A sensor array based on trigonal-selenium nanowires for the detection of gas mixtures

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Abstract

A simple array-type gas sensor was fabricated using trigonal-selenium nanowires and its ability to detect volatile organic compounds was investigated. The time delays between sensor signals resulting from the varying diffusion velocities of gaseous organic compounds were assessed. The analysis of a model mixture of acetone and benzene was demonstrated. This sensor can operate at room temperature without any heating requirements and shows potential as a device of low power consumption and a low cost gas analysis system capable of differentiating the components of mixed gases.

Keywords: Se nanowires, Sensor array, Time delays, Gas analysis, Gas mixture

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1. Introduction

Up to now, number of one-dimensional (1D) nanostructured materials (nanomaterials) [1-3], such as nanotubes [4], nanowires [5-8], nanobelts [9] and nanofibers [10], have been discovered and intensively researched. Recently, based on the significantly enhanced performance of 1D nanomaterials resulting from their high surface-volume ratio, together with the properties of semiconductors, gas sensors [11-22] have been devised for use in numerous applications, including electronic noses [23,24], clinical assaying, explosive detection, and workplace hazard monitoring.

Semiconducting gas sensors have primarily used metal oxides such as SnO_2 [11-13] and these sensors typically must operate at temperatures of 300 to 550 °C, which results in significant power consumption. The gas detection in these devices takes advantage of the change in electrical conductivity induced when gases are adsorbed on the metal oxide surface, and heating of the metal oxide is necessary to improve the sensitivity. Recently, however, we reported a new gas sensor using trigonal-selenium nanowires (t-SeNWs) that does not require heating [19-22] and so can operate with reduced power consumption (less than one micro-watt) [22]. This sensor is capable of detecting various organic gases at room temperature and determining individual organic gases using the sensor response. Unfortunately, these sensors cannot distinguish between gases that induce similar levels of conductivity change.

Improving the discrimination of this device between gas types by using arrays of sensors having different characteristics has been considered as a possible solution to this problem [13,25]. For example, a sensor array that combines palladium and platinum catalysts [26] and a sensor array based on metal-decorated carbon nanotubes [27] have both been reported, although the fabrication of such devices is complicated and the discrimination of various gases depends on the quantity and types of gases to which these devices are exposed. Recently, the benefits of using chemosensory transduction over gas chromatography (GC) systems have been demonstrated by using a metal oxide gas sensor array for turbulent gas mixtures [28].

In this paper, we propose a uni-array gas sensor, in which one side of the electrode consists of a uni-electrode and the other side is composed of an array-electrode, based on the use of t-SeNWs. This device may be operated at room temperature and is also compact (the main part of the sensor is approximately $3.0 \times 5.5 \text{ mm}^2$ in size) and has the ability to discriminate between different types of gases. Herein we demonstrate that this sensor, even though physically small in size and uni-array gas sensor, can measure the time delay between sensor responses caused by the varying diffusion velocities of gaseous volatile organic compounds (VOCs) [29]. We also provide typical examples of the analysis of mixed gases generated by dropping mixtures of liquid acetone and benzene onto a cotton swab.

2. Experimental

The t-SeNWs used in this work were fabricated using the simple method developed by Ohtani et al. [8], employing commercially-available amorphous Se shots (a-Se, 99.9999% purity, Rare Metallic) and ethanol (99.5% purity) [19]. Approximately 18.0 mg of the a-Se material was ground into a powder in an agate mortar and transferred to a glass vial, following which ethanol (1 mL) was added. The vials were maintained at room temperature and, after several weeks, the a-Se powder was converted into t-SeNWs. The obtained t-SeNWs crystals were observed by high-resolution field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6490 operated at 30 kV. A typical FE-SEM image of t-SeNWs crystals is shown in Fig. 1. The average sizes of the t-SeNWs used in the experiments were diameter of 151 nm and length of 2.66 μm .

