

Computational Model Of Plasma-Organic-Polymer-Film-Coated QCR Sensor For Analysing Its Dynamic Response

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Abstract—This paper proposes a computational model of the mass-sensitive chemical sensor with plasma-organic-polymer-film-coated quartz crystal resonators for use in sensor signal processing to develop a high-performance electronic nose system. Assuming one-dimensional Fickian diffusion of sample gas molecules, diffusion equation is applied to sample gas molecules in the sensor film bulk to describe the responses of the chemical sensor to the sample gas. Green's function is introduced to solve the diffusion equation, and the computational model of the chemical sensor response is derived. A computational experiment of the chemical sensor response is conducted to compare the sensor responses calculated by the proposed model with the experimental results obtained by the gas sensing system using water vapour as sample gas. The result shows the feasibility of the proposed model to estimate the responses of the chemical sensor.

Keywords—chemical sensor; quartz crystal resonator; plasma-organic-polymer film; diffusion equation; Green's function

I. INTRODUCTION

An electronic nose, which is based on chemical sensor technologies, has been utilized in various applications, such as distinguishing volatile organic compounds to evaluate indoor air quality, investigating the freshness/staleness of foods and diagnosing human health/activity with biogas [1], [2], [3], [4]. Many studies on chemical materials, sensor devices, sensor systems and their signal processing algorithms have been investigated because of the need for a highly accurate classification of gases and odours in practical applications of electronic noses. To develop a high-performance electronic nose system, a mathematical model of the chemical sensor dynamics is important to analyse the time response of the sensor and to design signal processing applications such as filtering, prediction and pattern recognition [5], [6], [7].

The authors have presented gas monitoring applications [8] that use mass-sensitive chemical sensors based on an array of quartz crystal resonators (QCRs), which are coated with plasma organic polymer films [9] (Fig. 1). The response of the mass-sensitive chemical sensor consists of a combination of physical and chemical phenomena. The QCR resonance frequency shift is proportional to the sample gas concentration change within the sensor film because of the sorption/desorption of the sample gas molecules to the sensor film surface: the molecules crossing the phase boundary between the external (vapour) phase and film surface; the diffusion of molecules from the film surface into the bulk;

and the reversible binding of molecules in the film by chemical reactions. This process was described using the well-known Fickian diffusion equation for the diffusion and binding of molecules in the film. In our previous work [10], we have proposed a computational model of the chemical sensor where the sample gas distribution was determined using an analytic function in the boundary condition of the diffusion equation. However, the computational model required numerical convolution integrals in each term of the alternating series. This was because the diffusion equation was solved using Laplace transforms.

In this paper, we discuss a computational model of the mass-sensitive chemical sensor with plasma-organic-polymer-film-coated QCRs. In section 2, diffusion equation is used to describe the governing equation for the concentration of sample gas molecules in the sensor film bulk and its solution is given using the Green's function that satisfies the boundary conditions. In section 3, computational experiments on the calculation of the chemical sensor response are conducted to confirm the feasibility of the proposed model.

II. DIFFUSION MODEL OF CHEMICAL SENSOR

Figure 2 illustrates the diffusion model of the sample gas molecules in the sensor film bulk. To obtain the computational model of the chemical sensor, a pure diffusion model is assumed where the sensor film is assumed to be thin, homogeneous and uniform. Assuming Fickian diffusion of sample gas molecules, the dynamics of molecule concentration, $\psi(x, t)$, at position x and time t can be given by the

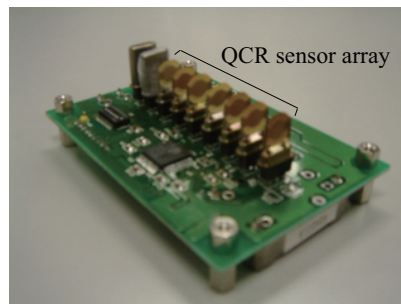


Fig. 1. Overview of plasma-organic-polymer-film-coated QCR sensor.

