Constant-phase-mode operation of the light-addressable potentiometric sensor

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ABSTRACT

The constant-phase-mode operation of the light-addressable potentiometric sensor (LAPS) is proposed and demonstrated. In this new operation mode, the temporal change and the spatial distribution of the analyte concentration are recorded in the form of the bias voltage applied to the LAPS sensor plate, which is servo-controlled to maintain the phase of the photocurrent at a constant value with respect to the light modulation. The constant-phase-mode LAPS is advantageous for its wider measurement range and reduction of artifacts.

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1. Introduction

The light-addressable potentiometric sensor (LAPS) [1,2] is a chemical sensor based on the field effect in the electrolyte–insulator–semiconductor (EIS) structure shown in Fig. 1(a). The width of the depletion layer at the insulator–semiconductor interface changes in response to the variation of the analyte concentration of the solution in contact with the sensing surface. In LAPS measurement, the sensor plate is illuminated with a modulated light, and the alternating photocurrent is measured to detect the variation of the capacitance of the depletion layer.

Fig. 1(b) shows an example of current–voltage (I–V) curves of an n-type LAPS for different pH values. The analyte concentration (or pH in this case) can be determined by measuring the shift of the I–V curve along the voltage axis. The LAPS can be also operated in both the constant-bias mode and the constant-current mode [3–16]. In the constant-bias mode, the voltage applied to the sensor is fixed, and the variation of the photocurrent is recorded and converted into the shift of the I–V curve, which can be further converted into the analyte concentration. This mode has been used in chemical imaging sensors [7,13–16], in which a laser beam scans the sensor plate under a fixed bias voltage and the photocurrent is recorded at each pixel to generate a two-dimensional map of the analyte concentration. In the constant-bias mode, however, the photocurrent reaches its maximum or minimum for a large shift of the I–V curve,

and therefore, a large variation of the analyte concentration cannot be precisely recorded. In the constant-current mode [8–12], on the other hand, a feedback loop controls the bias voltage so that the photocurrent is maintained at a constant value. In this case, the servo-controlled voltage can follow even a large shift of the I–V curve.

In the conventional LAPS measurement (including the constant-bias mode and the constant-current mode), the amplitude of the alternating photocurrent is measured as the sensor signal. However, the amplitude varies not only with the shift of the I–V curve, but also with the impedance of the solution, fluctuation of the light intensity, and loss of photocarriers due to recombination inside the semiconductor layer, which may result in artifacts.

In our previous study [17], we proposed a phase-mode LAPS, in which the phase of the alternating photocurrent with respect to the light modulation was detected instead of its amplitude. It was demonstrated that the shift of the phase–voltage (ϕ–V) curve was essentially the same as that of the I–V curve, and that the phase was much less sensitive to the fluctuation of the light intensity and loss of photocarriers at defects in the semiconductor layer [18].

In the present study, we developed the constant-phase-mode operation of LAPS, which combines the advantages of the constant-current-mode and the phase-mode LAPS.

2. Experiment

The LAPS sensor plate used in this study is made of 200-μm-thick n-type Si with a resistivity of 10–20 Ω cm and is covered with a 50-nm-thick thermal SiO_2 layer and a pH-sensitive layer
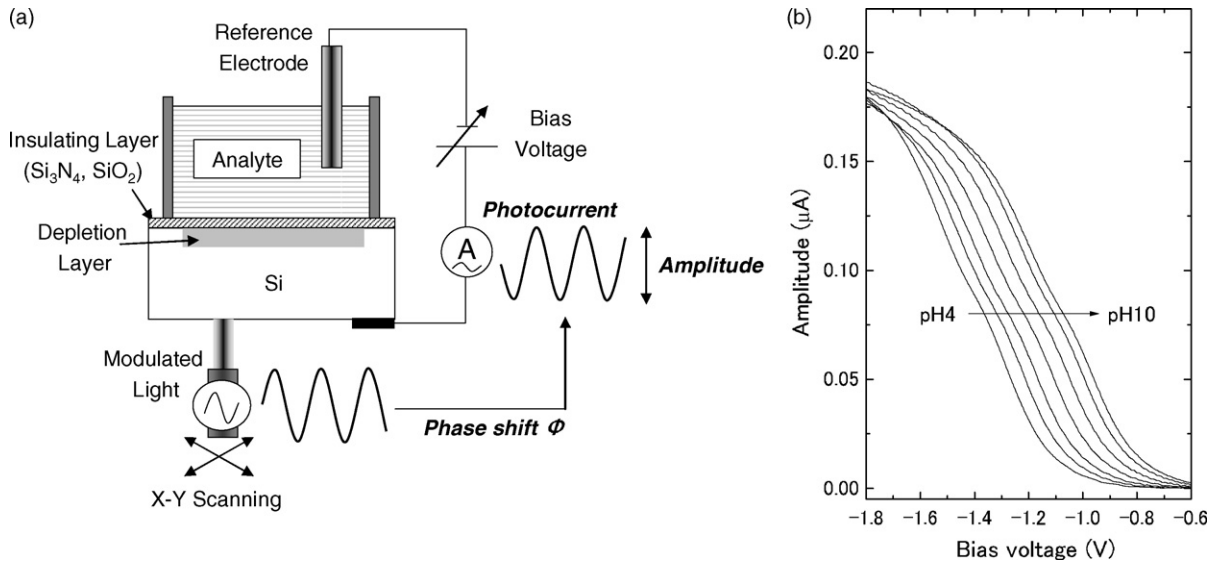