Fig. 2(a) and (b) show a schematic diagram of the uni-array electrical gas sensor and its photograph, respectively. The most important aspect of this sensor is that it consists of t-SeNWs combined with two electrodes. One of these is a uni-electrode (1.0 mm wide by 12.4 mm in length) with two drains (with a cross sectional area of $0.220 \times 0.700 \text{ mm}^2$) to allow gas flow on both sides.

The gas flows parallel to the long axis of the uni-electrode, as shown in Figs. 2(a) and (c). The uni-electrode was constructed from carbon tape (Nissin EM, size $1.2 \times 8.0 \text{ mm}^2$, 0.16 mm thick) on a thin Au layer (approximately 0.26 μm) electroplated on a thin Cu plate. The t-SeNWs were subsequently placed on the carbon tape to a thickness of approximately 26 μm .

Actually, the other electrode consisted of 16 array-electrodes as shown in Fig. 2(b), each 0.20 mm wide and separated by 0.20 mm, arranged along the gas flow direction, though the other electrode was drew with 8 array-electrodes as shown in Figs. 2(a) and (c). The array-electrodes were composed of a thin Au layer (approximately 0.26 μm) electroplated on a thin Cu plate. The gap between the two electrodes (the distance between the surface of the thin Au layer of the array-electrodes and the carbon tape on the uni-electrode) was approximately 0.20 mm. Since the side surface of the integrated t-SeNWs layer was situated parallel to the gas flow direction, the t-SeNWs functioned in the same manner as the adsorbent column of a GC system partially.

Sensor patterns were made using a mill/drill plotter system (ProtoMat S63, LPKF Laser & Electronics AG) typically employed for manufacturing circuit boards. Herein the individual sensors in the sensor array are denoted by detector number as det 1, det 2 and so on, starting from the gas inlet side. The main part of the sensor in which the two gas flows occurred was approximately $3.0 \times 5.5 \text{ mm}^2$ in size as shown in Fig. 2(b).

The current, I , generated by the sensor at a constant applied voltage, V , was measured using a semi-automated system constructed using several digital multimeters (ADC 7461A, time resolution 0.05 s) controlled by a computer, as shown in Fig. 2(c). Gaseous VOCs were generated by dropping pure liquid organic compounds onto a cotton swab (5 mm Φ , 10 mm in length) placed approximately 1 mm from the sensor. Controlled concentrations of gaseous VOCs were generated with a permeator (GASTEC PD-1B) by dilution with the purified air as a carrier gas or with an air bag (Tedlar, 5 L) to inject the desired quantity of the organic compound. A gas flow produced with a mini-pump (Shibata MP- Σ 30N for flow rate 0.2 L/min or MP- Σ 300N for 0.8 L/min). In

order to investigate the responses of individual sensors in the sensor array, detectors 1, 5, 9, 11 and 13 (det 1, det, 5, det, 9, det 11 and det 13) were selected. These data were obtained by using digital multimeter 1, 5, 9, 11 and 13, respectively.

3. Results and discussion

Fig. 3(a) shows typical results obtained from the sensor at $V=5.0$ V when gaseous methanol was produced by dropping methanol onto a cotton swab placed approximately 1 mm from the sensor. The gas concentration N (ppm) of methanol at cotton swab is 167000 ppm as listed in Table 1. Here the value of N was calculated using $10^6 P_B / P$ (ppm), where P_B (kPa) is the value of saturation vapor pressure listed in Table 1 and P ($= 101.325$ kPa) is the standard pressure at T ($= 298.15$ K) is the absolute temperature at room temperature [30]. In this plot each detector signal has been normalized by I_0 ($=0.566$ μ A for det 1, 18.210 μ A for det 5, 16.549 μ A for det 9, 33.561 μ A for det 11, and 1.524 μ A for det 13), the initial current measured before introducing the gas. In addition, the individual signals are offset vertically to avoid overlapping. When the methanol gas was introduced (as denoted by “gas on”) at 0 s, the electric current rapidly decreased from the initial value of I/I_0 to a minimum value I_m/I_0 . In addition, when the gas was cut off (“gas off”), the electric current returned rapidly to its initial value. The decrease in the electric current was likely caused by a decrease in the number of nanowire surface holes, which was compensated for by electrons released from the adsorbed organic molecules [19]. However, in this study, we were interested in the onset time of the current decrease at each detector rather than the signal intensity. Fig. 3(b) shows a magnification of the I/I_0 signal in the region just after introducing the gas. Here, each signal position is again shifted to avoid overlapping. As indicated by the arrows in this figure, the onset of the current decrease at each detection point varied with the detector number, meaning that we can measure a time delay associated with each detector. Fig. 3(c) summarizes the time delay at each detector, obtained from the difference between the onset time at the detector and the onset time of