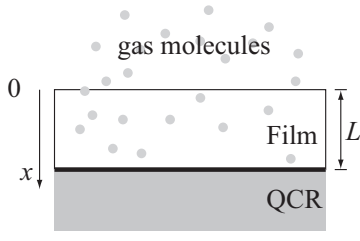


Fig. 2. Diffusion process model of the chemical sensor.

following diffusion equation:

$$\frac{\partial \psi(\mathbf{x}, t)}{\partial t} = D \nabla^2 \psi(\mathbf{x}, t) - \text{div}(\mathbf{v} \psi(\mathbf{x}, t)) \quad (1)$$

where D is the effective diffusion coefficient and \mathbf{v} is the velocity of QCR's vibration. Here the QCR vibrates with in-plane sliding mode. The concentration gradients with respect to the position in y and z axes are zero and those with respect to the velocity are also zero. Thus, the following one-dimensional diffusion equation can be obtained:

$$\frac{\partial \psi(x, t)}{\partial t} = D \frac{\partial^2 \psi(x, t)}{\partial x^2} \quad (2)$$

The initial and boundary conditions of molecule concentration are as follows:

$$\psi(x, t_0) = \psi_0(x), \quad (3)$$

$$\psi(0, t) = f(t), \quad (4)$$

$$\frac{\partial \psi(L, t)}{\partial x} = 0, \quad (5)$$

where $f(t)$ is the function that expresses the concentration of arbitrary sample gas molecules at the sensor film surface in the sorption/desorption process and L is the sensor film thickness.

Substituting $\phi(x, t) = \psi(x, t) - f(t)$ for transforming the variable, the governing equation, initial condition and boundary conditions can be rewritten as follows:

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{D} \frac{\partial}{\partial t} \right) \phi(x, t) = \frac{1}{D} \frac{df(t)}{dt}, \quad (6)$$

$$\phi(x, t_0) = \psi_0(x) - f(t_0), \quad (7)$$

$$\phi(0, t) = 0, \quad (8)$$

$$\frac{\partial \phi(L, t)}{\partial x} = 0. \quad (9)$$

Defining the operator $\mathcal{L} = \partial^2/\partial x^2 - (1/D)\partial/\partial t$, Green's function $G(x, t, x', t')$ satisfies the following equation and boundary conditions:

$$\mathcal{L}G(x, t, x', t') = -\delta(x - x')\delta(t - t'), \quad (10)$$

$$G(x, t, 0, t') = 0, \quad (11)$$

$$\frac{\partial G(x, t, L, t')}{\partial x'} = 0, \quad (12)$$

where $\delta(\cdot)$ is the Dirac delta function. Assuming orthogonal functions $\xi_n(\cdot)$ which satisfy the boundary conditions, the following form can be obtained:

$$\delta(z - z') = \sum_{n=1}^{\infty} \xi_n(z)\xi_n(z'), \quad (13)$$

where

$$\xi_n(z) = \sqrt{\frac{2}{L}} \sin p_n z \quad (14)$$

and $p_n = \frac{(2n-1)\pi}{2L}$. Green's function satisfying the boundary conditions can be assumed as follows:

$$G(z, t, z', t') = \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{g_n(\omega, z') e^{i\omega(t-t')} \xi_n(z)}{2\pi} d\omega, \quad (15)$$

where the following relationship is introduced:

$$\delta(t - t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega(t-t')} d\omega. \quad (16)$$

Substituting Eqs. (13), (15) and (16) into Eq. (10), the function $g_n(\cdot)$ can be obtained as follows:

$$g_n(\omega, z') = \frac{D}{i\omega + Dp_n^2} \xi_n(z') \quad (17)$$

As a result, Green's function satisfying the boundary conditions can be defined as follows:

$$G(x, t, x', t') = D \sum_{n=1}^{\infty} q_n(x) q_n(x') e^{-Dp_n^2(t-t')}. \quad (18)$$

Using Green's function, the governing equation solution can be given as follows:

$$\begin{aligned} \phi(x, t) = & \int_{t_0}^t dt' \int_0^L dx' G(x, t, x', t') \left\{ -\frac{1}{D} \frac{df(t')}{dt'} \right\} \\ & + \frac{1}{D} \int_0^L dx' G(x, t, x', t_0) \phi(x', t_0). \end{aligned} \quad (19)$$

Finally, the solution of the diffusion equation (Eq. (2)) can be obtained as follows:

$$\begin{aligned} \psi(x, t) = & f(t) - \frac{2}{L} \sum_{n=1}^{\infty} \frac{\sin p_n x}{p_n} \\ & \times \left\{ f(t) - Dp_n^2 e^{-Dp_n^2 t} \int_{t_0}^t f(t') e^{Dp_n^2 t'} dt' \right. \\ & \left. - e^{-Dp_n^2(t-t_0)} p_n \int_0^L \psi_0(x') \sin p_n x' dx' \right\}. \end{aligned} \quad (20)$$

