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Chemical vapor detection using nanomechanical platform

S. H. Lim*

*School of Mechanical and Automotive Engineering,
Kookmin University, Seoul, Korea*

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Abstract

For high sensitive and multiplexed chemical analysis, an opto-mechanical detection platform has been built. To check the performance of the platform, we performed water vapor response measurements for the cantilevers coated with alkane thiols having different functional end groups. Furthermore, for the exposure of 50 ppb toluene vapor to carboxylic benzene thiol coating layer, nanoscale static deflection of the cantilever sensors has been measured simultaneously. The nanomechanical platform using cantilever sensors can be miniaturized to be used for high sensitive and selective environmental monitoring for indoor or outdoor air pollutants, mold, heavy metals, and other health hazard materials.

Keywords: Multiplexed chemical analysis; Molecular interaction; Nanomechanical platform; Sensitivity; Selectivity; Environmental monitoring

1. Introduction

Chemically functionalized nanomechanical transducers such as microcantilever beams can detect surface stresses created by target-receptor binding at very low concentration with sufficiently high signal-to-noise ratio. Such a high sensitivity opens many applications such as detection of explosives and chemical warfare agents, as well as environmental contaminants, which can have very low vapor pressures [1].

Low concentration of chemical vapor detection using a commercial AFM tip has been demonstrated [2]. Also, a 1-D microcantilever sensor array coated with different types of polymers as chemical sensing layers was used to try to identify unique deflection signatures for each target chemical [3]. To solve the low selectivity problem as well as degradation of the polymer coating materials, we need to find a high selective and robust receptor. For target specific receptors, sequence-specific recognition motifs have been identified through directed evolution methods [4]. To screen high selective receptors in an efficient way, we need to have a denser sensor array. A dense sensor array like 2-D microcantilever sensors can be individually coated with different test receptors using inkjet printing techniques.

For multiplexed chemical analysis in low concentration of chemical vapor environment, we have developed a nanomechanical sensor array platform. It consists of (1) 2-D microcantilever sensor array chip fabricated using surface and bulk micromachining, (2) low concentration vapor generation system, (3) temperature controlled sensing chamber, (4) optical measurement setup using laser and CCD, etc. Each microcantilever sensor can be coated with different candidate receptors manually or automatically and the vapor phase reaction with target molecules can be measured in a multiplexed way. A vapor phase chemical detection experiment has been performed for various thiolated coating materials including alkane and benzene thiols. Chemically

*Corresponding author. Tel.: +82 2 910 4672
E-mail address: shlim@kookmin.ac.kr

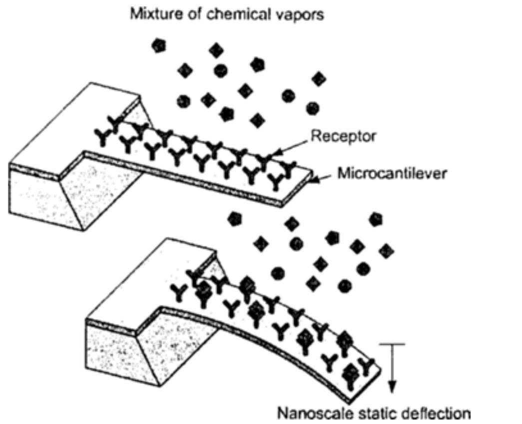


Fig. 1. Nanoscale static deflection of microcantilever induced by molecular interaction between receptor and target chemical vapor.

induced nanoscale motion of cantilevers having different coating materials has been measured in sub 10 nm noise level.

2. Nanomechanics and sensor array

The total surface free energy change ΔG_{total} during the molecular interaction between the target and receptor molecules can be written as the sum of the mechanical free energy change ΔG_{mech} and chemical free energy change ΔG_{chem}:

$$\Delta G = \Delta G_{mech} + \Delta G_{chem} \quad (1)$$

The mechanical free energy change ΔG_{mech} can be expressed as

$$\Delta G_{mech} = C / R^2 , \quad (2)$$

where C depends on the thickness of the cantilever and the modulus of its material and R denotes the radius of curvature of the shape adopted by the cantilever. It can be thought as strain energy change which is proportional to the square of the curvature. Therefore, it will increase as the curvature increases. Also, the chemical free energy change ΔG_{chem} can be calculated from the molecular interaction forces like electrostatic repulsion, hydrogen bonding, and van der Waals forces. For a detailed form of chemical free energy terms, refer to [5]. As shown in Fig. 2, the equilibrium curvature of the structure ($1/R_{eq}$) is determined at the point where the total free energy change is minimized.

