Identification of gas species and their concentrations by using sorption kinetics of viscoelastic film

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***Abstract*—Nanomechanical sensors and their arrays have been attracting significant attention for detecting, distinguishing, and identifying target analytes. In the static mode operation, sensing signals are obtained by a concentration-dependent sorption-induced mechanical stress/strain. Recently, we derived an analytical solution, which is applicable to multistep injection-purge cycles in the static mode nanomechanical sensing with viscoelastic receptor layers. The model can be utilized for extracting viscoelastic properties and the concentrations of analytes more accurately by fitting a couple of injection purge curves obtained from experimental data. Here, we show the utility of the optimized parameters directly not only for the identification of gas species but also for their concentrations.**

***Index Terms*—gas identification, gas concentration identification, sorption kinetics, nanomechanical sensors, Membrane-type Surface stress Sensor (MSS)**

I. INTRODUCTION

Nanomechanical sensors have gained significant attention as powerful tools for detecting target analytes [1]–[3], especially odors that are composed of a complex mixture of gaseous molecules [4]–[6]. An array of nanomechanical sensors can be potentially utilized as a sensing unit for artificial olfaction. In the so-called static operation, sensing signals are obtained by measuring mechanical stress/strain induced by the sorption of target molecules in a receptor material. The materials coated on the nanomechanical sensors often exhibit viscoelastic nature, and hence the dynamic response of nanomechanical sensing reflects the sorption kinetics along with the viscoelastic stress relaxation. On the basis of the theoretical model proposed by Wenzel et al. [7], we recently derived the general analytical expression that includes the sorption kinetics and the viscoelastic stress relaxation [8]. This model is applicable to the multistep injection-purge cycles without reaching a steady-state, allowing us to effectively analyze the sensor responses and extract more accurate optimized parameters.

In this study, we demonstrate the direct identification of gas species as well as their concentrations using the optimized parameters obtained from the derived equation in [8]. Our previous report [9] clearly shows that one of the optimized parameters can be utilized for the identification of gas species using Wenzel's model; however the model is limited for optimizing the parameters accurately from the signal that reaches a steady-state. In contrast to the model, our analytical model [8] agrees well with sensor responses experimentally measured using a nanomechanical Membrane-type Surface stress Sensor (MSS) [10] coated with viscoelastic materials. The curve fitting provides not only the several physical parameters but also the features of the analyte species as well as their concentrations, leading to the accurate identification of the gas species and their concentrations without using any multivariate analyses.

II. GOVERNING EQUATIONS

In the case of the static mode operation of a micro-cantilever plate, the sorption-induced expansion makes the cantilever beam bend [1]. Several analytical solutions have been proposed for the theoretical formulations of the static mode nanomechanical sensing, especially for a microcantilever model, which clearly shows that the signal responses of the nanomechanical sensors are directly proportional to the internal strain ϵ_f.

In the case of the sorption-induced nanomechanical sensing, there are several investigations using microcantilever sensors [7]. In the model, the concentration-dependent sorption-induced internal strain in a coating film $\epsilon_f(C_g)$ is approximated as $\epsilon_f = \lambda C_g$ (with $\lambda = \frac{1}{3}\nu_a$) for small volume expansion (i.e., $\epsilon_f \ll 1$), where ν_a is the specific volume of the absorbed analyte. The absorption-induced strain can, therefore, be assumed to be directly proportional to the analyte concentration in the gas phase C_g.

Among a large variety of materials, viscoelastic properties arise from dynamic differences on molecular rearrangements. Wenzel et al. proposed a theoretical model for a cantilever-type nanomechanical sensor coated with a viscoelastic material [7]. The theoretical models are derived from the simplest three-parameter solid model:

$$\tau_r E_U \frac{d}{dt}\epsilon(t) + E_R\epsilon(t) = \tau_r \frac{d}{dt}\sigma(t) + \sigma(t), \tag{1}$$

where E_U and E_R denote the unrelaxed (instantaneous) modulus and relaxed (asymptotic) modulus, respectively, and τ_r is the time constant of stress relaxation.

