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

Journal:	*Molecular Systems Design & Engineering*
Manuscript ID	ME-COM-11-2018-000097.R1
Article Type:	Communication
Date Submitted by the Author:	08-Jan-2019
Complete List of Authors:	Yoshizumi, Toshihiro; Tokyo Medical and Dental University, Institute of Biomaterials and Bioengineering Goda, Tatsuro; Tokyo Medical and Dental University, Institute of Biomaterials and Bioengineering Yatabe, Rui; Kyushu University Oki, Akio; National Institute for Materials Science, ; Panasonic Corporation, Bioscience Technology Development Office Matsumoto, Akira; Tokyo Medical and Dental University, Oka, Hiroaki; Panasonic Automotive & Industrial Systems Company Washio, Takashi; Osaka University Toko, Kiyoshi; Kyushu University Miyahara, Yuji; Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University

In this work “Field-effect transistor array modified by a stationary phase to generate informative signal patterns for machine learning-assisted recognition of gas-phase chemicals”, we report a new AI chemical sensing system for recognition of gaseous analytes. The system consists of a porous gate FET (PGFET) sensor array modified by gas chromatography (GC) stationary phase materials, and a supervised machine learning technique. Interaction between PGFET and gaseous molecules can be tuned by selecting GC stationary phase materials. Signal patterns generated from GC stationary phasemodified PGFET sensor array were applied for machine learning-assisted recognition of gaseous molecules. The system has attractive potential for applications to mobile AI chemical sensing devices.

Mol. Syst. Des. Eng.

COMMUNICATION

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Toshihiro Yoshizumi,[a] Tatsuro Goda,[a] Rui Yatabe,[b] Akio Oki,[c] Akira Matsumoto,[a,d] Hiroaki Oka,[c] Takashi Washio,[e] Kiyoshi Toko,[b] and Yuji Miyahara*[a]

We propose an artificial intelligence-based chemical-sensing system integrating a porous gate field-effect transistor (PGFET) array modified by gas chromatography stationary phase materials and machine-learning techniques. The chemically sensitive PGFET array generates cross-reactive signals for computational analysis and shows potential for applications to compact intelligent sensing devices, including mobile electronic noses.

The sensing of gas-phase chemicals is becoming important in many fields including medical diagnosis, food/agricultural safety, industrial process, and home security together with the *Internet of Things* (*IoT*).[1] Artificial intelligent (AI) sensing systems aided by statistical/computational analytical methods are a promising approach to recognition and quantification of gaseous chemicals from the signal patterns of sensor arrays.[2,3] Disease diagnostics by identifying volatile organic compounds (VOCs) as biomarkers from exhaled breath is a modern research field, which takes advantage of AI-based sensing systems through the application of cross-reactive sensor arrays.[4–6] Artificial nose technologies, including electronic noses (e-noses), require an array consisting of cross-reactive sensors to mimic the mammalian olfactory system, which can generate broad (i.e., non-selective) and differentiated responsive signals. Such cross-reactive signals are compatible with pattern recognition techniques, such as principal component analysis, artificial neural networks, among others.[3,4] Therefore, the development of cross-reactive sensor arrays is a key research theme in the development of intelligent chemical-sensing systems.

Field-effect transistor (FET)-based sensors show great potential as highly sensitive sensing devices.[7] Furthermore, these devices possess advantages for developing compact electronic devices owing to miniaturization and large-scale integration in one chip, because semiconductor processes can be applied to fabricate FET-based sensors. In fact, chemically sensitive FETs have shown potential for applications to multiplexed sensors for gas molecules at room temperature and in applications to drones for aerial sensing of chemicals.[8] According to the previous report, selective targeting of gases, such as H_2, H_2S, and NO_2, has been archived with chemical-sensitive nanosized metallic layers, including Pd-Au, Ni-Pd, and Ni. Recently, we reported a polyethylene glycol (PEG)-modified porous gate FET (PGFET).[9] The chemically sensitive PGFET incorporated a PEG layer, which interacted with VOCs, and a porous Pt gate electrode in the gate structure. Changes in the drain current and threshold gate voltage were chemically gated through capacitance changes in the gate structure by adsorbing gaseous molecules into the stationary phase layer and porous Pt gate.