det 1. It is evident that the time delay increased in a nonlinear manner with increasing detector number. We believe that this nonlinear variation was caused by the gradual decrease in gas concentration that occurred as the organic molecules were adsorbed on the surfaces of the t-SeNWs during the gas flow process, because the values of I_m/I_0 decreased with increasing detector number.

Fig. 4 shows typical I/I_0 data for det 1 and det 9 at $V=5.0$ V, when various gases (acetone, 1-propanol and 1-butanol) were produced by dropping these independently onto a cotton swab placed approximately 1 mm from the sensor. The gas concentrations of acetone, 1-propanol and 1-butanol are 304000, 27200, and 8500 ppm, respectively, as listed in Table 1. Each signal is once again vertically offset in this figure. It can be seen that the time delays between det 1 and det 9 are 0.55, 4.55 and 22.90 s for acetone, 1-propanol and 1-butanol, respectively. Thus, even though the sensor is quite small, there were measureable and characteristic differences in time delays between these gases. We subsequently measured the time delays between det 1 and det 9, $\Delta t_{1,9}$, for several other VOCs (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, benzene, toluene and acetone) at $V=5.0$ V and plotted the $\Delta t_{1,9}$ values for those gases against the inverse of the gas diffusion rates, V_D^{-1} ($s\ g^{-1}$), of these same gases in Fig. 5, applying logarithmic scales to both the vertical and a horizontal axes. The values of V_D applied in this plot were calculated using an equation for the diffusion rate of a vapor out of a tube [31,32]:

$$V_D = \beta \left(\frac{D_{AB} PM}{RT} \right) \cdot \ln \left(\frac{P}{P - P_B} \right), \quad (1)$$

where β is given by $\beta = A/L$, in which A (cm^2) is the cross-section of the flow path and L (cm) is the length of the flow path. The term D_{AB} ($cm^2\ s^{-1}$) is the vapor diffusion coefficient in air under standard pressure, P ($= 101.325$ kPa), in which the subscripts A and B represent air and the organic

compound, respectively, M (g mol^{-1}) is the molecular weight of the vapor, R ($\text{cm}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$) is the gas constant, T ($= 298.15 \text{ K}$) is the absolute temperature at room temperature and P_B (kPa) is the partial pressure of organic compound B at T [30]. Here, when $(P_B/P) \ll 1$, the value of V_D is approximately proportional to P_B/P ($=10^{-6}N$).

We calculated the value of D_{AB} ($\text{cm}^2 \text{ s}^{-1}$) in Eq. (1) using the Fuller-Schettler-Giddings equation [33]:

$$D_{AB} = \frac{1.00 \times 10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P \left[(\Sigma_V)_A^{1/3} + (\Sigma_V)_B^{1/3} \right]^2}, \quad (2)$$

where Σ_V is the sum of the atomic diffusion volumes [Table 1 in Ref. 33]. The value of V_D^{-1} (s g^{-1}) was then calculated using gas parameters listed in Table 1, employing $M_A = 28.97 \text{ g mol}^{-1}$, $(\Sigma_V)_A = 20.1 \text{ cm}^3 \text{ mol}^{-1}$ for air, a cross-section value $A = 0.220 \times 0.700 \text{ mm}^2$ and $L = 0.340 \text{ mm}$.

