Resonant frequency temperature dependence of polymer-based cantilever sensor for monitoring VOC

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We investigated the temperature dependence of the resonant frequency of a polycarbonate (PC)-based cantilever and the phenomena governing the resonant frequency shift of the PC-based cantilever, in order to obtain fundamental data for polymer-based VOC (volatile organic compound) sensors. First the Polymer-based cantilever sensor, which consists of a PC cantilever and a PVDF (polyvinylidene fluoride) piezoelectric film, was fabricated. Then the resonant frequency shift of the polymer-based cantilever sensor induced by change in temperature was measured. The measured resonant frequency of the PC cantilever tends to decrease linearly in step with increases in temperature. Finally, we examined the temperature dependence of the Young's modulus using a bulk PC plate made from the same materials as those of the PC-cantilever. The temp erature dependence on the measured resonance frequency of the PC cantilever correlated well with the theoretical resonance frequency calculated using the Young's modulus of the bulk PC plate.

1. Introduction

Much attention has been devoted to the development of chemical sensors for detecting VOC (volatile organic compound) species in environmental monitoring of chemicals to prevent risk. Resonant mass sensors of vibrating cantilevers based on MEMS (microelectromechanical systems) are believed to show good potential for this purpose in terms of low power consumption and miniaturization [1, 2].

Most resonant cantilever sensors so far reported have been made of silicon-based materials, namely, silicon, silicon nitride, or silicon oxide [1-7]. Yet silicon-based cantilever sensors are invariably expensive to fabricate and have strong environmental impact during fabrication. This might limit their industrial use for real-time local monitoring.

Polymer-based cantilevers offer such advantages as low cost and an environmentally friendly fabrication process in micro-factories [8-14]. We fabricated polymer cantilevers using our own low-cost, reliable micro-fabrication technique [15] by combining the processes of hot embossing, bonding, and polishing. 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 and show temperature dependability in material properties.

Our investigations into the dynamic properties of polymer cantilevers support the feasibility of polymer-based cantilever sensors for VOC monitoring [15]. We 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. The PC cantilever had a maximum quality factor of more than 100. From this result, we deduced that PC-based cantilever sensors feasibly could be used for VOC monitoring in fabrication facilities.

In this paper, polymer-based cantilever sensor with micro thermometer was first fabricated. We then measured the resonant frequency shift of the PC cantilever in the polymer-based cantilever sensor induced by temperature change. Finally, we examined the phenomena governing the resonant frequency shift of the PC cantilever and the possibility of applying them as VOC sensors for environmental monitoring in semiconductor facilities.

2. Structure of PC-based cantilever sensor

2.1. Principle of VOC sensing using PC-based cantilever sensor

Figure 1 shows the principle of VOC sensing using a polymer-based cantilever sensor. The sensor consists of PC (polycarbonate) cantilevers and piezoelectric films of PVDF (polyvinylidene fluoride). 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 cantilevers vibrate at their resonant frequencies. The vibration powers of both the cantilevers in resonance are transmitted to the each PVDF piezoelectric film. 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 Δf_r is determined by the mass detection Δm. It can be expressed as [3],

$$\Delta f_r = -\Delta m \frac{f_r}{2m} \qquad (1)$$

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.

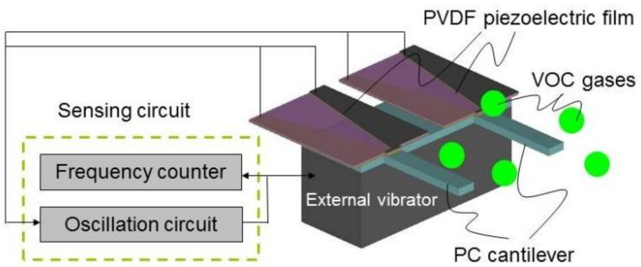
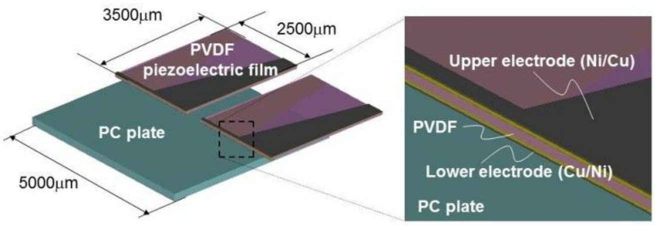


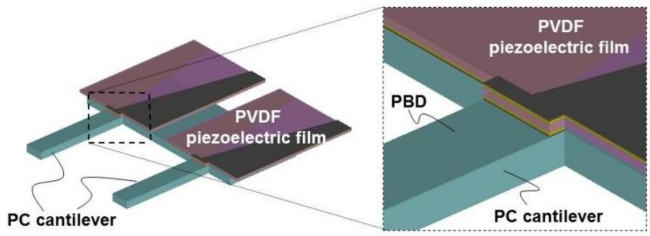
Fig. 1 Schematic showing how the PC-based cantilever sensor detects VOC gases