Here, we provide a machine learning-aided intelligent sensing system based on a PGFET sensor array modified with a polymeric material used for a gas chromatography (GC) stationary phase. The chemical responsiveness of the PGFET sensor was tuned by selection of GC stationary phase materials. This tunability enabled cross-reactive sensing of gas-phase chemicals. We applied a machine-learning technique to classify the differentiated signal patterns and identify a few aldehydes with similar chemical structures, namely nonanal, hexanal, and benzaldehyde.

The experimental procedure is briefly described below (for more details, see ESI†). Fig. 1a shows a schematic illustration of the GC stationary phase-modified PGFETs. The stationary phase layer was formed on the surface of the top insulating layer as a gas molecule-

---

[a] Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda, Tokyo, 101-0062, Japan.
E-mail: miyahara.bsr@tmd.ac.jp

[b] Research and Development Center for Taste and Odor Sensing, Kyushu University, 744 Motooka, Nishiku, Fukuoka, 819-0395, Japan.

[c] Sensing Solutions Development Center, Panasonic Automotive and Industrial Systems Company, 1006 Kadoma, Kadoma, Osaka, 571-8506, Japan.

[d] Kanagawa Institute of Industrial Science and Technology, 3-2-1 Sakado, Takatsu-ku, Kawasaki, 213-0012, Japan.

[e] The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Osaka, 567-0047, Japan.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

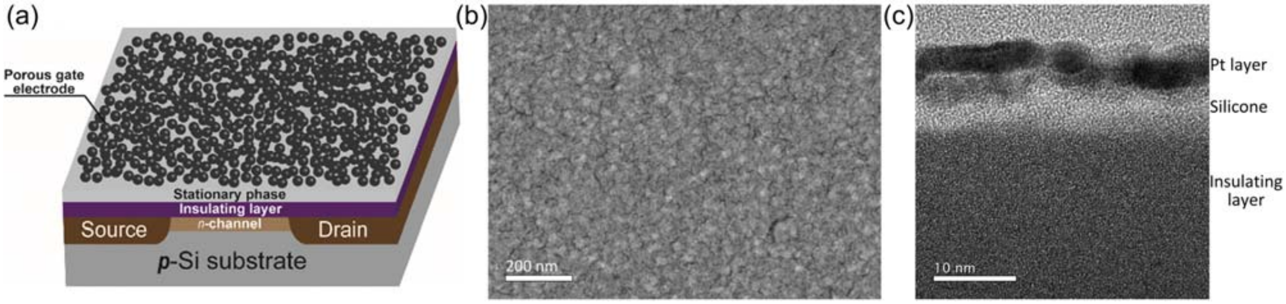


Fig. 1. Stationary-phase material-modified PGFET sensor. (a) Schematic illustration of the PGFET gate structure. The PGFET is an *n*-channel depletion mode device. (b) SEM observation of the porous Pt gate electrode. Scale bar is 200 nm (c) Cross-sectional TEM observation of the gate structure showing the stationary phase layer sandwiched between the insulating layer and porous gate electrode. Scale bar is 10 nm.

interaction layer. As shown in Table 1, dimethyl poly siloxane (silicone OV-1), PEG 4000, diethylene glycol succinate (DEGS) and tetrakis hydroxyethyl ethylene diamine (THEED), which are stationary phase materials typically used in GC columns,[11] were applied in this layer. Furthermore, a porous gate electrode consisting of a network of Pt nanoparticles (NPs) to enable gas molecules to access the stationary phase layer, was formed by a short-time radio-frequency sputtering process. The PGFET gate structure was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM) imaging. Aldehyde compounds, including nonanal, hexanal, and benzaldehyde (Table 2) were used as model gas-phase chemical analytes. Each vapor analyte was introduced under a dry N_2 carrier gas flow into the gas flow cell that arrayed and housed the stationary phase-modified PGFET sensors.

The real-time responses of the PGFET sensors to the different aldehydes at room temperature were monitored from the output voltage (V_{out}) of a dedicated electronic circuit.[9] In processing signals from the cross-reactive PGFET array, we extracted feature vectors through a discrete Fourier transform (DFT) process for a supervised learning approach. The data set of feature vectors were used for a machine-learning technique based on an algorithm of random forests for classification of signal patterns to recognize each aldehydic functionalized compound.

Table 1. List of stationary phase materials applied for PGFET sensors. GC general polarities P_{gen} based on McReynolds constants from ref. 10.