From Fig. 5, for released gases at the saturation vapor pressure with pure organic solution, we see that the time delay $\Delta t_{1,9}$ at $V=5.0 \text{ V}$ was proportional to V_D^{-1} and the relationship between these two variables may be described by a straight line, meaning that the volatile gas flows through the small drain in the sensor in the same manner as vapor moves through a diffusion tube. The exception is 1-pentanol, which required a long time to move through the sensor and deviates from the line. This deviation from the linear relationship occurred due to dilution of the gas concentration, because the concentration was decreased by adsorption to the t-SeNWs as the gas flowed through the sensor. In fact, according to Eq. (1), as the partial pressure P_B decreases, the value of V_D^{-1} increases.

The most important aspect of Fig. 5 is the demonstration that we can measure the characteristic time delays of individual gases using this small gas sensor. To date, simple gas sensors have typically measured a response, S , equal to $\Delta I/I_0$, where ΔI ($=I_0 - I_m$) is the change in electric current

induced by gas adsorption and I_0 is the initial current before the introduction of the gas. As a result, such sensors cannot distinguish gases having the same S values. In the present case, however, measuring the time delays between the sensor signals associated with various gases allows the sensor to differentiate gases with the same S values. As an example, Fig. 5 in Ref. 19 states that benzene and acetone produced by dropping methanol onto a cotton swab placed approximately 1 mm from the sensor have the same S value (about 0.2) but Fig. 5 illustrates that the present sensor can differentiate their mixture. As shown in Fig. 5, the time delays of benzene and acetone were 1.40 s and 0.55 s, respectively, and thus we can separate these gases in the sensor.

In the case of gases with similar $\Delta t_{1,9}$ values, we can tell them apart by measuring $\Delta t_{1,n}$ ($n > 9$) values, because $\Delta t_{1,n}$ will vary in a nonlinear manner with detector number. As an example, the $\Delta t_{1,9}$ for benzene and ethanol are 1.40 s and 1.25 s in Fig. 5, respectively, but the $\Delta t_{1,11}$ values are 3.00 s and 1.55 s. Therefore, we can readily distinguish these gases.

Fig. 6 (a) shows the typical magnification of the I/I_0 signal for det 1 and det 13 at $V=5.0$ V in the region just after introducing the mixed gases of acetone and benzene (gas on). Here, gaseous VOCs for mixtures of acetone and benzene were generated by dropping mixed these organic liquid compounds onto a cotton swab (5 mm Φ , 10 mm in length) placed approximately 1 mm from the sensor. In this case, the gas concentration of acetone and benzene are 304000 and 125000 ppm, respectively. As indicated by the arrows in Fig. 6(a), the onset of the current decrease at the detector number 13 decreased with increasing the ratio of liquid acetone in the mixture x . Fig. 6(b) shows the experimental results obtained from measuring the time delays between det 1 and det 13, $\Delta t_{1,13}$ (closed circles), and S value at det 1, S_1 (closed lozenges), against x . The $\Delta t_{1,13}$ values for benzene and acetone under these conditions were 5.73 s and 2.04 s, respectively, and the characteristic value obtained for the mixture of liquid acetone and liquid benzene is seen to change with x . From this result, if the composition of a gas mixture is known, we can use the sensor to identify the mixing ratio for these liquids by measuring the time delay.

