Doppler Vibratometer (LDV) is the commonly used tool for measurement of the resonant frequency of a microcantilever. The cantilever die is placed below the laser source perfectly parallel to the piezo-buzzer. The buzzer oscillates the cantilever and the frequency versus amplitude curve is obtained. The first peak indicates the resonant frequency of the cantilever. Alternatively, the frequency measurements may also be carried out using a standard AFM setup [18]. The cantilever under test is fitted to the cantilever holder of the AFM and hence gets coupled with the piezo stage of the AFM setup. The vibrations of the cantilever are sensed optically using phototransistors. The amplitude of AC component of the voltage as seen at the phototransistor is proportional to the amplitude of the cantilever vibrations. To enable efficient optical measurements, it is essential to make the outer surface of the cantilever as reflective by sputtering a thin layer of gold. This layer should be thin enough so as not to affect the mechanical properties of the cantilever.

5.2.2. Determination of Q-Point

Another parameter of relevance in dynamic mode is the Q point of the cantilever [14, 46]. The Q point is the ratio of the resonant frequency to the frequency at -3dB. Low values of Q point indicates a narrow amplitude frequency spectrum implying that a small energy is sufficient to resonate the cantilever whereas a high value of Q indicates a wide frequency spectrum which implying lesser amplitude vibrations for the same resonant input energy. This factor is critical in determining damping of the cantilever in viscous environments.

5.2.3. Determination of Deflection Sensitivity

Determination of gauge factor of an affinity cantilever stack is an essential parameter in predicting its sensitivity. For a piezo cantilever stack of length L_c, piezo layer length L_p, width *w*, invidual layer thickness h_i, distance of the piezo layer from the neutral axis Z_{nr}, the value of strain may be calculated for step deflection using equation (13) and (6)

$$\frac{\Delta R}{R} = -Kz\frac{\left[1-\frac{1}{2}.\frac{L_p}{L_c}\right]L_c.\,Z_{NR}.\,K}{EI} \tag{13}$$

Where K is the gauge factor.

Actual measurements are carried out using a micromanipulator needle measurements and control of which can be achieved up to atomic precision. Simultaneous measurement of change in current and voltage as a function of deflection is taken. Thus a plot of a change in resistance to the deflection may be obtained. The slope of this curve gives the deflection sensitivity which is to be compared with the simulation results obtained using the earlier method and a co-relative analysis has to be evaluated.

5.3. Modified surface characterization

The functionalized surface needs to be characterized by fourier transform infrared spectroscopy FTIR to verify the functional groups and nature of bonds formed on the surface. Contact mode atomic force microscopy (AFM) may be used to investigate the profile of the functionalized layer and check for its consistency throughout the profile. Fluorescence microscopy may also be used to evaluate the nature of grafting of the receptor molecules to ensure uniform sensing throughout the entire surface.

6. ENCAPSULATED PIZEORESISTIVE CANTILEVERS AS BIO/VOC SENSORS

Over the past decade, studies have been conducted on developing ultra-sensitive gas sensors (tuned to the order of ppb) using micro cantilevers. In [29, 38] is reported a CB-Su8 encapsulated pizeoresistive polymeric cantilever coated with Fe(III) Porphyrin for selective detection of CO. A very similar cantilever with polyaniline nanofibers for detection of soil moisture has been reported in [47]. The cantilevers developed are highly selective with response and recovery times in the order of a few tens of seconds. Similar cantilevers have been reported for detection of TNT [39]. These cantilevers have encapsulated Graphene-Su8 as the piezoresistor which processes a gauge factor of 144, several orders higher than the CB-Su8 piezoresistors. The reported device has excellent selectivity with a detection capacity of a few ppb. The response and recovery times of these cantilevers are in the order of a few minutes. Several other papers such as [40] have reported trace detection of explosives by sensing organophosphorous vapors on functionalized SiO_2 cantilevers with crystalline silicon as the encapsulated pizoresistor. These cantilevers were found to be sensitive to 20ppb of DMMP vapours with reputable response and recovery of around ten minutes. The scope and application of microcantilevers in trace detection of volatile organic compounds and noxious gases is vast but commercial device fabrication remains limited owing to long term stability of such sensors. Affinity cantilevers also find tremendous applications in testing food quality such as in [48] is reported a monocrystalline silicon encapsulated sensor for both vapour and liquid phase detection of trimethylamine. Recent developments [49] have also made it possible for detection of 'vibrio cholera' from food samples which is known caused severe life threatening diarrhea. Affinity micro cantilevers offer relatively simple transduction principles and are ultra-sensitive. Research now is directed in developing handheld sensing devices with affinity cantilevers functioning as core components.

7. CONCLUSION

The cantilevers reviewed in this paper work on the principle that when a target analyte is adsorbed on the functionalized cantilever surface, stresses in the order of 0.5N/m to 5 N/m are produced. For efficient and effective transduction these stresses need to be translated to strain of the pizeoresistive layer so as to be trasnducted as a recordable change in resistance. Su8 is being investigated intensely as the structural layer because of its inertness to wet processes, cost effective and ease of fabrication (it can be easily spun on a substrate) and low Young's modulus (around 5GPa). The low young's modulus implies that Su8 cantilevers would bend easily for a relatively smaller surface stress than conventional silicon oxide or silicon nitride cantilevers. However as Su8 is to be spun, the overall stack length increases considerably. Early studies with encapsulated pizeoresistor have been reported using gold or titanium but then studies have found silicon to have much higher gauge factor. Polysilicon is the most commonly reported piezo element as it can be easily deposited to a uniform thickness using a standard sputtering/ HWCVD system; the design being cost effective. A highly deflecting cantilever stack may not always be ultra-sensitive; it is the design parameters which define the deflection sensitivity. For affinity cantilevers, it is always desirable to have the piezoresistive layer and the encapsulation layer on the other side of the neutral axis to achieve high sensitivity. It has been observed that deflection saturates for increasing surface stresses for a given surface area in oxide-poly cantilevers where the piezo layer is placed just slightly away from the neutral axis. This is however avoided in stack encapsulated cantilever structures. Apart from a strong background of surface functionalization and adsorption, a thorough understanding and tuning of the design parameters is essential in commercial device development using cantilevers.

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