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Zeolite-modified microcantilever gas sensor for indoor air quality control

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Abstract

To control indoor air quality, a novel freon gas sensor of piezoelectric microcantilever coated with zeolite has been developed in this paper. Excited by an ac voltage, the microcantilever is employed to detect the concentration of sample freon-12 gas ranged from 0 to 100 ppm by the effect of the specific MFI zeolite modification. High selectivity and sensitivity combined with excellent repeatable and reversible performances are shown. The relationship between the frequency shift in percent and the concentration of freon gas is linear. The minimum mass changing of 3.5×10^{-9} g and the sensitivity of -0.0024%/ppm are determined from the experimental results.

Keywords: Microcantilever; Zeolite; Gas sensor; Freon

1. Introduction

A micro-total analysis system (μ-TAS) or a "Lab-On-Chip" for integrated chemical and biochemical analysis has grown dramatically in the past decade. The concept extends the scope since its introduction by Manz at Transducers'89 and now encompasses analysis and synthesis for applications ranging from chemistry through to biology. By using a high degree of parallelism in the designs it has become clear that automation of high sample throughput is possible. Meanwhile, an enormous amount of researches have been devoted to the development to miniaturize chemical and biochemical sensors, which has great effect on expanding the application fields, such as quality and process control, disposable diagnostic biosensor for medical analysis, fragrance design, oenology, and as sensing devices for gaseous analytes. However, the miniaturization of chemical sensor is of great complexity, functionality and compactness, and the sensitivity of the device and consequently the analytical power should be enhanced. Therefore, it is important to find a sensor with a high sensitivity and easy to be miniaturized and mass-produced.

A microcantilever in resonating mode has attracted intensive interest these years on account of its much higher sensitivity than the classical methods [1–3]. Cantilevers used as nanoscale sensors for atomic force microscope (AFM) have recently been extended beyond those of a surface-imaging tool. The masses of such sensors are typically in nanogram range, thus enabling short response time (milliseconds) and high sensitivity well beyond what is achievable with standard techniques. Such micromechanical sensors have been configured to be used as calorimeters and surface stress sensors. A piezoelectric microcantilever in resonating mode, which shifts its resonance frequency due to mass loading, has shown very high sensitivity for sensing chemicals and has broad and potential application areas related to environmental control [4], artificial nose [5], drug discovery [6], etc. Air quality is one aspect of environmental control. With the extensive use of air conditioner, problems with freon gas emission have increased in recent years. Rapidly and accurately determining the concentration of freon gas plays an important role on air quality control and assay, especially on indoor air quality control.

Although cantilever presents high sensitivity, in order to recognise different specific chemicals, improving the sensor's selectivity becomes one of the critical factors. A great many researches of sensing materials have been done to increase selectivity, including polymer [7,8], metal [3], oxide [4] and so on. Zeolites are the subject of intense

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interest as chemical sensors and as advanced materials. The nano-sized channel system of the zeolites provides a size and shape-selective matrix for absorbed molecules while maintaining a high surface-to-mass ratio. Microcomposite coatings with molecular sieving properties have been deposited on surface acoustic wave devices [9], quartz microbalances [10], and zeolite composites [11].

In this paper, as a special application of indoor air quality control, study on novel microcantilever sensor with a piezoelectric layer working in the resonating mode modified with a thin-layer MFI type zeolite to determine freon-12 gas is firstly to be reported. Such microcantilever shows high selectivity and sensitivity for the determination of freon-12.

2. Theoretical Background

A straight elastic beam model is applied here. Its resonance frequency is calculated by using Newton's second equation of motion. The details are given in [12] and later.