2.2. Fabrication of polymer-based cantilever sensor

The process for fabricating the polymer-based cantilever sensor is illustrated in Fig. 2 (a) to 2 (b). The first step is to form the PVDF piezoelectric film. The PVDF piezoelectric film consisted of an upper electrode (Ni/Cu), PVDF, and lower electrode (Cu/Ni). Once fabricated, the film had external dimensions of 3500 µm × 2500 µm. The thicknesses of the Ni electrode, Cu electrode, and interposed PVDF were 10 nm, 70 nm, and 9 µm, respectively. The upper and lower electrodes were etched with a ferric chloride solution using a polyimide mask. In the second step, the PVDF piezoelectric film was 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. Both the PC cantilevers were fabricated to the same dimensions using this micro-fabrication process. An overlapping area between the upper and lower electrodes of the PVDF piezoelectric film was arranged on the fixed end of the PC cantilever. The overlapping length between the PC cantilever and PVDF piezoelectric film with upper and lower electrodes measured 50 µm. The photograph in Fig. 3 shows the polymer-based cantilever sensor at the completion of fabrication. The cantilevers measured 1500 µm (length) x 300 µm (width). The overlapping area between the PC cantilever and PVDF piezoelectric film with upper and lower electrodes measured 50 µm × 300 µm. The polymer-based 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. A thermal sensor (PT100, DM-314) was arranged on the package to monitor temperature.



(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 polymer-based cantilever sensor

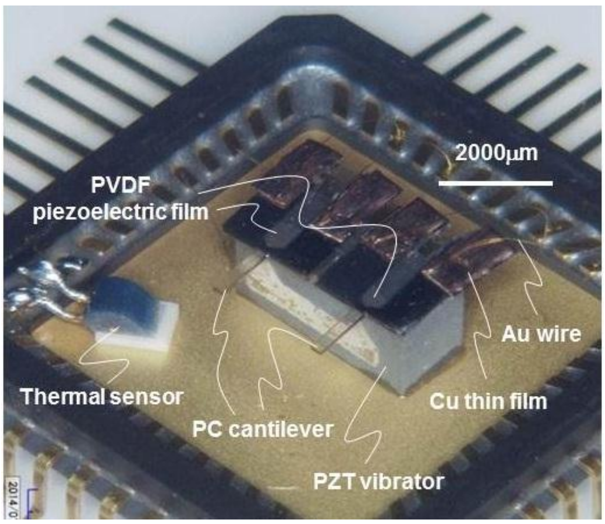


Fig. 3 External view of the polymer-based cantilever sensor fixed on a PZT vibrator

2.3 Dynamic property of the polymer-based cantilever sensor

We investigated the dynamic properties of the polymer-based cantilever sensor under atmospheric pressure at room temperature. The PC cantilever on the left side in Fig. 3 was used to obtain fundamental data for evaluating dependence on temperature. A schematic view of the evaluation system is shown in Fig. 4. The frequency response was measured and analyzed using 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.

Figure 5 shows the frequency response of the PC cantilever. The vibration modes of the PC cantilever were identified from the results by using the finite element method (FEM) analysis. The evaluation system identified clear peaks for the 1st to 4th flexural vibration modes from the PC cantilever, with output voltages of 0.02 mV, 0.22 mV, 0.77 mV, and 1.25 mV. The resonant frequency of the 1 to 4th flexural vibration modes from the PC cantilever were 8 kHz, 765 kHz 147 kHz and 297 kHz, respectively. A higher resonance frequency has the advantage of a higher sensitivity for detecting VOC [16]. Therefore, we applied the 4th flexural vibration mode to evaluate the temperature dependability.

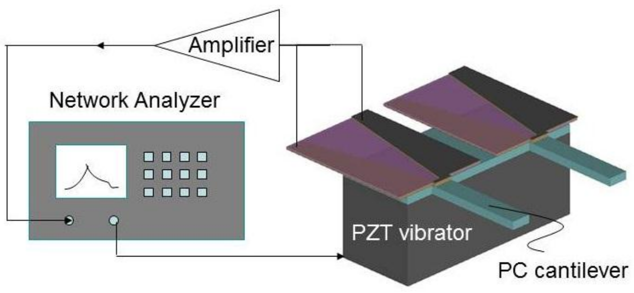


Fig. 4 Schematic view of the system for evaluating the dynamic properties of the polymer-based cantilever sensor