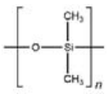
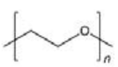
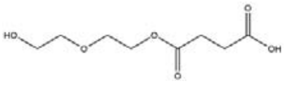
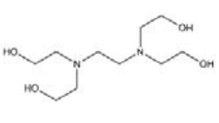
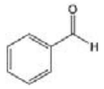
Sensor No.	Stationary phase	Chemical structure	P_{gen} in ref.10
s1	Dimethyl poly siloxane (silicone OV-1)		229
s2	Polyethylene glycol (PEG 4000)		2353
s3	Diethylene glycol succinate (DEGS)		3300
s4	Tetrakis hydroxyethyl ethylene diamine (THEED)		3725

Fig. S1 and Fig. 1b show top view images of the FET sensor and porous gate structure of s1 (See Table 1), respectively. We confirmed the porous morphology of the Pt gate electrode, as shown in Fig. 1b. Cross-sectional TEM images of the gate structure at scales of 10 and 200 nm are shown in Fig. 1c and Fig. S2, respectively. Furthermore, we confirmed the formation of the as-designed gate structure with the stationary phase layer sandwiched between the insulating layer and porous gate electrode. Representative real-time responsive measurements of the PGFET sensors to nonanal, hexanal, and benzaldehyde are shown in Fig. 2. The regions highlighted in red are the intervals during which the VOC analyte flowed. Exposure to each analyte provoked a chemical gating effect in the PGFET sensors and increased V_{out} in the circuit.[9] The response peaks of the PGFET sensors were reversible and repeatable for exposure to the aldehydes. Notably, each PGFET generated different peak patterns including fingerprint information such as peak height, width, kurtosis, response and recovery speed. Thus, the responsive properties of the PGFET-based sensor could be tuned by selection of the GC stationary phase material. The different peak heights generated from each stationary phase-modified PGFET device at room temperature are shown in Fig. S4.

The peak height from the silicone OV-1 modified PGFET (s1) at room temperature was higher than those of the other three PGFETs. We presume that this different response is caused by different interactions between the VOCs and stationary phases owing to

Table 2. Aldehydes as VOC analytes and their concentrations.

VOC analyte	Chemical structure	Gas-phase concentrations (ppm)
Nonanal		0.4, 0.8, 2
Hexanal		4, 7, 13
Benzaldehyde		0.7, 1, 6

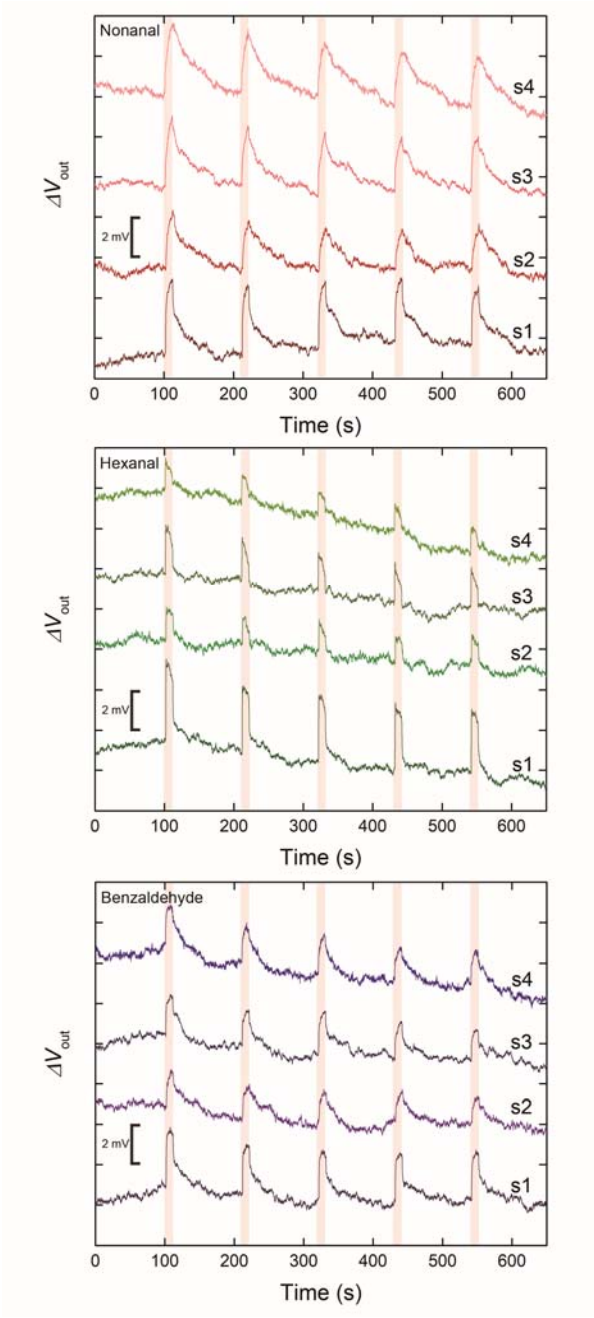


Fig. 2. Representative real-time responsive measurements of the PGFET sensors of s1–s4 to nonanal (0.8 ppm), hexanal (4 ppm), and benzaldehyde (1ppm).