$$c^2 \frac{\partial^4 w}{\partial x^4}(x,t) + \frac{\partial^2 w}{\partial x^2}(x,t) = 0 \qquad c = \sqrt{\frac{EI}{\rho A}} \tag{1}$$

where $w(x, t)$ is the motion of the beam, ρ the density of the beam, A the cross-sectional area, E and I are the Young's modulus and the moment of inertia of the beam. By solving Eq. (1), we obtain the following solutions:

$$w(x,t) = W(x)T(t) \qquad T(t) = A\cos(\omega t) + B\sin(\omega t)$$
$$W(x) = C_1\cos(\beta x) + C_2\sin(\beta x) + C_3\cosh(\beta x) + C_4\sinh(\beta x)$$
$$\omega_i = (\beta_i L)^2\sqrt{\frac{EI}{\rho A L^4}} \qquad \omega_i = 2\pi f_i \tag{2}$$

where f_i is the resonant frequency of the beam, L the length of the beam. With the boundary condition of the one end fixed cantilever beam, i.e. $\cos(\beta_i L)\cosh(\beta_i L) = -1$ its natural frequency f_i in hertz can be expressed as follows [11]:

$$f_i = \frac{\lambda_i^2}{2\pi L^2}\sqrt{\frac{EI}{\rho A}} \tag{3}$$

where λ_i is a dimensionless parameter tabulated in [13].

Table 1
Theoretical and experimental resonance frequencies

Frequency (Hz)	Mode index i			
	1	2	3	4
Theoretical	1697	10634	29815	58426
Experimental	1646	9276	28500	–

As can be seen from the cross-sectional view of the microcantilever in Fig. 1, the microcantilever is composed of five different materials. Here we assume the properties of such a multilayer structure follow a rule of mixtures approach [14]. Therefore, the natural frequency of the composite beam can be expressed as follows:

$$f_i = \frac{\lambda_i^2}{2\pi L^2}\sqrt{\frac{\sum E_i I_i}{A\rho_c}} = \frac{\lambda_i^2}{2\pi L^2}\sqrt{\frac{\sum E_i I_i}{m_c/L}}$$
$$\rho_c t_c = \sum \rho_i t_i \qquad m_c = \rho_c A L \tag{4}$$

where m_c, ρ_c and t_c are the mass, density and thickness of the composite beam, E_i, I_i, ρ_i and t_i are the Young's modulus, the moment of inertia, the density and the thickness of each layer, respectively.

Table 1 gives the resonance frequencies of our microcantilevers. The resonance frequencies from experiments show some shift-down comparing to their theoretical ones, which relates to the deposition of the zeolite layer.

Working as a mass-sensitive transducer, the microcantilever translates the mass changing by the adsorption of the zeolite layer to specific gas molecules to mechanical frequency shift and finally to electrical signal output. The relationship between the frequency shift Δf_i and mass loading Δm_c can be calculated from the equation followed accordingly:

$$\frac{\Delta f_i}{f_i} = \sqrt{\frac{1}{\Delta m_c/m_c + 1}} - 1 \tag{5}$$

The above equation can be developed as a series

$$\frac{\Delta f_i}{f_i} = \frac{1}{2}\frac{\Delta m_c}{m_c} + \frac{3}{8}\left(\frac{\Delta m_c}{m_c}\right)^2 + \frac{15}{48}\left(\frac{\Delta m_c}{m_c}\right)^3 + \cdots \tag{6}$$

when $\Delta m_c/m_c$ is small enough, the first item on the right can approximate the relationship between $\Delta f_i/f_i$ and

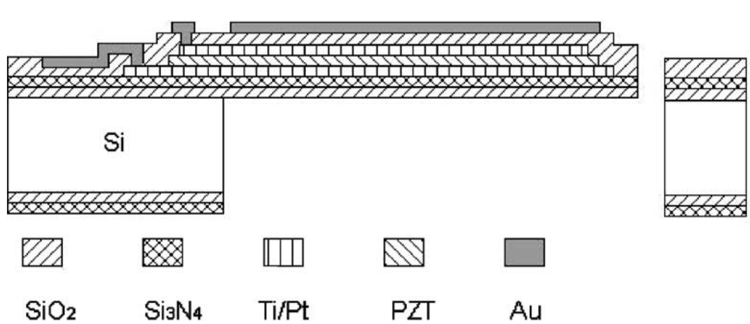

Fig. 1. Structure of the piezoelectric microcantilever. The dimensions are length 970 μm, width 300 μm and thickness 3 μm.