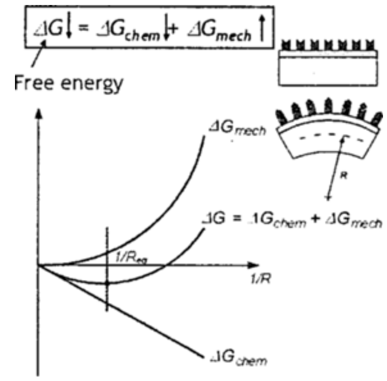


Fig. 2. Principle of nanoscale deflection. Total surface free energy determines the curvature of the microcantilever sensor.

On the other hand, for a known surface stress change $\Delta\sigma$, the cantilever deflection Δh can be written as

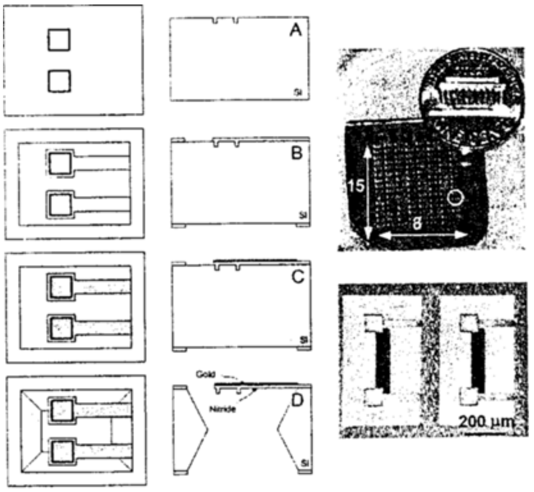
$$\Delta h = \frac{3(1-\nu)}{E}\left(\frac{L}{t}\right)^2 \Delta\sigma , \quad (3)$$

where ν is Poisson's ratio, E is Young's modulus, L is length, and t is thickness of structural layer. For a silicon nitride cantilever 200 μm long, 0.5 μm thick, with E = 85 GPa, ν= 0.27, a surface stress change of 1 mJ/m^2 will result in a deflection of 4 nm at the cantilever end, which can be easily detected with an optical readout system similar to that of an atomic force microscope.

As shown in Fig. 3, the 2-D cantilever sensor array chip (size 1 in × 1 in), which has about 720 microcantilevers, is fabricated by using surface and bulk micromachining techniques. A 200 μm long microcantilever is made of 0.5 μm thick silicon nitride structural layer coated with 30 nm thick gold coating layer. Also, the paddle at the end of the microcantilever has a ridge-like structure that makes the paddle flat and gives a clear spot image. Four masking steps are required as well as wet and dry etching steps, a low pressure chemical deposition (LPCVD) step and metal evaporation. For detailed microcantilever design and fabrication process, refer to [6].

3. Optical detection system design

An expanded He–Ne laser beam is used to illuminate the entire sensor array and the reflection from the rigid square paddle at the end of each



(a) (b)

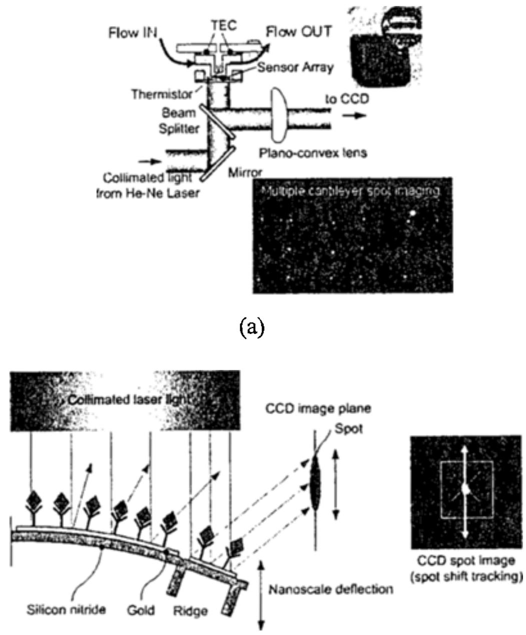
Fig. 3. 2-D microcantilever sensor array chip. (a) Four mask step fabrication process. (b) Fabricated 2-D microcantilever sensor array chip (size 1 in × 1 in) and its SEM image.

