Basic characteristics of polycarbonate-based dual cantilever sensors for detecting VOC

Naoki SHIRAISHI*, Mutsumi KIMURA** and Yasuhisa ANDO***

Abstract

We have developed and evaluated polycarbonate (PC)-based dual cantilever sensors as part of a low-cost sensor network system for monitoring VOCs (volatile organic compounds). The PC-based dual cantilever sensor consists of a PC cantilever and a PBD (polybutadiene)-coated PC cantilever with PVDF (polyvinylidene fluoride) piezoelectric films. We began by investigating the size and mode dependences of resonant frequencies and quality factors of PC cantilevers and PBD-coated PC cantilever as output signal of PVDF piezoelectric film. Next, we examined the change of resonance frequency in the presence of VOCs vapor by setting up a resonance sensor evaluation system equipped with a dilution flow system, temperature-controlled chamber, oscillation circuit, and frequency counter. The resonant frequency of both PC cantilever and PBD-coated PC cantilever shifted significantly downward depending VOCs.

Key words: Cantilever, Polycarbonate, Polybutadiene, Polyvinylidene fluoride, Frequency shift, Sensor network system

1. Introduction

Much attention has been devoted to the development of chemical sensors to detect VOC (volatile organic compound) species for the environmental monitoring of chemicals for risk prevention. The MOS (metal oxide semiconductor) sensor, the most widely used sensor for VOC detection to date, consumes power at levels too high to permit practical use for real-time local monitoring. As an alternative, resonant mass sensors of vibrating cantilevers based on MEMS (microelectromechanical systems) are believed to have good potential for this purpose (Maute, et al., 1999, Spitzer, et al., 2012).

Most resonant cantilever sensors so far reported have been made of silicon-based materials, namely, silicon, silicon nitride, or silicon oxide. They are available in a great variety of shapes, dimensions, and sensitivities, and for a great variety of target gases (Blom, et al., 1992, Datar, et al., 2009, Lu, et al., 2007, Lu, et al., 2008, Ziegler,. 2004). Yet silicon-based cantilever sensors have strong environmental impact during fabrication. This might limit their industrial use for real-time local monitoring.

Polymer-based cantilevers offer advantages such as low cost and environmentally friendly fabrication process (Amaya, et al., 2011, Calleja, et al., 2003, Johansson, et al., 2005, Mouaziz, et al., 2006, Suter, et al., 2011). Furthermore, the polymer-based cantilevers have the potential of reactive layer-less VOC sensor, because the polymer cantilever of polymeric material adsorbs VOC in itself, whereas silicon-based cantilever sensors absolutely need reactive layer of PBD (polybutadiene) or TiO2 (Titanium dioxide). Moreover, the cantilever sensor composed by different polymer has the feasibility of selecting VOC species, because the characteristics of VOC absorption depend on each polymeric material.
Though polymer-based cantilevers offer several advantages, polymers have not been applied as base materials for resonant mass sensors. Polymer materials generally have dynamic viscoelasticity, a property that compromises the resonant frequency and quality factor of polymer-based sensors (Lochon, et al., 2005). Specifically, a sensor requires a high resonant frequency and a high quality factor to reach a high sensitivity and a low detection limit. This requirement has precluded the development of polymer-based resonant sensors for mass detection.

Our investigations into the dynamic properties of polymer cantilevers support the feasibility of polymer-based cantilever sensors for VOC monitoring (Shiraishi, et al., 2013). We have looked at both the size- and mode-dependencies of the resonant frequencies and quality factors of the polycarbonate (PC) cantilevers under atmospheric pressure. A higher mode tended to coincide with a higher resonance frequency and higher quality factor. From this result, we deduced that PC-based cantilever sensors can be feasibly used for VOC monitoring in fabrication facilities.

In this paper, PC-based dual cantilever sensors were first fabricated by using bonding, laser fabrication and polymer coating techniques. We then measured the resonance frequencies and quality factors of PC-based dual cantilever sensors composed of PC cantilevers and PBD-coated PC cantilevers with piezoelectric films of PVDF (polyvinylidene fluoride). Finally, we examined the frequency shift of the PC-based dual cantilever sensor induced by the adsorption of VOC molecules using VOC dilution flow system.