polarity differences. The GC polarity based on McReynolds constants, which is a polarity scale for classifying GC stationary phases,[10] could be helpful for discussion of the responsive properties of stationary phase-modified PGFET. The reported values[10] of general polarities P_{gen} calculated from McReynolds constants of the GC stationary phases are summarized, as shown in Table 1. The P_{gen} value of silicone OV-1 is much smaller than those of the other three stationary phases. Therefore, at room temperature, hydrophobic interactions of alkyl or phenyl groups in the three aldehydic compounds might control their interactions with the PGFET modified with silicone OV-1, which has a relatively low GC polarity. To assist recognition of each aldehyde by machine learning, feature vectors extracted in signal processing were used to classify the peak patterns. For recognition of nonanal, hexanal, and benzaldehyde the F-measure, which relates to classification precision in the machine learning based on a random forest algorithm, was 62.8%. If classification of peak patterns from three aldehydes was conducted randomly, the classification precision was 33.3%. More precise classification precision was achieved in the stationary phase-modified PGFET sensing system. Notably, this machine learning-assisted recognition was conducted in three aldehydes that have similar chemical structures (Table 1). Although the precision based on the array consisting of four stationary phase-modified PGFETs in the preliminary work was low, we expect that increasing the number of PGFET sensors and their modification with various stationary phase materials might improve recognition precision of gas-phase chemicals based on an intelligent sensing system.

Conclusions

We report an intelligent sensing system consisting of cross-reactive chemical sensor array based on a GC stationary phase material-modified PGFETs. Each PGFET was modified with silicone OV-1, PEG 4000, DEGS, or THEED. The devices generated different response profiles owing to differences in the interaction of the stationary phase materials and the gaseous molecules. The sensing results indicate that the response of the chemical-sensitive PGFET can be tuned by selection of stationary phase materials. The data sets of feature vectors, extracted through DFT calculations, from individual PGFET sensor signals were applied in a supervised machine-learning approach to classify signal patterns for recognition of each aldehydic functionalized compound, namely nonanal, hexanal, and benzaldehyde. Notably, all three aldehydes had similar chemical structures. The classification precision for recognizing each aldehyde might be improved by increasing the number of PGFET sensors and data points. Long-term stabilities of PGFET sensors and quantifications of gas-phase chemicals should be tested for usability evaluations in future researches. Because FET-based sensors can be fabricated by semiconductor processes for miniaturization and large-scale integration on one chip, the intelligent sensing system shows attractive potential for compact electronic devices including mobile e-noses for environmental monitoring toward *IoT*.

This work was supported by the Impulsing Paradigm Change through Disruptive Technologies (ImPACT) Miyata Program from the Japan Science and Technology (JST) Agency.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 R. A. Potyralio, *Chem. Rev.*, 2016, **116**, 11877; A. Al-Fuqaha, M. Guizani, M. Mohammadi, M. Aledhari and M. Ayyash, *IEEE Commun.*, 2015, **17**, 2347.

2 W. Göpel, *Sens. Actuators, B* 1998, **52**, 125.

3 P. C. Jurs, G. A. Bakken and H. E. McClelland, *Chem. Rev.*, 2000, **100**, 2649; M. Bicego, G. Tessari, G. Tecchiolli and M. Bettinelli, *Sens. Actuators, B* 2002, **85**, 137; K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid and D. R. Walt, *Chem. Rev.*, 2000, **100**, 2595.

