Electronic Supplementary Information for *Molecular System Design & Engineering*

Field-effect transistor array modified by a stationary phase to generate informative signal patterns for machine learning-assisted recognition of gas-phase chemicals

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Contents

1. Experimental details.

1.1. Fabrication of gas chromatograph (GC) stationary phase-modified porous gate field-effect transistor (PGFET) samples

To fabricate the GC stationary phase material-modified PGFETs, we used an *n*-channel depletion mode FET-based sample (ISFET com., Japan), with no gate electrode. GC stationary phase materials, such as dimethyl poly siloxane (silicone OV-1; Shinwa Chemical Industries, Japan), polyethylene glycol (PEG; PEG4000, USP, USA), diethylene glycol succinate (DEGS; SUPELCO, USA), and tetrakis(hydroxyethyl)ethylene diamine (THEED; GL Sciences, Japan) were applied as layers to modulate interactions with gaseous molecules in the FET gate structure. PEG was dissolved in pure water at a concentration of 0.1 g L^{-1}. Silicone OV-1, THEED, and DEGS were dissolved in tetrahydrofuran (THF; Fujifilm Wako Pure Chemical, Japan) at 0.1 g L^{-1}. A 2-μL portion of the solution was dropped onto the surface of the top insulating layer in the planner FET gate structure at room temperature. After dropping of the stationary phase material-dissolved solution, the FET sample was heated at 110 °C for 20 min in an oven to evaporate the solution. After evaporation of the solution, the stationary phase layer was formed. Then, a short (30 s) treatment by a radio-frequency (RF) sputtering process was applied to form a porous Pt gate electrode as the top layer of the PGFET structure. The conditions for RF sputtering included a power of 50 W in a vacuum chamber with a ~1 Pa Ar atmosphere.

1.2. Real-time volatile organic compound (VOC) sensing by stationary phase-modified PGFETs

For real-time VOC vapor sensing by the stationary phase material-modified PGFET, we used a dedicated electronic circuit. For real-time monitoring, the drain-source voltage (V_{DS}) and gate voltage (V_G) of the FET were fixed at 40 and 400 mV, respectively. The sampling frequency was set to be 10 Hz (i.e., a sampling period of 0.1 s). The chemical-sensitive FET samples were arrayed and housed in a gas-flow cell, as shown in Fig. S3. Aldehydic functional compounds such as nonanal, hexanal, and benzaldehyde were used as the VOC analytes. The VOC vapor was generated by a vapor-generating apparatus (Permeater PD-1B-2, GASTEC, Japan) and added to the gas-flow cell under the flow of dry N_2 carrier gas. The concentration of the vapor analyte (nonanal 0.4, 0.8, 2 ppm; hexanal 4, 7, 13 ppm; benzaldehyde 0.7, 1, 6 ppm) was conditioned by selecting the glass tube size, which contained the VOC, and the heating temperature. The sample flow rate of the VOC vapor under a dry N_2 carrier gas was fixed at 0.5 L min^{-1}. After stabilization of the measurement equipment in all measurements, sensing measurements by the four PGFET sensors were started. The sample-flow interval was 10 s. The introduction of VOC analyte to the gas-flow cell was repeated five times in one measurement. All sensing measurements were conducted two times.

1.3. Electron microscope observations of the PGFET sample

A representative PGFET, sample s1, was observed by electron microscope imaging. Top view observations of the PGFET sensor and porous Pt gate electrode (Fig. S1 and 1b) were acquired on a scanning electron microscope (SEM; JSM-7800F, JEOL, Japan) operating at accelerating voltages of 5 and 10 kV. After SEM observations, the sample was processed by a focused ion beam (FIB) system (JIB-4501, JEOL, Japan) to obtain cross sections of the FET gate structure. To protect the configuration in the FIB cutting process, the sample was protected with resin. The cross-sectional gate structure (Fig. 1c and S2) was observed by transmission electron microscope (TEM; JEM-2100F, JEOL,

Japan) imaging operating at an accelerating voltage of 200 kV.