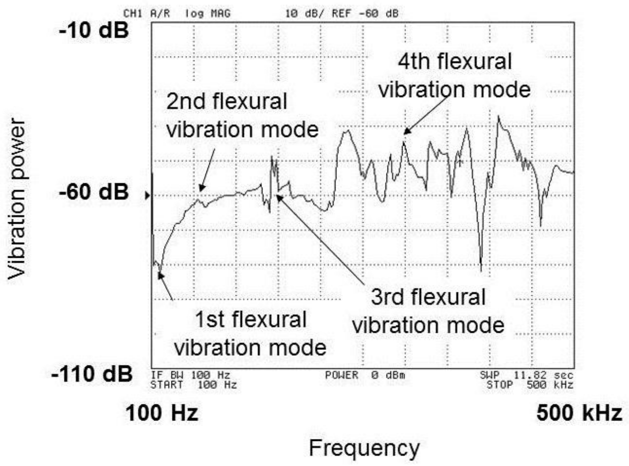


Fig. 5 Frequency responses of the PC cantilever

3. Resonant frequency temperature dependence of the PC cantilever

Figure 6 is a schematic view of our system for evaluating the temperature dependence of the PC cantilever. The apparatus consists of a temperature-controlled chamber, oscillation circuit, frequency counter (53131A, Agilent Technologies, Inc.) and data logger. The polymer-based 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 capacity of the micro camber is 15.6 mm × 15.6 mm × 3.38 mm. The PC cantilever was 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 data logger recorded the resonant frequency from frequency counter and temperature from thermal sensor at 2 sec intervals.

Figure 7 shows the resonant frequency temperature dependence of the PC cantilever. The measurement was conducted within a temperature range of 19–26 °C to investigate the potential for use in industrial applications. The temperature of the chamber was continuously increased from 19 °C to 26 °C at programming rate of 0.42 °C/min. Subsequently, the temperature was continuously decreased from 26 °C to 19 °C at programming rate of 0.42 °C/min. The measurement was repeated 2 times. The resonant frequency shifted significantly downward during increasing temperature at a rate of about -300 Hz/°C. The downward shift of the resonant frequency was 2100 Hz. Subsequently, during decreasing temperature the resonant frequency increased at the rate of 300 Hz//°C. The amount of the upward shift of the resonant frequency was 2100 Hz. In spite of the measurement being repeated, no significant changes were confirmed.

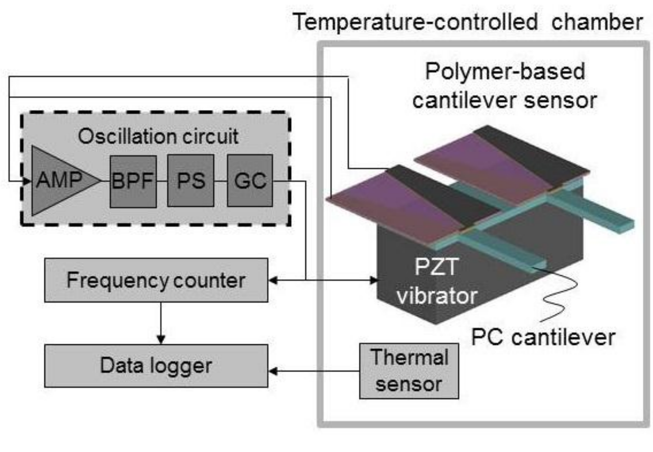


Fig. 6 Schematic view of our system for evaluating dependence on temperature

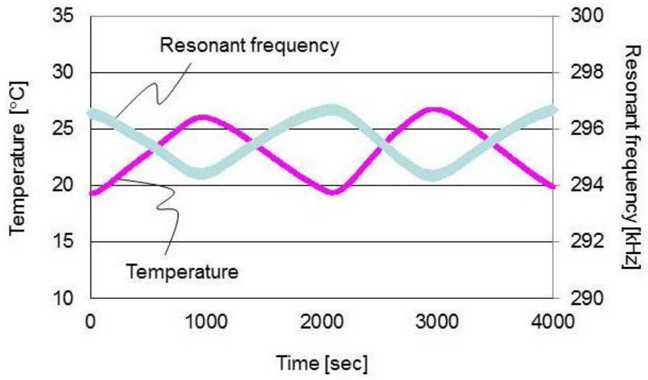


Fig. 7 Temperature dependence of the resonant frequency of the PC cantilever

4. Evaluation of the Young's modulus temperature dependence using dynamic mechanical analyzer

We examined the Young's modulus temperature dependence of the PC material using a bulk PC plate (10 mm × 5 mm× 0.2 mm) made from the same materials as those of the cantilevers (PC-1000 from SEKISUI SEIKEI Co., Ltd.). The bulk PC plate was set on a dynamic mechanical analyzer (RSA3 from TA Instruments Japan Inc.) and the Young's modulus temperature dependence of the PC plate was measured directly by applying tensile excitation. The measurement was conducted within a temperature range of -30-180 °C. The programming rate and angular velocity were 2 °C/min and 62.8 rad/sec, respectively.