III. COMPUTATIONAL EXPERIMENT OF THE CHEMICAL SENSOR RESPONSE

Computational experiments of the plasma-organic-polymer-film-coated QCR sensor were conducted to investigate the feasibility of the proposed model. In the experiments, the response of the computational model is calculated with the following conditions: the initial condition is set to 0 ($\psi_0(x) = 0$) and the function $f(t)$ in the boundary condition was assumed by the combination of a Heaviside function $\theta(t)$ and a first-order model as follows:

$$f(t) = F_g \{ \alpha \theta(t) + (1 - \alpha)(1 - e^{-Tt}) \}, \quad (21)$$

where F_g is the magnitude of the sample gas concentration, α is a weight parameter and T is a dead time coefficient of the sample gas's sorption in the sensor film surface. The Heaviside function represents rapid sorption of the sample gas molecules to the sensor film surface while the first-order model represents slow sorption. The mass of the sample gas molecule in the sensor film bulk $m(t)$ for the boundary condition Eq. (21) can be calculated by integrating the function $\psi(x, t)$ from 0 to L with respect to x as follows:

$$\begin{aligned} m(t) &= \int_0^L \psi(x, t) dx \\ &= LF_g \{ \alpha \theta(t) + (1 - \alpha)(1 - e^{-Tt}) \} \\ &\quad - \frac{2F_g}{L} \sum_{n=1}^{\infty} \frac{1}{p_n^2 (Dp_n^2 - T)} \{ (\alpha Dp_n^2 - T) e^{-Dp_n^2 t} \\ &\quad + (1 - \alpha) T e^{-Tt} \}. \end{aligned} \quad (22)$$

The diffusion coefficient D , the dead time coefficient T and the weight parameter α are important parameters to define the response of the chemical sensor. When water vapour is used as sample gas, the diffusion coefficient of water vapour in air is $D = 0.219 \times 10^{-4}$; however, that in the material of plasma organic polymer films has not yet been reported even though many studies of the transport phenomena through polymers have been investigated [11] (e.g. polymethyl methacrylate, which is a glassy polymer, shows a diffusion for water with $D = 3.35 \times 10^{-12}$ [12]). The dead time coefficient and the weight parameter which represent the sorption phenomena are also unknown parameter. In this study, these parameters were estimated by using the steepest descent method simultaneously so as to fit the computational model with the sensor responses obtained with the gas sensing system constructed in our previous study [9] where water vapour was used as sample gas and the sensor films were coated with D-phenylalanine (s1), D-tyrosine (s2), D-glucose (s3), DL-histidine (s4), adenine (s5), polyethylene (s6) and polychlorotrifluoroethylene (s7). In the steepest descent method, the cost function is defined as follows:

$$J = \frac{1}{2} \sum_{t=0}^{t_e} \{ \Delta \bar{F}(t) - \bar{m}(t) \}^2, \quad (23)$$

where $\Delta \bar{F}(t)$ is the resonance frequency shift (RFS) of the experimental sensor response normalized with the maximum

TABLE I
ESTIMATION RESULTS OF DIFFUSION COEFFICIENT AND TIME CONSTANT
IN THE SENSOR CELL.

sensor cell	$D(\times 10^{-12})$	T	α
s1	3.83314	0.000956096	0.167920
s2	4.07051	0.000880820	0.222010
s3	7.63455	0.000901280	0.377863
s4	7.37898	0.000948749	0.440270
s5	7.57980	0.001062300	0.499214
s6	10.7844	0.001028110	0.506225
s7	5.42601	0.000953812	0.522635

RFS and $\bar{m}(t)$ is the response of the computational model normalized with the final value of $m(\infty) = LF_g$. This is because that the RFS of the QCR ΔF [Hz] is in proportion to mass variation of the sensor film Δm [ng] (it is defined by Sauerbrey equation). The parameters were updated by the following form:

$$\mathbf{W}(p+1) = \mathbf{W}(p) - \gamma \frac{\partial J}{\partial \mathbf{W}(p)}, \quad (24)$$

where p is the iteration number, γ is the step size and the vector \mathbf{W} is composed of the parameters D , T and α .