For the derivation of the equations governing the concentration of an analyte into a receptor material coated on a nanomechanical sensor during absorption/desorption processes, we assume a first-order absorption. The reaction rate of a concentration of an analyte in the coating film $C(t)$ is given by

$$\frac{d}{dt}C(t) = \frac{1}{\tau_s}\left[K_p C_g(t) - C(t)\right], \tag{2}$$

where τ_s is diffusion time constant; K_p is known as the partition coefficient in the case of a polymer coating film. In the case of gas sensing using nanomechanical sensors, the sample gas is usually introduced by carrier gas; subsequently, the gas line is switched to the purge gas line to promote the desorption of the sample gases. Since the injection of analyte is generally controlled by the continuous flow of headspace gas or bubbling liquid samples, it can be assumed to be homogeneous in time. Thus, for the multistep injection-purge cycles, we consider a rectangular wave-like sequence (see also Fig. 4 in [8]). Then, the concentration of an analyte in the gas phase $C_g(t)$ can be described as a step function [8]:

$$C_g(t) = \begin{cases} 0, & t < t_0 \\ C_g, & t_{2(n-1)} \leq t < t_{2n-1} \quad (n = 1, 2, \cdots). \\ 0, & t_{2n-1} \leq t < t_{2n} \end{cases} \tag{3}$$

According to the formulation derived by Wenzel et al. [7], the derived general differential equation in Eq. (1) can be extended to the rectangular wave-like injection models. Substituting Eq. (2) with Eq. (3) into Eq. (1), the general differential equations of stress can be rewritten at the *n*-th injection and purge processes as a step function [8]. Then, the recurrence relations of the stresses between the *n*-th and (*n*+1)-th purge and the relations between *n*-th purge and (*n*+1)-th injection can be found. The recurrence formula can be solved, and hence the stresses at the *n*-th injection and purge processes can be obtained as

$$\sigma(t) = \begin{cases} 0, & t < t_0 \\ -\sigma_{\text{sat.}} + \sigma_{\text{sat.}}\alpha \displaystyle\sum_{i=0}^{2(n-1)} (-1)^i e^{-\frac{t-t_i}{\tau_s}} & \\ \quad + \sigma_{\text{sat.}}(1-\alpha) \displaystyle\sum_{i=0}^{2(n-1)} (-1)^i e^{-\frac{t-t_i}{\tau_r}}, & \\ & t_{2(n-1)} \leq t < t_{2n-1} \\ \sigma_{\text{sat.}}\alpha \displaystyle\sum_{i=0}^{2n-1} (-1)^i e^{-\frac{t-t_i}{\tau_s}} & \\ \quad + \sigma_{\text{sat.}}(1-\alpha) \displaystyle\sum_{i=0}^{2n-1} (-1)^i e^{-\frac{t-t_i}{\tau_r}}, & \\ & t_{2n-1} \leq t < t_{2n} \end{cases}, \tag{4}$$

with

$$\sigma_{\text{sat.}} = E_R \lambda K_p C_g, \tag{5a}$$

$$\alpha = \frac{1}{\tau_s}\left(\frac{E_U}{E_R} - \frac{\tau_s}{\tau_r}\right)\left(\frac{1}{\tau_s} - \frac{1}{\tau_r}\right)^{-1}, \tag{5b}$$

where $\sigma_{\text{sat.}}$ denotes the stress at the saturated or the equilibrium state when the initial internal stress is zero [8]. The models given in Eq. (4) are assumed to be proportional to the concentration of analyte in the gas phase C_g and $\sigma_{\text{sat.}}$ is related to the amplitude of the signal. Since the signal output of the nanomechanical sensing is directly proportional to the concentration $C(t)$ as described above, the signal output is analytically derived for the rectangular multistep injection-purge cycles with viscoelastic materials.