2. Principle of VOC sensing using PC-based dual cantilever sensor

Figure 1 shows the principle of VOC sensing with the PC-based dual cantilever sensor. The sensor consists of the PC cantilever and the PBD-coated PC cantilever with PVDF piezoelectric films. The sensor is set onto the PZT vibrator over a sensing circuit composed of an oscillating circuit and frequency counter. When the driving signal from the oscillating circuit is applied to the PZT vibrator, the PC cantilever and PBD-coated PC cantilever vibrate at its resonant frequencies. The vibration powers of the both cantilevers in resonance are transmitted to the each PVDF piezoelectric films. Resonant mass sensors detect target VOC gases by measuring variations in the resonant frequency of the sensing structure due to mass loading. When the cantilever adsorbs the VOC gas molecules, the mass increases and the resonant frequency decreases. Hence, the VOC gas can be detected by measuring the resonant frequency shift. The resonant frequency shift $\Delta f_r$ is determined by the mass detection $\Delta m$. It can be expressed as (Lu, et al., 2008),

$$
\Delta f_r = -\Delta m \frac{f_r}{2m}
$$

where $f_r$ and $m$ are the resonant frequency and mass of the cantilever, respectively. The resonant frequency shift is detected by a frequency counter.

Fig. 1 Schematic showing how the PC-based dual cantilever sensor detects VOC gases

3. Fabrication of PC-based dual cantilever sensor

The process for fabricating the PC-based dual cantilever sensor is illustrated in Fig. 2 (a) to 2 (b). The first step is to form the PVDF piezoelectric film (1-1003702-7, TOKYO SENSOR CO., Ltd.). The PVDF piezoelectric film consisted of an upper electrode (Ni/Cu), PVDF, and lower electrode (Cu/Ni). The thicknesses of the Ni electrode and
Cu electrode were 10 nm and 70 nm, respectively. The upper and lower electrodes were etched with a ferric chloride solution using a polyimide mask. In the second step, the PVDF piezoelectric films were bonded to a PC plate (PC-1000, SEKISUI SEIKEI Co., Ltd.) with glue (EPOCLEAR, KONISHI Co., Ltd.) (Fig. 2 (a)). In the third step, the PC cantilevers were fabricated with an excimer laser. The overlapped area between the upper and lower electrodes of the PVDF piezoelectric film was arranged on the fixed end of the PC cantilever. The overlapped length between the PC cantilever and PVDF piezoelectric film with upper and lower electrodes measured 100 μm. Finally, a thin film of PBD (181382, Sigma-Aldrich Co., LLC.) was diluted with tetralin at 6 weight % and coated on the upper surface of one PC cantilever (Fig. 2 (b)).

Two kinds of PC-based dual cantilever sensors were fabricated using this micro-fabrication process. Each of the PC-based dual cantilever sensors had a PC cantilever and a PBD-coated PC cantilever. Table 1 summarizes the dimensions of the PC cantilevers and the PBD-coated PC cantilevers in the PC-based dual cantilever sensors used for measurement. The photograph in Fig. 3 (a) shows the PC-based dual cantilever sensor of sensor 1 in Table 1 at the completion of fabrication. The PC-based dual cantilever sensor was fixed onto a PZT vibrator with glue (EPOCLEAR, KONISHI Co., Ltd.) and placed in a package for evaluation. Cu thin film and Au wire were adopted for the electric connection. The enlarged micrographs in Fig. 3 (b) and (c) show the fabricated PC cantilever in sensor 2 and PBD-coated PC cantilever in sensor 2.