In the computational experiment, the thickness of each sensor film was shown in Table I and the order of series in Eq. (22) was 20. The sensor responses using the gas sensing system were collected with the sampling rate of 2 second for 3600 seconds. In the estimation of the parameters using the steepest descent method, the experimental data was sampled with the interval of 10 seconds to evaluate the cost function and the total number of the sample from each sensor was 360. In the calculation of updating the parameters, the step sizes were $\gamma_D = 1 \times 10^{-21}$, $\gamma_T = 1 \times 10^{-7}$ and $\gamma_\alpha = 1 \times 10^{-3}$, and the initial conditions were $D(0) = 1 \times 10^{-12}$, $T(0) = 0.001$ and $\alpha(0) = 0.1$. The computational experiments were conducted using Mathematica™ version 8 (Wolfram Research, Inc.).

Table I shows the estimated parameters and the responses of the computational model are illustrated in Fig. 3. Although approximation errors are observed at the start of the responses, the computational model can approximate the responses observed in the experimental results. These results show the feasibility of the proposed model of the plasma-organic-polymer-film-coated QCR sensor. As shown in Table II, the difference of the ratio between the diffusion coefficient and the thickness of the sensor film, D/L^2 , indicates that the diffusion of the gas molecules in the sensor film bulk is affected with the sensor cell's materials. The weight parameters are different with respect to the ratio D/L^2 while the dead time coefficients are almost same values. This means that the rapid sorption of sample gas molecules to the sensor film surface becomes dominant according to increasing the ratio D/L^2 in the sensor response represented by the proposed computational model. In the slow sorption, the effect caused from the difference of sensor cell's materials seems to be small.

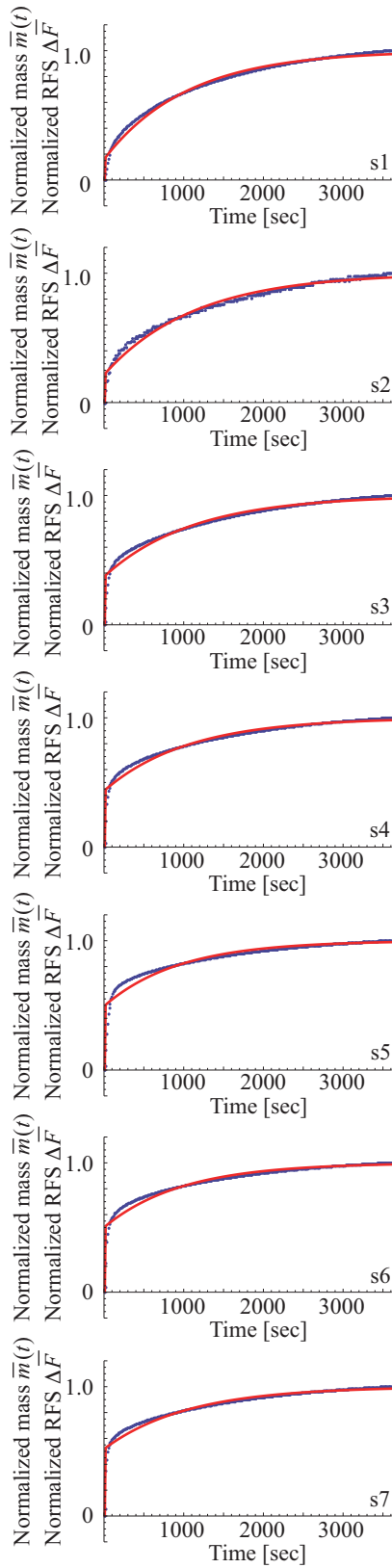


Fig. 3. Transient response of plasma-organic-polymer-film-coated QCR sensor, where blue dot indicates the experimental result and red line indicates the simulation result.

TABLE II
RATIO BETWEEN THE DIFFUSION COEFFICIENT AND THE THICKNESS OF THE SENSOR FILM.

sensor cell	L (Å)	D/L^2 (s^{-1})
s1	9889	3.91967
s2	8948	5.08390
s3	11159	6.13102
s4	9324	8.48773
s5	8275	11.0693
s6	11349	8.37299
s7	5646	17.0215

IV. CONCLUSIONS

This paper investigated a computational model of the mass-sensitive chemical sensor with plasma-organic-polymer-film-coated QCRs for application in the development of a high-performance electronic nose system. To describe the responses of the chemical sensor to sample gas molecules, Fickian diffusion equation was applied to the sample gas molecules in the sensor film bulk. The computational model of the chemical sensor response was obtained by solving the governing equation using Green's function. The computational experiment, in which water vapour was used as sample gas, proved the feasibility of the proposed model in the estimation of the chemical sensor responses.

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