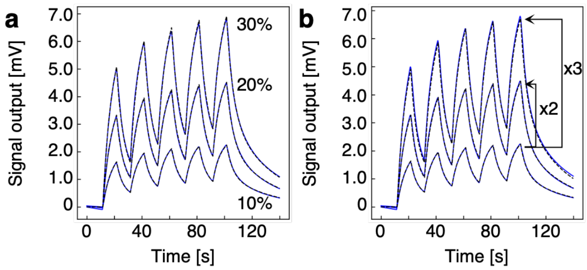

Fig. 1. Experimentally measured signal responses of PCL-coated MSS to ODCB. (a) Fitting curves with optimized paramters calculated from each concentration (10, 20 and 30%). (b) Fitting curves with optimized prameters calculated from 10% signal response. Corresponding $\gamma\sigma_{\text{sat.}}$ is multiplied by 20%/10% and 30%/10%, respectively.

III. EXPERIEMENTAL

A. Preparation of MSS

In this study, we used MSS as a sensing unit because of the high robustness and sensitivity [10]. The construction of the MSS chips and its working principle have been previously reported [10], [11]. Briefly, MSS consists of a silicon-based membrane suspended by four piezoresistive beams, composing a full Wheatstone bridge. The membrane is coated with a receptor material, which generates the surface stress caused by the sorption-induced expansion. The surface stress on the membrane is transduced to the four sensing beams as amplified uniaxial stresses, resulting in the changes in the electrical resistance of the piezoresistors embedded in the beams.

Polycaprolactone (PCL) and alkyl-functionalized nanoparticles (C18-STNPs) [4] were coated directly onto the MSS membrane using an inkjet spotter (LabJet-500SP, Microjet Corporation) equipped with a nozzle (IJHBS-300, Microjet Corporation). Each receptor material was dissolved in *N,N*-dimethylformaide (DMF) at a concentration of 1 mg mL^{-1}, and the resulting solutions were deposited onto each channel of the MSS. The injection speed, volume of a droplet, and numbers of inkjet shots were fixed at ca. 5 m s^{-1}, ca. 300 pL, and 300 shots, respectively. A stage of the inkjet spotter was heated at 80 °C to promote evaporation of DMF. The thicknesses of the receptor layers were ca. 1 μm.

B. Sensing

The coated MSS chips were placed in a Teflon chamber, which was placed in an incubator with a controlled temperature of 25.00 ± 0.02 °C. The chamber was connected to a gas system consisting of two mass flow controllers (MFCs), a mixing chamber, a purging gas line, and a vial for a solvent liquid. The vapor of each solvent was produced by bubbling carrier gas. Pure nitrogen gas was used as carrier and purging gases. The total flow rate was maintained at 100 mL min^{-1} during the experiments. The duration time was precisely controlled and the concentrations of the four different solvent vapors were controlled using MFC-1 at P_a/P_0 of 0.1, 0.2, and 0.3, where P_a and P_0 denote the partial vapor pressure and saturated vapor pressure of the solvent, respectively (Table I). Before measuring MSS signals, pure nitrogen gas was introduced into the MSS chamber for 1 min. Subsequently, MFC-1 (injection line) was switched on/off at each duration time (10 [s]) with a controlled total flow rate of 100 mL min^{-1} using MFC-2 for up to 20 injection-purge cycles to obtain constant gas concentration given in Eq. (3). Data were measured with a bridge voltage of –0.5 V and recorded with a sampling rate of 100 Hz. The data collection program was designed using LabVIEW (NI Corporation).

TABLE I
CONCENTRATIONS OF GASES USED IN THIS STUDY

VOC	P_0 [ppm] [a]	P_a/P_0 [ppm] [b]		
		10%	20%	30%
Water	31300	3130	6270	9400
Ethanol	86300	8630	17300	25900
n-Dodecane	196	19.6	39.1	58.7
1,2-dichlorobenzene	1950	195	390	585

[a] Saturated vapor pressure in the unit of ppm is estimated by using Antoine equation [12].