![Fabrication of the PC-based dual cantilever sensor](image)

(a) The PVDF piezoelectric films were formed and bonded to the PC plate

(b) The PC cantilevers were fabricated and a PBD film was coated on one PC cantilever

Fig. 2 Fabrication of the PC-based dual cantilever sensor

| Table 1 Dimensions of the PC cantilevers and the PBD-coated PC cantilevers in the PC-based dual cantilever sensors [unit: μm] |
|---|---|---|---|---|---|
| | Cantilever length | Cantilever width | Cantilever thickness | PVDF thickness | PBD thickness |
| Sensor 1 | PC cantilever | 2498 | 498 | 200 | 28 |
| | PBD-coated PC cantilever | 2496 | 497 | 200 | 28 |
| Sensor 2 | PC cantilever | 1496 | 296 | 100 | 9 |
| | PBD-coated PC cantilever | 1498 | 297 | 100 | 9 |

4. Evaluation of dynamic characteristics of cantilever sensor using PVDF piezoelectric films

First, we carried out modal analysis using the finite element method (FEM) to identify the relationship between the vibration mode and resonant frequency of the PC cantilever in sensor 1 and sensor 2. FEA by COVENTOR® was used to simulate the vibration mode and resonant frequency. Figure 4 shows FEM simulated deformation of the 1st to 4th flexural vibration modes of the PC cantilever in sensor 1. Mesh type is hexahedron elements and number of nodes in
PC cantilever in sensor 1 and sensor 2 are 45551 and 41261, respectively. The Young’s modulus of PC was 2.25 GPa and the density of the PC was $1.2 \times 10^3 \text{kg/m}^3$ from data sheet of PC-1000. The resonant frequency of the 1 to 4th flexural vibration modes from the PC cantilever in sensor 1 were (a) 7 kHz, (b) 43 kHz, (c) 116 kHz and (d) 214 kHz, respectively. The resonant frequency of the 1 to 4th flexural vibration modes from the PC cantilever in sensor 2 were (a) 10 kHz, (b) 61 kHz, (c) 165 kHz and (d) 311 kHz, respectively.

We then investigated the dynamic characteristics of the PC-based dual cantilever sensors under atmospheric pressure at room temperature to obtain fundamental data for sensing VOCs. A schematic view of the evaluation system is shown in Fig. 5. The frequency response was measured and analyzed with a network analyzer (4395A, Agilent Technologies, Inc.). The excitation frequency was continuously switched between 100 Hz to 500 kHz at measurement intervals of 10 Hz. A driving signal of 224 mV from the network analyzer was applied to the PZT vibrator. The output voltage of the PVDF piezoelectric film was amplified by 10 dB and recorded with the excitation frequency to measure each resonance peak and its bandwidth at high resolution. The sweeping measurement was repeated 16 times and the frequency response curves were obtained by averaging the 16 measurement data for each resonance peak of the PC cantilevers and PBD-coated PC cantilever listed in Table 1.

We measured the size and mode dependences of resonance frequencies and quality factors of PC cantilevers as output signal of PVDF piezoelectric film. Fig. 6 shows the measured frequency responses of the PC cantilevers. The vibration modes of the PC cantilevers were refined by FEM and experimental results. The evaluation system identified clear peaks of the 1st to 4th flexural vibration modes from the PC cantilever in the sensor 1, with output voltages of 0.04 mV, 0.89 mV, 1.78 mV, and 0.50 mV. The PC cantilever in the sensor 2, on the other hand, clear peaks of the 3rd and 4th flexural vibration modes were detected, with output voltages of 0.79 mV and 2.00 mV. The resonant peaks of the 1st and 2nd flexural vibration mode of the PC cantilever in the sensor 2 were not measured in our evaluation system. The PC cantilever length of sensor 2 is shorter than that of Sensor1, but the overlapped length of PC cantilever and PVDF is the same 100um. In addition, the spring constant of the PC cantilever in the sensor 2 is lower than that of sensor 1. Therefore, the output voltage of the non-resonance of the sensor 2 is higher than that of sens01. Furthermore, a lower mode tends to exhibit a lower output voltage. Accordingly, we assumed that the output voltage of 1st and 2nd flexural vibration mode in Sensor2 was lower than that of the non-resonance.