cantilever is imaged as a spot on the CCD screen as shown in Fig. 4. The mechanical deflection generated by chemical interaction is detected by measuring the shift in the position of the spots on the CCD screen. For cantilever deflection measurement, a Matlab program calculates the displacement of the reflected spots in real time. Using our current setup, 18 cantilever sensors can be imaged on CCD simultaneously as shown in Fig. 4 (a). The maximum number of cantilever reflection spots that can be imaged is limited by the physical dimensions of a CCD.

4. Chemical vapor transport

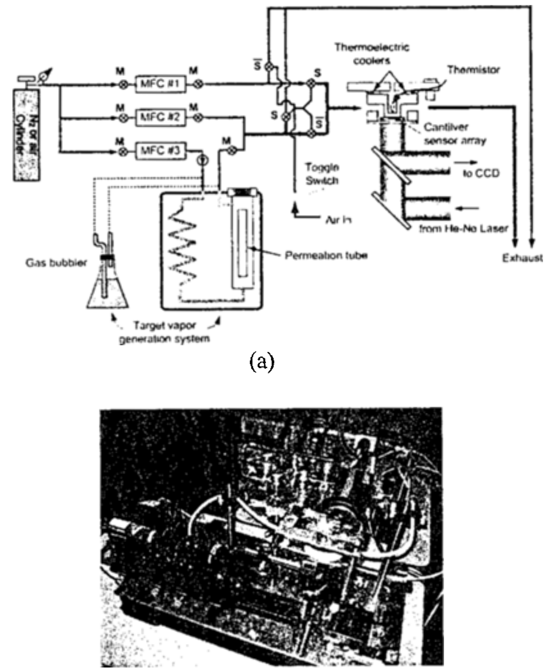
As shown in Fig. 5, the chemical vapor transport system consists of mass flow controllers, on/off manual valves (M), solenoid valves (S, $\bar{S}$), target vapor generation system using a permeation tube, etc. Three mass flow controllers (0–200 sccm, accuracy ±1%, Tylan Inc., calibrated by Coastal Instruments) are used to control the flow rate for purging and vapor dilution lines. The permeation tube (Kin-Tek Inc.) is inserted in a quartz tube, and it is heated at a specific temperature to generate a fixed concentration of a chemical inside.

In the toggle switch OFF state, the purging line through MFC #1 is connected to the chemical chamber. In the toggle switch ON state, the purging line is closed and the dilution line through MFC #2



(b)

Fig. 4. (a) Overall optical detection setup. (b) Individual spot formation and tracking.



(b)

Fig. 5. (a) Schematic diagram of experiment setup (M: manual ON/OFF valve, $S/\bar{S}$: normally ON/OFF solenoid valve). (b) Real experiment setup.

and MFC #3 is connected to the chemical chamber. During the flow line switch, the flow rate to the chemical chamber is kept as constant to remove the unwanted sensor response from the flow rate change.

5. Experiment

To check the system performance, water and toluene vapors were flown into temperature controlled chemical chamber using a chemical vapor transport system. For water vapor flow, a gas bubbler was used instead of permeation tube gas generation setup. Using micropipette, cantilever sensors were manually coated with alkane thiols [SH-$(CH_2)_{11}$-R] and benzene thiols [SH-(C_6H_5)-R] having different functional end group (R) for water and toluene vapors. Each cantilever was coated by injecting 0.5 μL and 5 mM alkane or benzene thiols on the gold surface. To remove physically adsorbed thiols, each cantilever was washed by ethanol solution. Then, the whole chip was dried using critical point dryer to remove potential stiction problem. During experiment, the flow rate was kept to 100 sccm and the temperature of the cantilever sensors was kept constant using a commercial temperature controller.