Fig. 7(a) shows typical results of the I/I_0 signal for det 1 (broken line) and det 13 (solid line) at various concentration of gaseous ethanol under the gas flow condition of 0.2 L/min. When the ethanol gas was introduced (as denoted by “gas on”) at 0 s, the electric current rapidly decreased from the initial value of I/I_0 to a minimum value. In addition, when the gas was cut off (“gas off”), the electric current returned rapidly to its initial value. Fig. 7 (b) shows a magnification of the I/I_0 signal for det 1 (broken line) and det 13 (solid line) in the region just after introducing the ethanol gas. The value of $\Delta t_{1,13}$ as indicated by the thin parallel lines in this figure increases with decreasing gas concentration, while the slope of the I/I_0 signal decreases with decreasing the gas concentration. The closed triangles and open circles in Fig. 7(c) show the gas concentration dependences of the value of $\Delta t_{1,5}$ and $\Delta t_{1,13}$ at $V=5.0$ V, respectively, under the gas flow condition of applying gaseous ethanol at 0.2 L/min. The values of $\Delta t_{1,5}$ and $\Delta t_{1,13}$ are approximately proportional to the inverse of the gas concentration, that is, these data indicate that the gas diffusion velocity is reduced at lower concentrations. Therefore, in order to analyze for gases with long time delays during a short time period, a reduced quantity of detectors and high flow speed should be employed. For example, as the closed circles in Fig. 7(c), adopting the gas flow condition of applying gaseous ethanol at 0.8 L/min, the value of $\Delta t_{1,5}$ in the region of low concentration can be detected during a short time period. The decrease of the slope of the I/I_0 signal with decreasing the gas concentration is caused by the gas adsorption of the integrated t-SeNWs layer situated parallel to the gas flow direction as like the adsorbent column of a GC system.

The distinguishing ability of our sensor has been investigated and visualized using Principal Component Analysis (PCA) which is well known and widely used for processing of multidimensional data sets obtained in chemical applications [13,14,25,26,34]. PCA operates on a set of data to create a new coordinate system. The first principal component (PC1) captures the

maximum amount of variance possible in the original data set. The second PC (PC2) captures the maximum possible amount of the residual variance, and so on.

First, PCA was based on the data sets of $\Delta t_{1,5}$, $\Delta t_{1,9}$, $\Delta t_{1,11}$, $\Delta t_{1,13}$, and S_1 for 8 gases of VOCs in Table 1. Here, in order to improve the distinguishing ability of our sensor, the S_1 value for 8 gases was added to the measurement set. The S_1 value for 8 gases was the same value of Fig. 5 in Ref. 19. In the data sets of $\Delta t_{1,5}$, $\Delta t_{1,9}$, $\Delta t_{1,11}$, $\Delta t_{1,13}$, and S_1 , most variance was in the first two PCs (PC1+PC2= 88.24+11.73= 99.97 %), that is, the information could be represented reasonably well with the first two principal components. On the other hand, we have also analyzed the data sets of $\Delta t_{1,9}$ and S_1 for 8 gases of VOCs. In this case, the relative contribution of the PC1 and PC2 was 80.52 % and 19.48 %, respectively. Fig. 8 presents the resulting PCA score plot. This was the same pattern of the PCA score plot obtained from the data sets of $\Delta t_{1,5}$, $\Delta t_{1,9}$, $\Delta t_{1,11}$, $\Delta t_{1,13}$, and S_1 . A size of circles in Fig. 8 shows the magnitude difference of V_D^{-1} for 8 gases. Since the circles in Fig. 8 distribute almost regularly, the relation of Fig. 5 is supported. Using PCA, particularly, 8 gases of VOCs can be classified with alcoholic gas group (open circles) and the other (closed circles). Second, PCA was based on the data sets of $\Delta t_{1,9}$ and S_1 for mixtures of acetone and benzene in Fig. 6(b). Fig. 9 presents the resulting PCA score plot. The relative contribution of the PC1 and PC2 is 84.39 % and 15.61 %, respectively. Since the circles distribute regularly for x , we could use the sensor to identify the mixing ratio for these liquids by measuring the time delay as shown in Fig. 6(b), if the composition of a gas mixture is known. Third, PCA was based on the data sets of $\Delta t_{1,5}$, $\Delta t_{1,13}$ and S_1 for ethanol gas concentrations from 168 ppm to 16772 ppm. Fig. 10 presents the resulting PCA score plot. The relative contribution of the PC1 and PC2 is 79.28 % and 20.70 %, respectively. Since the circles distribute regularly, we could use the sensor to identify the gas concentration by measuring $\Delta t_{1,5}$ and $\Delta t_{1,13}$ as show in Fig. 7(c).