The measured resonant frequencies of the PC cantilevers are shown in Fig. 7. As Fig. 7 shows, the resonant frequencies depend on the vibration mode. The resonant frequency tends to increase in step with increases in the vibration mode (Shiraishi, et al., 2013). The quality factor were calculated at each resonance peak and shown in Fig. 8. The quality factor was calculated from the bandwidth at peak minus 3 dB in the power spectrum. The levels of energy dissipation in the cantilevers were evaluated by their quality factors $Q$ at resonant frequency, i.e., the ratio of the cantilever resonant frequency $f_{\text{resonance}}$ to the bandwidth of the peak at -3 dB power $\Delta f_{\text{-3db}}$ (Lu, et al., 2006):

$$Q = \frac{f_{\text{resonance}}}{\Delta f_{\text{-3db}}}$$  \hspace{1cm} (2)

As Fig. 8 shows, the quality factors depend on the vibration mode. The quality factor of the PC cantilever in the sensor 2 tends to increase in step with increases in the vibration mode. On the other hands, the quality factor of the 4th flexural vibration mode of the PC cantilever in the sensor 1 is smaller than that of 3rd flexural vibration mode. The quality factors of a polymer cantilevers are affected by the volume loss mechanism and support loss mechanism. Especially, the quality factors in higher order resonance mode depend on the support loss (Shiraishi, et al., 2013). The quality factors for support loss in micro-machined clamped-free beam cantilevers with length $L$ and thickness $T$ are expressed (Shiraishi, et al., 2013) as,

$$Q_{\text{support}} = \alpha_n \left( \frac{L}{T} \right)^3$$  \hspace{1cm} (3)

where $\alpha_n$ is the coefficient of nth-order vibration mode of the predicted support quality factors of a clamped-free cantilever. The coefficients of the predicted support quality factors of a clamped-free cantilever are $\alpha_1 = 2.08$, $\alpha_2 = 0.173$, $\alpha_3 = 0.064$ and $\alpha_4 = 0.033$. The theoretical quality factors ($Q_{\text{support}}$) were calculated from Eq. (3) using the dimensions shown in Table 1. The thickness ($L$) was defined as the sum of the cantilever thickness and the PVDF.
thickness. As the vibration mode increases from 3rd to 4th flexural vibration mode, $Q_{\text{support}}$ decreases from 84 to 44. The quality factor of the 4th flexural vibration mode of the PC cantilever in the sensor 1 seems to be affected by the support loss.

A cantilever with a higher resonance frequency has the advantage of a higher sensitivity. Meanwhile, the frequency shift detection is governed by the bandwidth of the vibration resonance. The value of frequency shift divided by resonant frequency is approximately proportional to the quality factor of the resonance (Ikehara, et al., 2007). Therefore, we applied the sensor 2 to evaluate the sensitivity with which the sensor detected VOC.

We then investigated the influence of PBD coating on the dynamic property of the PC cantilever under a higher order resonance mode at atmospheric pressure and room temperature. Fig. 9 shows the frequency response of the PC cantilever and the PBD-coated PC cantilever in the sensor 2. The PBD coating may have a problem with extinction and decline in the quality factor, however the evaluation system identified clear peaks of the 3rd to 4th flexural vibration modes from the both cantilever. The resonant frequency and the quality factor of the 4th flexural vibration mode in the PC cantilever were 294 kHz and 67. On the other hands, the resonant frequency and the quality factor of the 4th flexural vibration mode in the PBD-coated PC cantilever were 293 kHz and 87.

Fig. 4 Deformation of 1st to 4th flexural vibration modes of the PC cantilever in sensor 1 simulated by FEM

Fig. 5 Schematic view of the system for evaluating the dynamic properties of the PC-based dual cantilever sensors

Fig. 6 Frequency responses of the PC cantilevers
5. VOC detection by the PC-based dual cantilever sensor