The overall experiment was performed in two steps. The temperature response of each cantilever, Θ^i_{temp} (i=1~6), was measured for ΔT = 1K (Fig. 6 shows the temperature responses of 18 cantilevers for temperature change ΔT = - 2 K). Then, the chemical vapor response of each cantilever, Θ^i_{chem} (i =1~6), was measured. The measured response is the pixel shift in CCD image plane of each cantilever. The cantilever deflection Δh^i can be calculated as

$$\Delta h^i = S^i_T \cdot \Theta^i_{chem} / \Theta^i_{temp} \quad (i = 1 \sim 6), \tag{4}$$

where S^i_T is the known thermo-mechanical sensitivity of each cantilever [nm/K].

Fig. 7 shows the measured cantilever deflection for various humidity levels. Each line corresponds to the differential deflection (subtracted from the average deflection of six cantilevers coated with methyl alkane thiols) of the average measurement result of six cantilevers coated with the same alkane thiols. The measured data shows response differentiation for the different functional end groups of alkane thiols. Fig. 8 shows the deflection response of six cantilevers coated with carboxylic benzene thiols for the 50 ppb concentration of toluene vapor. Those cantilever deflection responses came from weak interaction between coated thiol molecules and target molecules. The weak interaction includes Van der Waals, electrostatic, and hydrogen bond interaction. The measured noise level was sub 10 nm, and the noise sources are chip temperature instability, flow rate fluctuation, stage vibration, etc.

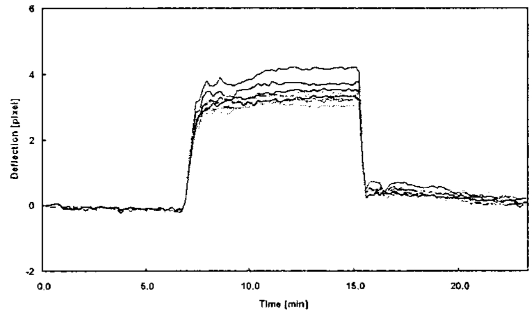


Fig. 6. Temperature responses of cantilevers for temperature change ΔT = 1 K.

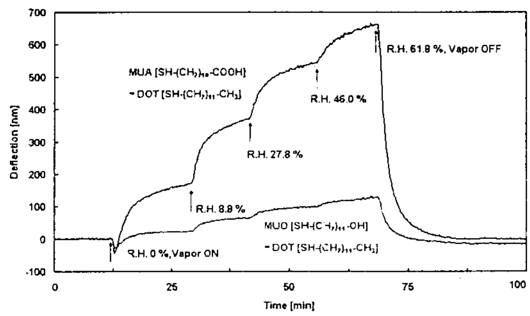


Fig. 7. Differential water vapor responses of cantilevers coated with alkane thiols for various humidity level.

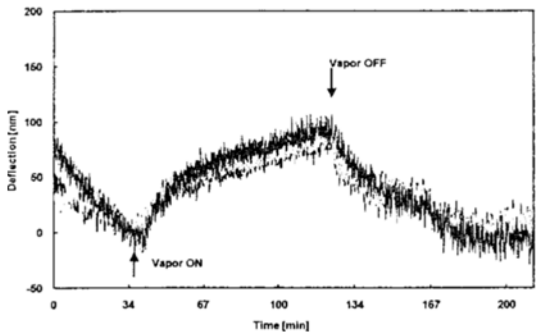


Fig. 8. 50 ppb concentration of toluene vapor responses of six cantilevers coated with carboxylic benzene thiols (SH-C_6H_5-COOH).

6. Conclusion

For high sensitive and multiplexed chemical analysis, an opto-mechanical detection platform has been built. The constructed platform includes a 2-D cantilever sensor array, laser, CCD, and low concentration chemical vapor generation and transport system. Each microcantilever sensor can be coated with different candidate receptors manually or automatically and the vapor phase reaction with target molecules can be measured in a multiplexed way. As a preliminary test, a vapor phase chemical detection experiment was performed for various thiolated coating materials including alkane thiols and benzene thiols. Chemically induced nanoscale motion of cantilevers having different coating materials was measured in sub 10 nm noise level.

Using the developed nanomechanical sensor array platform, we are planning to do multiplexed screening of target specific receptors, which are under development by our research group.

Also, a nanomechanical platform using cantilever sensors can be miniaturized to be used for high sensitive and selective environmental monitoring for indoor or outdoor air pollutants, mould, heavy metals, and other health hazard materials.

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