1.4. Classification of signal patterns derived from PGFET sensors by machine-learning technique for recognition of VOCs

The measured peaks (measured 2 times) were used for a supervised learning approach. Individual five-peak patterns were extracted from the sensing results in the manner shown in Fig. S5. In the peak pattern, the VOC-flow starting point and the point of the next VOC flow were defined as start and end-point, respectively. The extracted peak pattern is expressed as the follow function 1:

$$g(n) \quad n = 1, 2, \cdots, N, \qquad (1)$$

where *n* is time-series data index.

To generate feature vectors applied for a machine learning technique, signal processing was conducted through a discrete Fourier transform (DFT) with the following formula:

$$\mathrm{G(k)} = \sum_{n=0}^{N-1} g(n)w(n)exp\left(-j\frac{2\pi kn}{N}\right) = A_{i,k} - jB_{i,k}\,, \qquad (2)$$

where $w(n)$ is a Hann window function; frequency index, k = 0, 1, 2, …, N–1; channel index, i = 0, 1, 2, …, I; j is an imaginary unit. $A_{i,k}$ and $B_{i,k}$ are the real and imaginary part of a complex number, respectively.
In the spectrum, similar to DFT, the feature vector x is expressed by $A_{i,k}$ and $B_{i,k}$ as:

$$\begin{aligned}\mathrm{x} = [&A_{1,k_{min}}, A_{1,k_{min+1}}, \cdots, A_{1,k_{max}}, B_{1,k_{min}}, B_{1,k_{min+1}}, \cdots, B_{1,k_{max}},\\ &A_{2,k_{min}}, A_{2,k_{min+1}}, \cdots, A_{2,k_{max}}, B_{2,k_{min}}, B_{2,k_{min+1}}, \cdots, B_{2,k_{max}},\\ \cdots, &A_{I,k_{min}}, A_{I,k_{min+1}}, \cdots, A_{I,k_{max}}, B_{I,k_{min}}, B_{I,k_{min+1}}, \cdots, B_{I,k_{max}}]\end{aligned} \qquad (3)$$

where k_{max} (550) and k_{min} (0) are the upper and lower limit frequency, respectively. In this work, the dimensions of the feature vectors are $2\times(k_{max} - k_{min} +1)\times I$, where I = 4 (the number of stationary phase-modified PGFET sensors).

The data set of feature vectors was used to classify the signal patterns by an algorithm of random forest in a machine learning software of Waikato Environment for Knowledge Analysis: Weka. Cross-validations were conducted between each peak pattern except for peak 1. Parameters were tuned to optimize the value of the F-measure as a measure of classification precision.