5.1 Measurement

We used a VOC dilution flow system (Shiraishi, et al., 2014) to investigate the basic characteristics of a PC-based dual cantilever sensor. Fig. 10 is a schematic view of our system for evaluating the VOC sensitivity of the PC-based dual cantilever sensor. The apparatus consists of a VOC dilution flow system, temperature-controlled chamber, oscillation circuit, and frequency counter (53131A, Agilent Technologies, Inc.). The VOC dilution flow system is composed of a nitrogen source, mass flow controller (MFC), thermostat with VOC gases and 4 way valves (4 way V). The VOC dilution flow system mainly has two lines. One supplies pure nitrogen gas at specified flow rate. The other supplies VOCs at specified concentration and flow rate. These two lines can be diverted into a temperature-controlled
chamber or exhaust by 4 way valves, respectively. The line supplying VOCs at a specified concentration contains an interlaced thermostat with VOC gases that are diluted with nitrogen. The VOC dilution flow system creates and supplies the VOC gases into the chamber at a specified concentration and flow rate by adjusting the temperature of the thermostat and flow rate of the mass flow controller. The temperatures of the thermostat and flow rates of the mass flow controller are calculated by Antoine equation and saturated vapor pressure curve of VOCs. The PC-based dual cantilever sensor mounted on the PZT vibrator was installed in the temperature-controlled chamber. The temperature-controlled chamber composed of incubator and micro chamber. The chamber temperature is controlled by a Peltier element built into the incubator. The temperature error in the micro chamber for 1800 sec is within ±0.05°C.

The capacity of the micro chamber is 15.6 mm × 15.6 mm × 3.38 mm. The PC cantilever and PBD-coated PC cantilever were oscillated at the resonant frequency of the 4th flexural vibration mode by an oscillating circuit consisting of a 10 dB amplifier (AMP), phase shifter (PS), bandpass filter (BPF), and gain controller (GC). The frequency counter recorded the resonant frequency at 2 sec intervals. We selected toluene, octane and ethanol for the target VOC, as these VOCs are often used in industrial facilities. Moreover, the toluene and octane in gasoline and thinner are both well-known causes of health problems. The measurement was conducted at a temperature of 20°C to investigate the basic characteristics of PC-based dual cantilever sensor for detecting VOC. The capacity of the temperature-controlled chamber is less than 0.8 cc and flow quantity is 100 sccm. A delay of adsorption start by substitution can be disregarded in the ensuing resonant frequency shift, as the gas in the temperature-controlled chamber is substituted in less than 0.5 seconds. A temperature change due to the VOC gas in the micro chamber was not detected. Each line of VOC dilution flow system is isolated from the outside air to eliminate the influence of humidity.

Table 2 shows the measurement conditions for investigating the basic characteristic of the PC-based dual cantilever sensor of the sensor 2 in Table 1. We first investigated the resonant frequency shift of the PC cantilever. The PC cantilever oscillated at the 4th flexural vibration mode at 294 kHz. The frequency shift of the PC cantilever was recorded while injecting the chamber with pure nitrogen gas, followed by nitrogen diluted with toluene, octane and ethanol gases at a concentration of 5000 ppm (flow quantity of 100 sccm), followed by pure nitrogen. We then investigated the resonant frequency shift occurring under the three conditions of the PBD-coated PC cantilever. Consequently the PBD-coated PC cantilever oscillated at the 4th flexural vibration mode at 293 kHz.

5.2 Results

Figure 11 shows the resonant frequency shift of the PC cantilever. The PC cantilever was continuously exposed to each VOC for 180 seconds (gray zone in Fig. 11). The resonant frequency shifted significantly downward during the toluene, octane and ethanol exposure, reaching 47 Hz, 48 Hz and 12 Hz below baseline at the 3-minute point. Subsequently, in the absence of toluene, octane and ethanol, the resonant frequency shifted back up and returned to the baseline condition at the 3-minute point without heat treatment. The detection sensitivity for toluene, octane and ethanol were 0.009 Hz/ppm, 0.009 Hz/ppm and 0.002 Hz/ppm, respectively. The standard deviation of the resonant frequency response was 1.8 Hz. The detection limit for toluene, octane and ethanol were 192 ppm, 186 ppm and 777 ppm, respectively.