[b] Each concentration of vapor is calculated from saturated vapor pressure.

C. *Curve fitting and estimation of parameters*

To extract coating film properties from experimental data, we used least squares methods with trust region reflective algorithm using Python 3 with SciPy module. The amplitude constant $\sigma_{\text{sat.}}$, the diffusion time constant τ_s, the relaxation time constant τ_r, and the ratio of unrelaxed and relaxed moduli E_U/E_R in addition to the time when the first injection starts (t_0) were optimized using the derived formula in this study.

IV. RESULTS AND DISCUSSION

A. *Estimation of parameters*

Figure 1a shows one of the fitting results for the signal responses of PCL-coated MSS to 1,2-dichlorobenzene (ODCB) in different concentrations. The signal responses with different concentrations are well fitted with the derived equations for the five injection-purge cycles [8]. Importantly, the analyte/coating pair shows the amplitude parameter $\gamma\sigma_{\text{sat.}}$ proportional to the concentrations of analytes, where γ is a proportionality factor. As shown in Fig. 1b, the signal responses of different concentrations (20% and 30%) can be entirely predicted with the fitting parameters extracted from the 10% signal response by simply multiplying the amplitude parameter $\gamma\sigma_{\text{sat.}}$. The good agreement of the concentration dependence demonstrates that the predictive capabilities of the theoretical models.

When the measured signal responses are short (e.g., 30 s), then the parameters extracted from the experimental results cannot predict the entire signal responses (Fig. 2). Even if the signal response seems to reach the steady-state, the parameters extracted from a single injection procedure do not fit well to the experimental result (Fig. 2a). Conversely, in the case of the multistep injection-purge cycle system, the curves predicted by the extracted parameters fit well with the experimental results, even if the duration is relatively short (e.g., 90 s) as can be seen in Fig. 2b. Therefore, the optimized parameters extracted from a couple of injection-purge cycles can be clearly predicted by the experimental responses.

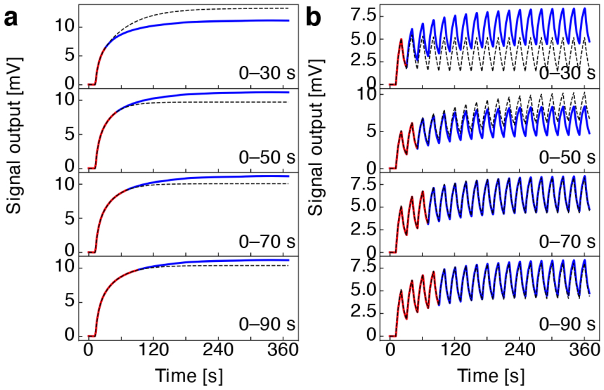

Fig. 2. Fitting accuracy between a single injection signal response and multistep injection-purge cycles. (a,b) Signal responses of PCL-coated MSS to ODCB are shown ($P_a/P_0 = 30\%$) for a single injection (a) and multistep injection-purge cycles (b). Red colored signal responses are used for optimizing each fitting curve, and blue colored signal responses are entire signal output. Black dashed lines are the corresponding fitting curves.

B. *Identification of gas species and their concentrations*

Among the intrinsic parameters, the diffusion constant τ_s is informative for gas identification as it reflects the physicochemical interaction between a receptor material and a gas. In our previous reports [9], we demonstrated that the two different time constants obtained from two different viscoelastic material-coated MSS can be utilized for the gas identification; however, the model for optimizing the parameters in [9] was based on the Wenzel's model [7], so that the signal responses have to reach the steady-state. In contrast, the present model for the multistep injection-purge cycles allows us to optimize the fitting parameters, including τ_s and $\gamma\sigma_{\text{sat.}}$, more accurately.