Fig. 1. (a) Schematic diagram of LAPS. (b) *I–V* curves of n-type LAPS for different pH values.

of 100-nm-thick Si_3N_4 in contact with the analyte solution to be measured. The sensor plate is illuminated with an infrared laser beam which is sinusoidally modulated at $f = 2.5$ kHz. The induced photocurrent is amplified at a gain of 10^6 V/A. The modulation signal and the photocurrent signal are simultaneously digitized at a sampling frequency of 100 kHz. The measurement time was 10 ms.

The measurement system used in this study is the same as the one described in our previous paper [18] except that the modulation signal and the photocurrent are simultaneously recorded for the calculation of the phase difference between them. In imaging experiments, a moving stage was used to scan the sensor plate with the focused laser beam (see Fig. 1(a)). In this study, the typical resolution of a chemical image was 64×64 pixels. The control software was developed with LabVIEW (National Instruments Corp.), which controlled the moving stage and recorded the photocurrent and the modulation signal simultaneously at each pixel.

3. Operation of the constant-phase-mode LAPS

3.1. Detection of phase difference

Fig. 2(a) shows a typical example of waveforms of photocurrent at various bias voltages. The amplitude of the photocurrent increases as the sensor is more negatively biased (see the *I–V* characteristics in Fig. 1(b)). At the same time, the phase of the photocurrent with respect to the light modulation also changes in response to the bias condition.

The phase of the photocurrent is calculated as follows. For the sampled data, the sine and cosine components of the modulation signal $A_1(t)$ and the photocurrent signal $A_2(t)$ are calculated as

$$\text{sine components}: \quad A_{i,\sin} = \frac{2}{N}\sum_{m=0}^{N-1} A_i(m\Delta t)\sin(2\pi f \cdot m\Delta t)$$

$$i = 1 \text{ or } 2 \tag{1}$$

and

$$\text{cosine components}: \quad A_{i,\cos} = \frac{2}{N}\sum_{m=0}^{N-1} A_i(m\Delta t)\cos(2\pi f \cdot m\Delta t)$$

$$i = 1 \text{ or } 2 \tag{2}$$

where N is the number of samples (=1000) and Δt is the sampling period (=10 μs). The phase terms of the modulation signal and the photocurrent signal are calculated respectively as

$$\phi_i = a\tan 2(A_{i,\sin}, A_{i,\cos}) \quad i = 1 \text{ or } 2 \tag{3}$$

and finally, the phase difference is calculated as

$$\phi = \phi_2 - \phi_1. \tag{4}$$

The phase difference ϕ is an indicator of the variation of the depletion layer, which responds to the applied bias voltage and the analyte concentration, as shown in Fig. 2(b).

3.2. Servo control

In the constant-phase-mode operation, the bias voltage applied to the EIS system is servo-controlled to maintain the phase difference ϕ at a constant value. Let ϕ_0 be the target value and assume that the ϕ–V curve can be linearly approximated with a slope s around $\phi = \phi_0$. If an error $\phi - \phi_0$ is observed at $t = t_n$, the bias voltage $V(t_n)$ is updated with a new value

$$V(t_{n+1}) = V(t_n) - (\phi - \phi_0)/s. \tag{5}$$

The sequence of $V(t_n)$ gives a temporal recording of the potential, which can be converted into the analyte concentration.

4. Results and discussion

4.1. Temporal recording

The constant-phase-mode LAPS measurement using the servo control of the bias voltage was applied to temporal recording of the ion concentration. Fig. 3 is an example of the temporal recording of the potential, in which different pH buffer solutions were successively brought into contact with the sensing surface. The pH value was changed from 5 to 9 in turn, and returned to pH 7 again. The plot of the bias voltage versus time (left panel in Fig. 3) shows that the bias voltage applied to the sensor was servo-controlled corresponding to the change of the pH value. Throughout this measurement, the phase of the photocurrent was maintained at a constant value of 137° by the servo control as observed in the right panel in Fig. 3.