Figure 12 shows the resonant frequency shift of the PBD-coated PC cantilever at the exposure densities of 1000 ppm and 5000 ppm. The PBD-coated PC cantilever was continuously exposed to each VOC for 180 seconds (gray zone in Fig. 11). At a concentration of 1000 ppm, the resonant frequency shifted downward during the toluene, octane and ethanol exposure reaching 47 Hz, 40 Hz and 10 Hz below baseline at the 3-minute point. Subsequently, in the absence of toluene, octane and ethanol, the resonant frequency shifted back up and returned to the baseline condition at the 3-minute point without heat treatment. The detection sensitivity for toluene, octane and ethanol were 0.047 Hz/ppm, 0.040 Hz/ppm and 0.010 Hz/ppm, respectively. The standard deviation of the resonant frequency response was 2.6 Hz. The detection limit for toluene, octane and ethanol were 55 ppm, 64 ppm and 252 ppm, respectively. In concentration of 5000 ppm, the resonant frequency shifted downward during the toluene exposure reaching 267 Hz below baseline and in the absence of toluene the resonant frequency shifted back up 49 Hz below baseline. Then, the PBD-coated PC cantilever was exposed to octane vapor; the resonant frequency reached 257 Hz and shifted back up 49 Hz below baseline in the absence of octane. And then, the PBD-coated PC cantilever was exposed to ethanol vapor; the resonant frequency reached 65 Hz. In the absence of ethanol, the resonant frequency returned to the baseline condition at the 3-minute point.
Figure 13 shows the resonant frequency shift of the PBD-coated PC cantilever at the exposure density of the VOC was 5000 ppm. The resonant frequency shift for exposing toluene, octane and ethanol in Fig. 11 is reported. The resonant frequency shift for exposing octane was added to compare the resonant frequency shift for the octane exposure after the toluene adsorption and single octane exposure. The amount of the resonant frequency shift for octane exposure after toluene adsorption was 208 Hz. On the other hand, the amount of the resonant frequency shift for the single octane exposure was 213 Hz. The difference in the amounts of the frequency shifts between octane exposure after toluene adsorption and single octane exposure was 2 %.

5.3 Discussion

The PC-based dual cantilever sensors used polymeric materials instead of silicon as the material for the resonant cantilever. The PC cantilever without PBD adsorbed the VOC and its resonant frequency shifted significantly downward during the toluene, octane and ethanol exposure. Therefore, it is not necessary to apply a reactive layer. Silicon-based cantilever sensors for VOC detecting, on the other hand, need a reactive layer for adsorbing VOCs. Therefore, this is a profitable low cost VOC sensor for environmental monitoring.

The quality factors of the PC cantilevers are considerably lower than the quality factors obtained for silicon cantilevers (typically 1000) (Ikehara, et al., 2007). The PC cantilevers have a detection limit for VOC gases of about one-tenth that of a silicon cantilever, when all other conditions are the same. This is explained by the dependency of the frequency shift detection on the bandwidth of the vibration resonance. We believe, however, that the PC-based dual cantilever sensors have sufficient potential for use in industry. The silicon cantilever, for example, has a detection limit for VOCs on the order of ppb (Mihara, et al., 2011), several orders of magnitude lower than mandatory detection limit on the order of ppm under the Industrial Safety and Health Law of Japan.

The detection sensitivity of the toluene was increased from 0.009 Hz/ppm to 0.047 Hz/ppm by a PBD coating. The standard deviation of the resonant frequency response was also increased from 1.8 Hz to 2.6 Hz by the PBD coating, however, the expected detection limits of the PC cantilever and PBD-coated PC cantilever corresponding to the resonant frequency shift and the standard deviation based on toluene exposure were 192 ppm and 55 ppm. A thin film of PBD is effective for detecting the VOC at low concentration.

The measurement was conducted at a temperature of 20°C to investigate the basic characteristics of the PC-based dual cantilever sensor. We assume that the sensitivity of the PC-based dual cantilever sensor varies with temperature, because the material properties of the polymer generally depend on the temperature. However, the temperature of fabrication facilities is much lower than the glass transition temperature of the polymer materials. While further studies will surely be needed, we expect the function of temperature correction to be accepted for integration in PC-based dual cantilever sensors.

In the absence of toluene, the resonant frequency of the PC cantilever and the PBD-coated PC cantilever shifted back up and returned to the baseline condition without heat treatment. This is a profitable characteristic for low consumption sensor network systems for monitoring VOC. The PBD-coated PC cantilever exposed to a 5000ppm concentration of VOC does not return to baseline completely in 3min. Meanwhile, the difference in the amount of frequency shifts between octane exposures after toluene adsorption and single octane exposure was 2 %. From this result, we deduced that a PBD-coated PC cantilever can still be feasibly used under the condition that the adsorbed VOC is not released completely.