It is not simple to estimate the limit of detection (LOD) [35] of our sensor, because our sensor is

relevant to the signal intensity of sensor and the different time $\Delta t_{1,N}$ between det 1 and det N . Considering the high gas concentration, since the signal intensity of sensor is thoroughly large, the LOD is mainly dominated by the time resolution of the detection of $\Delta t_{1,N}$. In this case, the estimated LOD value based on the standard deviation (factor $k=3.3$) [35] of the blank samples in Figs. 6(a) and 7(b) would be 0.165s. On the other hand, for low gas concentration, since the value of $\Delta t_{1,N}$ has thoroughly large, the LOD is mainly dominated by the signal intensity of sensor noise, which is mainly caused by current noise of SeNWs. Then, the estimated LOD value based on the standard deviation (factor $k=3.3$) [35] of the blank samples in Figs. 6(a) and 7(b) would be 2 ppm.

As discussed above, this compact uni-array-type gas sensor functions by assessing the time delays between sensors caused by the varying diffusion velocities of gases. Moreover, our sensor has good reproducibility upon repeated exposure to VOCs. Although the data are not included herein, it was also determined that this sensor was able to detect CO₂ in addition to VOCs [29].

4. Conclusion

We successfully fabricated a uni-array-type gas sensor using trigonal-selenium nanowires. This sensor can operate at room temperature without any heating requirements and so can operate with low-power consumption. Moreover, although our sensor is compact, it can measure the time delays between sensor signals associated with various gases. We found that we can differentiate specific organic compounds by measuring the signal time delays and were able to demonstrate this capability by analyzing a mixture of acetone and benzene generated by dropping mixed these organic compounds onto a cotton swab. This sensor shows potential as a portable gas analysis system.

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References

- [1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, One-dimensional nanostructures: synthesis, characterization, and applications, *Adv. Mater.* 15 (2003) 353–389.
- [2] W. Lu and C. M. Lieber, Semiconductor nanowires, *J. Phys. D* 39 (2006) R387–R406.
- [3] M. Batzill and U. Diebold, The surface and materials science of tin oxide, *Prog. Surf. Sci.* 79 (2005) 47–154.
- [4] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56–58.
- [5] A. M. Morales and C. M. Lieber, A Laser ablation method for the synthesis of crystalline semiconductor nanowires, *Science* 279 (1998) 208–211.
- [6] B. Gates, B. Mayers, A. Grossman, and Y. Xia, A sonochemical approach to the synthesis of crystalline selenium nanowires in solutions and on solid supports, *Adv. Mater.* 14 (2002) 1749–1752.
- [7] B. Mayers, B. Gates, and Y. Xia, One-dimensional nanostructures of chalcogens and chalcogenides, *Int. J. Nanotechnol.* 1 (2004) 86–104.
- [8] T. Ohtani, N. Takayama, K. Ikeda, and M. Araki, Unusual crystallization behavior of selenium in the presence of organic molecules at room temperature, *Chem. Lett.* 33 (2004) 100–101.
- [9] Z. W. Pan, Z. R. Dai, and Z. L. Wang, Nanobelts of semiconducting oxides, *Science* 291 (2001) 1947–1949.
- [10] C. H. Liang, G. W. Meng, Y. Lei, F. Phillipp, L. D. Zhang, Catalytic growth of semiconducting In_2O_3 nanofibers, *Adv. Mater.* 13 (2001) 1330–1333.
- [11] N. Yamazoe, Toward innovations of gas sensor technology, *Sens. Actuators B* 108 (2005) 2–14.
- [12] X. -J. Huang and Y. -K. Choi, Chemical sensors based on nanostructured materials, *Sens. Actuators B* 122 (2007) 659–671.