4 A. P. F. Turner and N. Magan, *Nat. Rev. Micro.*, 2004, **2**, 161; R. Vishinkin and H. Haick, *Small*, 2015, **11**, 6142; J. E. Fitzgerald, E. T. H. Bui, N. M. Simon and H. Fenniri, *Trends in Biotechnology*, 2017, **35**, 33; Ji-Wook and Jong-Heun Lee, *Lab Chip*, 2017, **17**, 3537; M. K. Nakhleh, H. Amal, R. Jeries, Y. Y. Broza, M. Aboud, A. Gharra, H. Ivgi, S. Khatib, S. Badarneh, L. Har-Shai, L. Glass-Marmor, I. Lejbkowicz, A. Miller, S. Badarny, R. Winer, J. Finberg, S. Cohen-Kaminsky, F. Perros, D. Montani, B. Girerd, G. Garcia, G.Simonneau, F. Nakhoul, S. Baram, R. Salim, M. Hakim, M. Gruber, O. Ronen, T. Marshak, I. Doweck, O. Nativ, Z. Bahouth, D. Shi, W. Zhang, Q. Hua, Y. Pan, L. Tao, H. Liu, A. Karban, E. Koifman, T. Rainis, R. Skapars, A. Sivins, G. Ancans, I. Liepniece-Karele, I. Kikuste, I. Lasina, I. Tolmanis, D. Johnson, S. Z. Millstone, J. Fulton, J. W. Wells, L. H. Wilf, M. Humbert, M. Leja, N. Peled and H. Haick, *ACS Nano*, 2017, **11**, 112.

5 H. Haick, Y. Y. Broza, P. Mochalski, V. Ruzsanyi and A. Amann, *Chem. Soc. Rev.*, 2014, **35**, 3523.

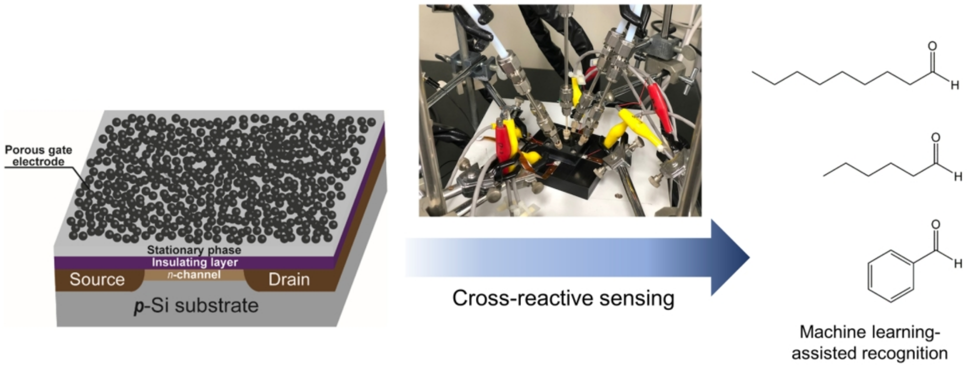
6 C. D. Natale, A. Macagnano, E. Martinelli, R. Paolesse, G. D‘Arcangelo, C. Roscioni, A. Finazzi-Agrò and A. D'Amico, *Biosens. Bioelectron.*, 2003, **18**, 1209; S. Dragonieri, M. P. van der Schee, T. Massaro, N. Schiavulli, P. Brinkman, A. Pinca, P. Carratú, A. Spanevello, O. Resta, M. Musti and P. J. Sterk, *Lung Cancer*, 2012, **75**, 326; A. T. Güntner, V. Koren, K. Chikkadi, M. Righettoni and S. E. Pratsinis, *ACS Sens.*, 2016, **1**, 528.

7 B. Wang, J. C. Cancilla, J. S. Torrecilla and H. Haick, *Nano Lett.*, 2014, **14**, 933; N. Shehada, G. Brönstrup, K. Funka, S. Christiansen, M. Leja and H. Haick, *Nano Lett.*, 2015, **15**, 1288.

8 H. M. Fahad, H. Shiraki, M. Amani, C. Zhang, V. S. Hebbar, W. Gao, H. Ota, M. Hettick, D. Kiriya, Y. Chen, Y. Chueh and A. Javey, *Sci. Adv.*, 2017, **3**, e1602557.

9 T. Yoshizumi, T. Goda, A. Matsumoto and Y. Miyahara, *Sens. Mater.*, 2018, **30**, 1001.

10 H. Rotzsche, *Stationary Phases in Gas Chromatography*, Elsevier Science, New York, 1991; E. F. Barry and R. L. Grob, *Columns for Gas Chromatography: Performance and Selection*, John Wiley and Sons, Hoboken, 2007.



79x40mm (600 x 600 DPI)