The PC-based dual cantilever sensor detects toluene, octane and ethanol gases. The amount of frequency shift depends on the VOC makeup. We assume that the difference in sensitivity was due to the molar weight of the VOCs. The molar weight of ethanol is lower than that of toluene and octane. Consequently, the sensitivity to ethanol was lower than that for toluene and octane. The sensitivity also depends on the cantilevers. The main application for this sensor is in environmental monitoring of fabrication facilities. In general, the VOC species used in the fabrication facilities are limited, therefore, a function for identifying the VOC is not necessary in many cases. However, if the identification of the VOC species is required, we assume that a dual cantilever sensor composed of different sensitivities would have the feasibility of identifying the VOC species.

Our PC-based dual cantilever sensor has successfully demonstrated its ability to function as a system for monitoring VOCs. We believe that PC-based dual cantilever sensors of this type have sufficient potential for industrial applications. Polymer-based cantilevers offer advantages such as low cost and an environmentally friendly fabrication...
process. In order to improve the sensitivity further, we believe that miniaturization of the PC cantilever will be effective. Our investigations into the dynamic properties of the polymer cantilevers support the feasibility of miniaturization of the PC cantilever (Shiraishi, et al., 2013). Furthermore, titanium oxide, a material with a large distribution factor can be applied as an adsorption layer (Kimura, et al., 2012). Although further studies are needed, the PC-based cantilever sensors will ultimately satisfy the regulatory requirements for VOC monitoring in semiconductor fabrication facilities.

![Fig. 10 Schematic view of our system for evaluating VOC sensitivity](image)

**Table 2 Measurement condition to investigate the basic characteristic of the PC-based dual cantilever sensor of Sensor 2**

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>VOC species</th>
<th>Concentration</th>
<th>Flow quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>toluene→octane→ethanol</td>
<td>5000 ppm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>PBD-coated PC</td>
<td>toluene→octane→ethanol</td>
<td>1000 ppm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>PBD-coated PC</td>
<td>toluene→octane→ethanol</td>
<td>5000 ppm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>PBD-coated PC</td>
<td>Octane</td>
<td>5000 ppm</td>
<td>100 sccm</td>
</tr>
</tbody>
</table>

![Fig. 11 Resonant frequency shift of the PC cantilever. The VOC concentration and flow quantity were 5000 ppm and 100 sccm, respectively (gray zone).](image)
Fig. 12 Resonant frequency shift of the PBD-coated PC cantilever. The VOC concentrations were 1000 ppm and 5000 ppm, respectively. The flow quantity was 100 sccm (gray zone).

Fig. 13 Resonant frequency shift of the PBD-coated PC cantilever. The frequency shift of octane exposure after toluene adsorption and single octane exposure are plotted. The VOC concentration and flow quantity were 5000 ppm and 100 sccm, respectively (gray zone).

6. Conclusion

We fabricated PC-based dual cantilever sensors consisting of a PC cantilever and a PBD-coated PC-cantilever with PVDF piezoelectric films by using bonding, laser fabrication and polymer coating techniques. The PC cantilever had a maximum resonant frequency and quality factor of 294 kHz and 67. Measurements of the frequencies and quality factors of the PBD-coated PC cantilever revealed a resonant frequency of 293 kHz and quality factor of 87. We examined the change in resonance frequency in the presence of VOC vapor by setting up the PC-based dual cantilever sensor evaluation system equipped with a dilution flow system, temperature-controlled chamber, oscillation circuit, and frequency counter. The resonant frequency of both the PC cantilever and PBD-coated PC cantilever shifted significantly downward during the toluene, octane and ethanol exposure. The detection sensitivity of the PC cantilever for toluene, octane and ethanol were 0.009 Hz/ppm, 0.009 Hz/ppm and 0.002 Hz/ppm, respectively. The detection sensitivity of the PBD-coated PC cantilever for toluene, octane and ethanol were 0.047 Hz/ppm, 0.040 Hz/ppm and 0.010 Hz/ppm, respectively.

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References