2. Supplemental figures

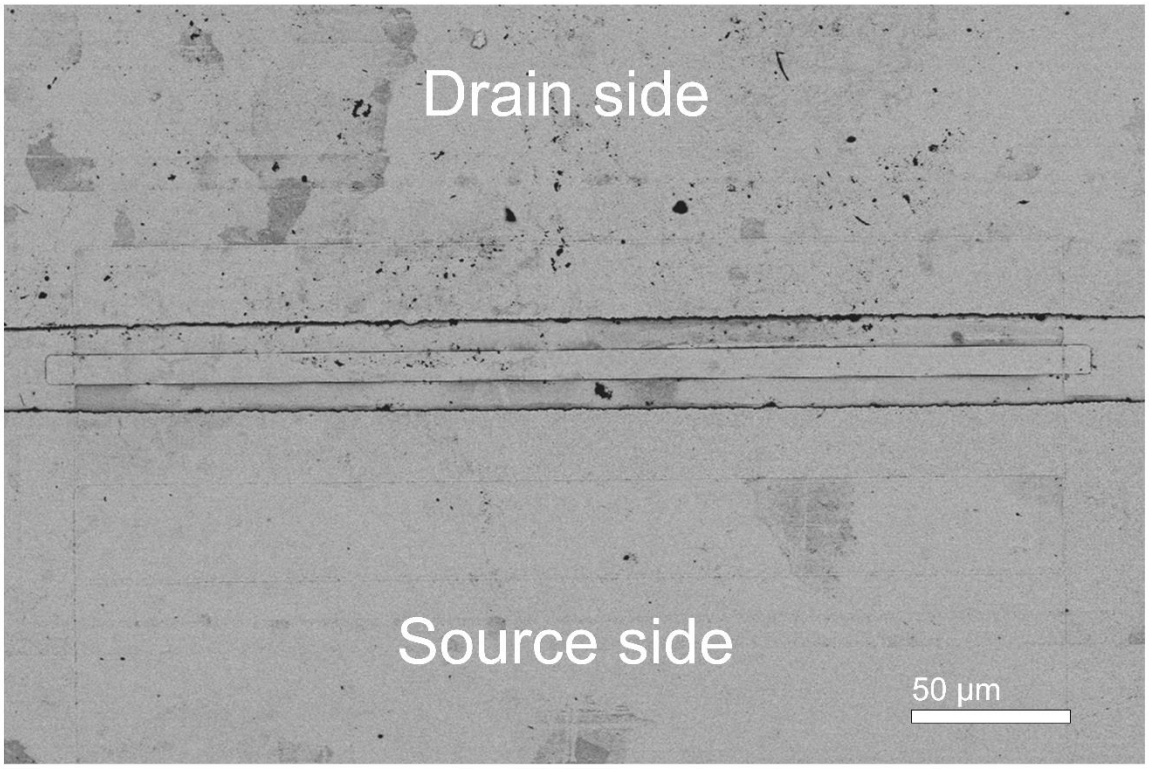

Fig. S1. Top view image of the PGFET of sensor 1. Scale bar is 50 µm.

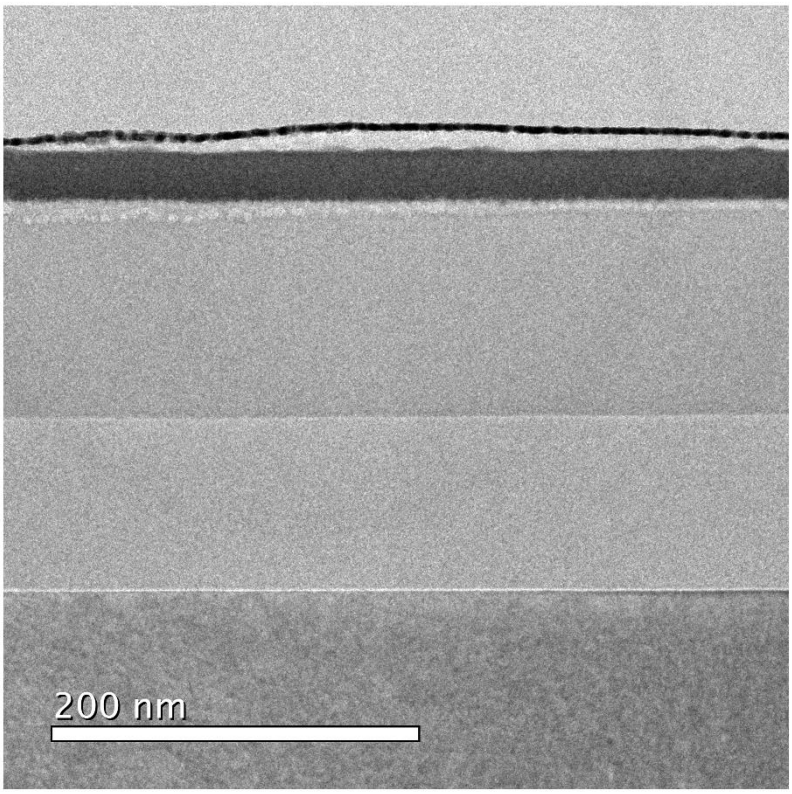

Fig. S2. Cross-sectional TEM image of the PGFET of sensor 1. Scale bar is 200 mm.