- [13] P. C. Chen, G. Shen, and C. Zhou, Chemical sensors and electronic noses based on 1-D metal oxide nanostructures, *IEEE trans. nanotechnology* 7 (2008) 668–682.
- [14] T. Zhang, S. Mubeen, N. V. Myung, and M. A. Deshusses, Recent progress in carbon nanotube-based gas sensors, *Nanotechnology* 19 (2008) 332001–332014.
- [15] X. Chen, C. K. Y. Wong, C. A. Yuan, G. Zhang, Nanowire-based gas sensors, *Sens. Actuators B* 177 (2013) 178–195.
- [16] T. Someya, J. Small, P. Kim, C. Nuckolls, and J. T. Yardley, Alcohol vapor sensors based on single-walled carbon nanotube field effect transistors, *Nano Lett.* 3 (2003) 877–881.
- [17] Z. Liu, T. Yamazaki, Y. Shen, T. Kikuta, N. Nakatani, and T. Kawabata, Room temperature gas sensing of *p*-type TeO₂ nanowires, *Appl. Phys. Lett.* 90 (2007) 173119–1-3.
- [18] E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan, Z. L. Wang, Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts, *Appl. Phys. Lett.* 81 (2002) 1869–1871.
- [19] N. Akiyama and T. Ohtani, Gas detection of volatile organic compounds using trigonal selenium nanowires, *Jpn. J. Appl. Phys.* 50 (2011) 015002–1-4.
- [20] N. Akiyama and T. Ohtani, Gas sensitive material comprising microcrystalline selenium and gas sensor using same, Japan Patent no.5120904 (2012). Korean Patent no.10-1447788 (2014). U.S. Patent Application 13-508292 (2012), German Patent Application 11-2010-004-279.9 (2012), based on International Application PCT/JP2010/069614.
- [21] N. Akiyama and T. Ohtani, Adsorption of primary alcohol molecules on trigonal selenium nanowires, *Jpn. J. Appl. Phys.* 52 (2013) 105001–1-5.
- [22] N. Akiyama, Gas sensor and gas sensor array, International Application PCT/JP2014/78760.
- [23] K. Persaud and G.H. Dodd, Analysis of discriminant mechanisms in the mammalian olfactory system using a model nose, *Nature* 299 (1982) 352–355.
- [24] J. Gardner and P. Bartlett (Eds.), *Electronic Noses Principles and Applications*, New York, Oxford University Press, 1999.

- [25] K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid, and D. R. Walt, Cross-reactive chemical sensor arrays, *Chem. Rev.* 100 (2000) 2595–2626.
- [26] T. Eklöv and I. Lundström, Distributed sensor system for quantification of individual components in a multiple gas mixture, *Anal. Chem.* 71 (1999) 3544–3550.
- [27] A. Star, V. Joshi, S. Skarupo, D. Thomas. J. C. Gabriel, Gas sensor array based on metal-decorated carbon nanotubes, *J. Phys. Chem. B* 26 (2006) 21014–21020.
- [28] J. Fonollosa, I. R-Luján, M. Trincavelli, A. Vergara and R. Huerta, Chemical discrimination in turbulent gas mixtures with MOX sensors validated by gas chromatography-mass spectrometry, *Sensors* 14 (2014) 19336–19353.
- [29] N. Akiyama, Gas sensor array, gas analysis method, and gas analysis system, Japan Patent Application 2014-533156 (2014), U.S. Patent Application 14-425560 (2015), based on International Application PCT/JP2013/073577.
- [30] W. M. Haynes (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 2012, 92th ed., Sect. 6.
- [31] J. M. Mckelvey, H. E. Hoelscher, Apparatus for preparation of very dilute gas mixtures, *Anal. Chem.* 29 (1957) 123–123.
- [32] A. P. Altshuller, I. R.Cohen, Application of diffusion cells to the production of known concentrations of gaseous hydrocarbons, *Anal. Chem.* 32 (1960) 802–810.
- [33] E. N. Fuller, P. D. Schettler, and J. C. Giddings, A new method for prediction of binary gas-phase diffusion coefficients, *Ind. Eng. Chem.* 58 (1966) 19–27.
- [34] S. Wold, K. Esbensen and P. Geladi, Principal component analysis, *Chemom. Intell. Lab. Syst.* 2 (1987) 37–52.
- [35] J. Fonollosa, A. Vergara, R. Huerta, S. Marco, Estimation of the limit of detection using information theory measures. *Analytica Chimica Acta*, 810 (2014) 1–9.