Figure 8 shows the temperature dependence of the Young's modulus for the bulk PC plate. The Young's modulus of the PC plate decreases rapidly at as it approaches the higher temperature of 150 °C. The polymeric material of the PC has a glass transition point. On the other hand, even if the temperature is lower than glass transition temperature, the Young's modulus of the PC depends on temperature. The Young's modulus of the PC gradually decreases linearly from 1.8 GPa to 1.2 GPa in the temperature range of -30–150°C.

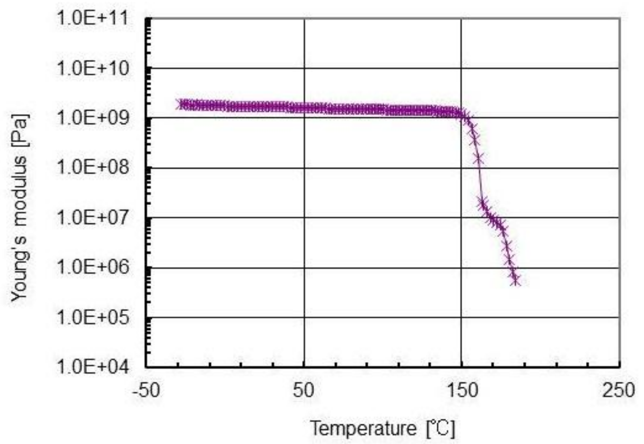


Fig. 8 Young's modulus temperature dependence of the bulk PC plate

5. Discussion

The theoretical resonant frequency of a cantilever of 4th flexural vibration mode with a length L and thickness T was calculated [15] to be,

$$f_4 = \frac{\kappa_4^2 T}{2\pi L^2}\sqrt{\frac{E}{12\rho}} \qquad (2)$$

where the coefficients of the 4th flexural vibration mode for the cantilever beam is κ_4 =10.996; and density of the PC ρ was 1.2×10^3 kg/m^3 [1]. E was Young's modulus.

Figure 9 shows a comparison between the measured resonant frequency of the PC cantilever and the theoretical resonant frequency. In Fig. 9, the resonant frequencies of the PC cantilever shown in Fig. 7 are rearranged as a function of temperature. The theoretically calculated resonant frequency (f_4) was calculated by Eq. (2) using the measured Young's modulus of the bulk PC plate and plotted in Fig. 9. The temperature dependence on the measured resonance frequency of the PC cantilever correlated well with the theoretical resonance frequency calculated using the Young's modulus of the bulk PC plate. The resonant frequency of the PC cantilever seems to be affected by the temperature dependence of the Young's modulus of the PC material.

While development of a temperature compensation function is surely needed, the polymer-based cantilever sensors will ultimately satisfy the regulatory requirements for VOC monitoring in semiconductor fabrication facilities.

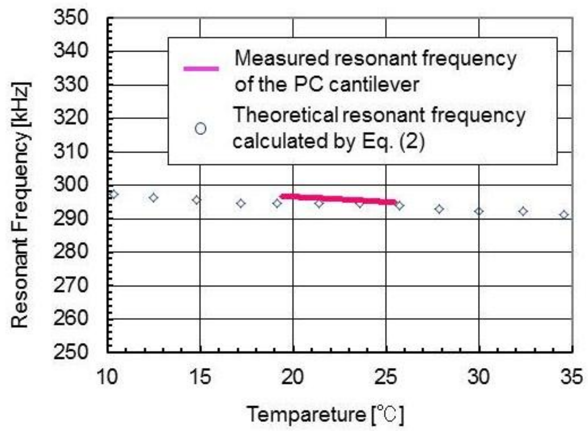


Fig. 9 Measured resonant frequency of the PC cantilever, and theoretical resonant frequency f_4 of Eq. (2)

6. Conclusion

We fabricated a polymer-based cantilever sensor consisting of PC cantilevers and PVDF piezoelectric films by using bonding, laser fabrication. We examined the change in resonant frequency due to temperature by setting up an evaluation system equipped with a temperature-controlled chamber, oscillation circuit, frequency counter and data logger. The resonant frequency of the PC cantilever tends to decrease linearly in step with increases in the temperature. We measured the Young's modulus temperature dependence directly using a bulk PC plate made from the same materials as those of the cantilevers. The resonant frequencies of the PC cantilever correlate well with the theoretical resonant frequencies calculated using the Young's modulus of the bulk PC plate. The resonant frequency of the PC cantilever seems to be affected by the Young's modulus temperature dependence of the PC material.

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