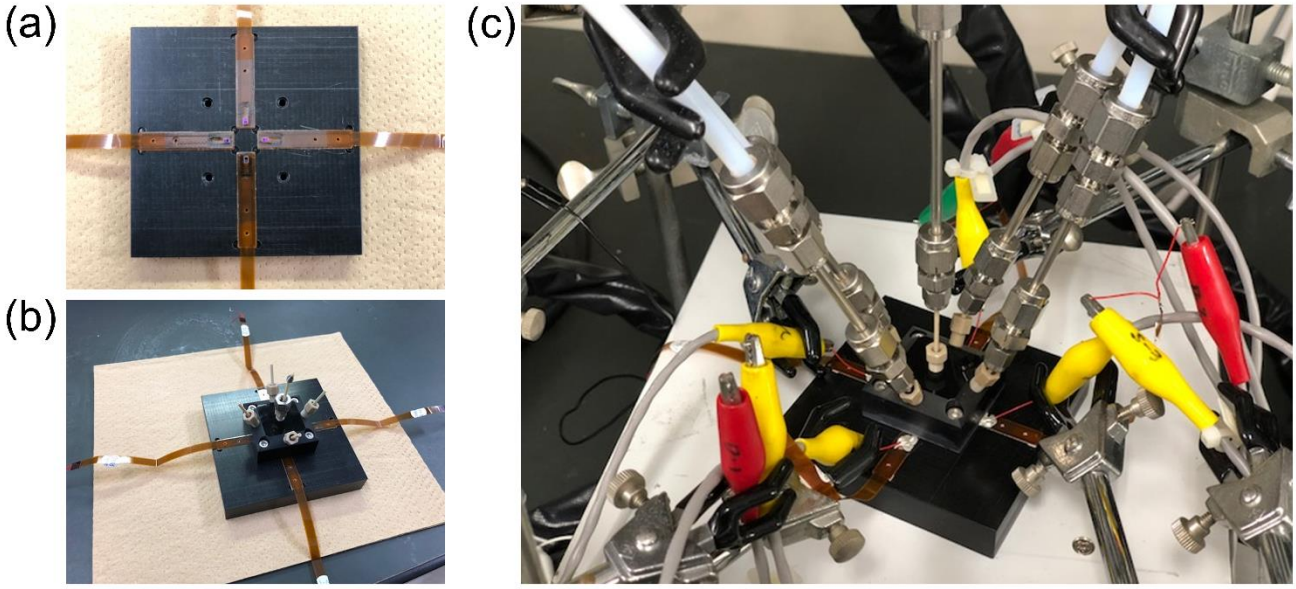

Fig. S3. Sensor array of developed stationary phase-modified PGFET sensors. (a) Arrayed PGFET sensors with no capping of the gas-flow cell, (b) with capping, and (c) appearance of real-time sensing measurement with the gas-flow cell containing the PGFET sensor array.