Figure 3 shows the plot of the two diffusion time constants obtained from two different materials-coated MSS for various volatile organic compounds (VOCs). It is clearly shown that each VOC forms well-separated clusters, even when the signal responses are obtained from different concentrations ranging from 10% to 30% (Fig. 3; see also Table I). More specifically, time constant $\tau_{s,\text{PCL}}$ obtained from PCL, which is a kind of polar hydrophobic polymers, shows the trend in the polarity, that is, polar/hydrophilic gases exhibited lower time constants while the hydrophobic gases, such as n-dodecane and ODCB yield higher time constants. In contrast to PCL, alkyl-functionalized nanoparticles (C18-STNPs) [4] have long alkyl chains, i.e., octadecyl functional groups, therefore, the time

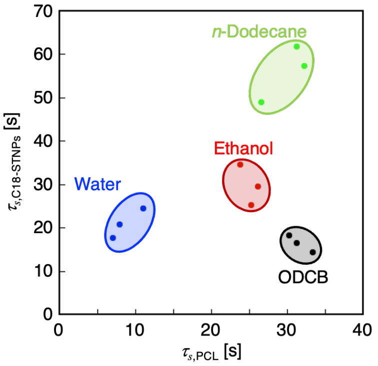

Fig. 3. Gas identification using the present viscoelastic model. Plot of $\tau_{s,\mathrm{PCL}}$ and $\tau_{s,\mathrm{C18\text{-}STNPs}}$ estimated by the curve fitting using Eq. (4). Each VOC contains the different concentratoins ranging from 10% to 30%.

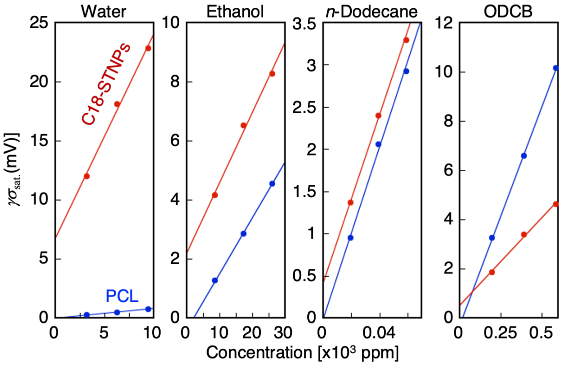

Fig. 4. Identification of gas concentrations using the present viscoelastic model. Concentration of target analyte from $\sigma_{\mathrm{sat.}}$ estimated by the curve fitting using Eq. (4).

constant $\tau_{s,\mathrm{C18\text{-}STNPs}}$ yields the well-separated clusters between non-polar aliphatic and aromatic gases (i.e., *n*-dodecane and ODCB), whereas it shows relatively similar values among the hydrophilic gases (i.e., water and ethanol).

Importantly, the amplitude parameters $\gamma\sigma_{\mathrm{sat.}}$ obtained from the receptor materials for the variety of VOCs clearly show the linear correlations to those of the concentrations (Fig. 4). This result clearly indicates that the optimized parameters τ_s and $\gamma\sigma_{\mathrm{sat.}}$ obtained from the present model [8] allow us to identify not only the gas species but also their concentrations without the use of the multivariate analyses.

V. CONCLUSION

The analytical model of the nanomechanical sensors coated with a viscoelastic material proposed by Wenzel et al. [7] was extended to the multistep injection-purge cycle system [8]. Wenzel's model includes the stress relaxation behaviors of the viscoelastic coating film and represents accurate signal responses. The present model can be used to analyze the absorption and desorption processes without measuring until the signal reaches the steady-state. By measuring a couple of injection-purge cycles, the accurate values of the coating parameters can be extracted. Therefore, the optimized parameters (i.e., τ_s and $\sigma_{\mathrm{sat.}}$) can be directly used as effective indices for the identification of gas species and their concentrations. The parameters obtained from the present model reflect the physical and chemical parameters of the coating film and the target gases. Thus, the present model can be utilized for the analyses of repeated injection-purge cycles, and the accurate optimized parameters can also be utilized as effective features for the pattern recognition-based analyses including machine learning approaches, contributing to the development of the practical artificial olfaction.

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