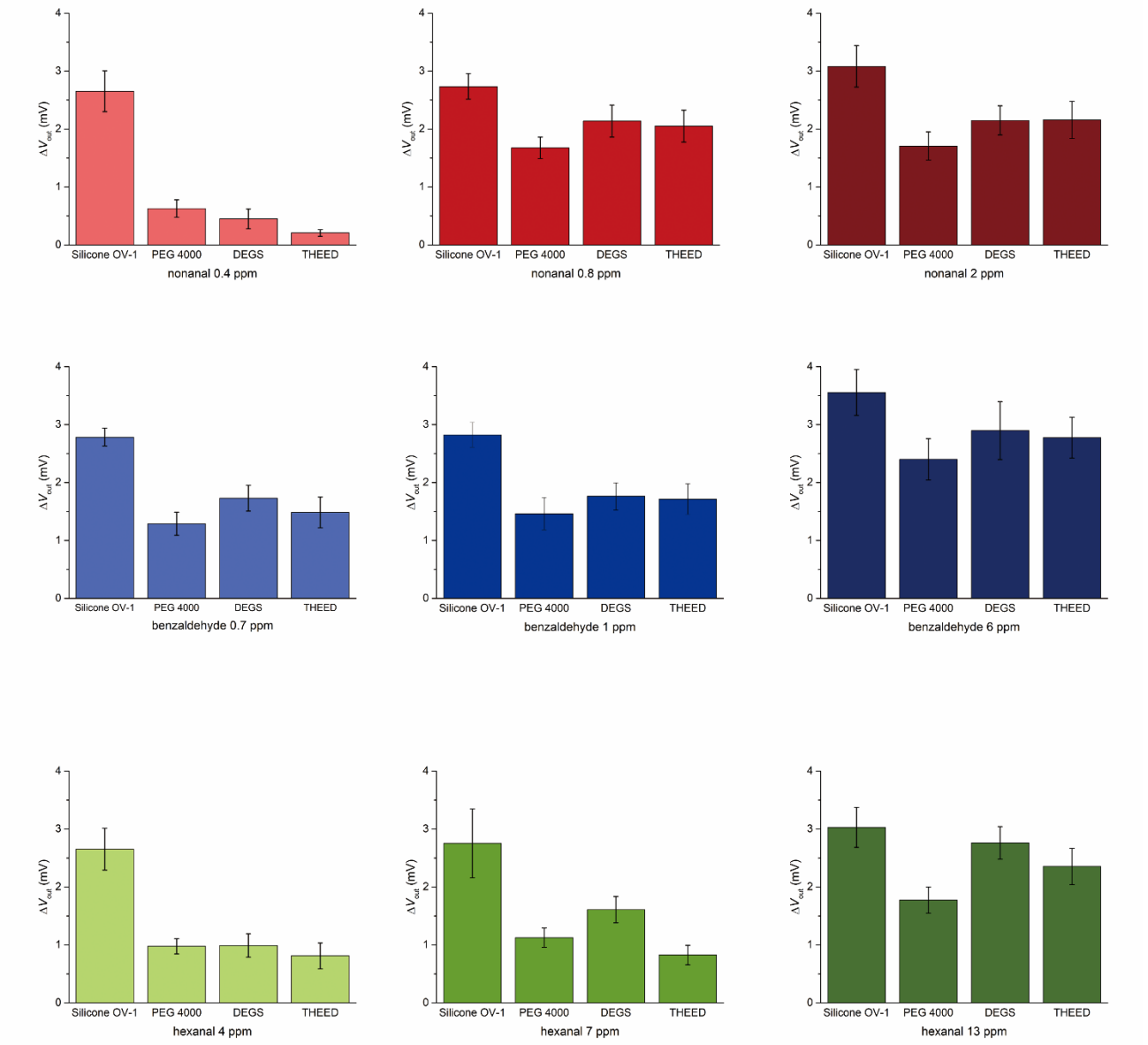

Fig. S4. Peak height differences from each stationary phase material-modified PGFETs at room temperature.

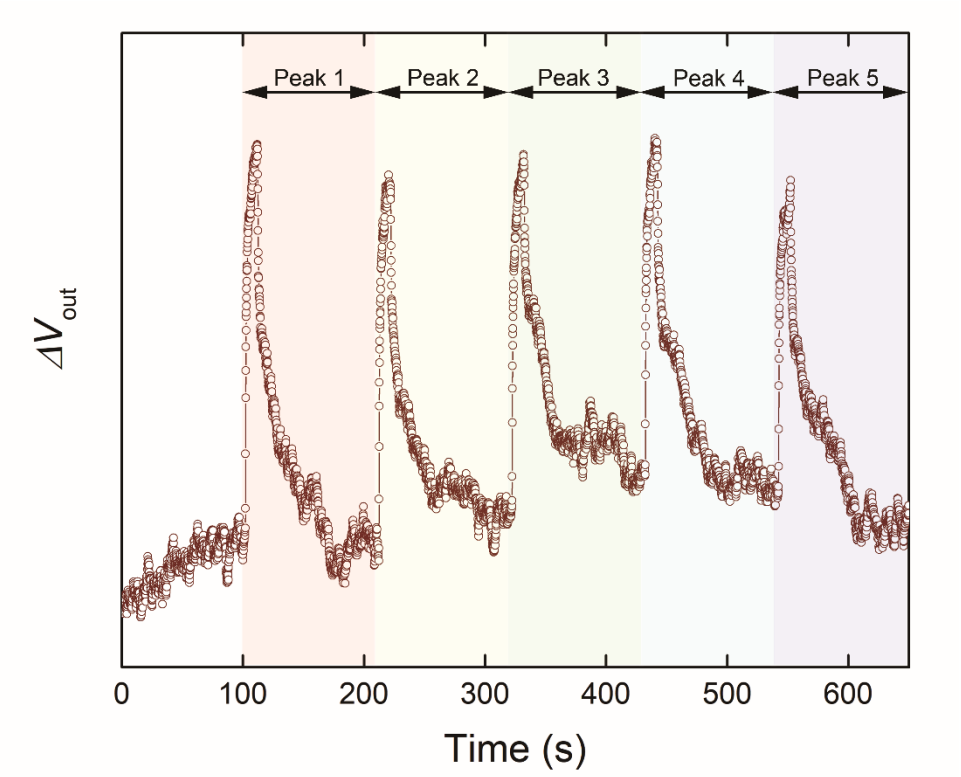

Fig. S5. Extraction of responsive peak patterns from a real-time measurement result.