Figure captions

Fig. 1. FE-SEM image of t-SeNWs. Scale bar = 0.5 μ m.

Fig. 2. Schematic diagram (a) and photograph (b) of the uni-array electrical gas sensor, and diagram detailing electrical current measurements in the gas sensor (c).

Fig. 3. Typical I/I_0 values (normalized by the initial current) on the application of gaseous methanol (a), I/I_0 values immediately after introducing the gas (b), and time delay as a function of the number of detectors (c). The signals in (a) and (b) have been shifted vertically to avoid overlap.

Fig. 4. Typical I/I_0 values (normalized by the initial current) obtained for gaseous acetone, 1-propanol and 1-butanol. The signals have been shifted vertically to avoid overlap.

Fig. 5. Time delays between det 1 and det 9 for methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, benzene, toluene and acetone, plotted against the inverse gas diffusion velocity, V_D^{-1} .

Fig. 6. Typical I/I_0 values (normalized by the initial current) immediately after introducing the gaseous acetone and benzene (a), and time delays between det 1 and det 13, $\Delta t_{1,13}$ (solid circles), and S value at det 1, S_1 (solid lozenges), for the ratio of acetone in the mixture x (b).

Fig. 7. Typical I/I_0 values (normalized by the initial current) obtained for various concentration of gaseous ethanol under the gas flow condition of 0.2 L/min (a), I/I_0 values immediately after introducing the gas (b), and gas concentration dependences of the time delay, $\Delta t_{1,5}$ and $\Delta t_{1,9}$, when applying gaseous ethanol at flow speed 0.8 L/min and 0.2 L/min (c).

Fig. 8. PCA score plot for time delays between det 1 and det 9 for methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, benzene, toluene and acetone. A size of circle shows the magnitude difference of V_D^{-1} for 8 gases.

Fig. 9. PCA score plot for mixtures of acetone and benzene.

Fig. 10. PCA score plot for several concentrations of ethanol.

Table 1

Calculated values of vapor diffusion coefficients, inverse gas diffusion velocities, experimental time delays and associated gas parameters used for calculations.

	M_B	P_B	$(\Sigma_V)_B$	D_{AB}	V_D^{-1}	$\Delta t_{1,9}$	N
	(g mol ⁻¹)	(kPa)	(cm ³ mol ⁻¹)	(cm ² s ⁻¹)	($\times 10^7$ s g ⁻¹)	(s)	(ppm)
Methanol	32.042	16.9	29.9	0.1618	0.571	0.95	167000
Ethanol	46.068	7.87	50.36	0.1234	1.175	1.25	77700
1-Propanol	60.095	2.76	70.82	0.1029	3.162	4.55	27200
1-Butanol	74.121	0.86	91.28	0.0899	9.512	22.90	8500
1-Pentanol	88.148	0.259	111.74	0.0807	29.675	158.50	2560
Benzene	78.112	12.7	90.68	0.0895	0.577	1.40	125000
Toluene	92.139	3.79	111.14	0.0804	1.912	4.50	37400
Acetone	58.079	30.8	66.86	0.1059	0.242	0.55	304000

Fig. 1

Fig.2(a)

Fig. 2(b)

Fig.2(c)

Fig.3(a)

Fig.3(b)

Fig.3(c)

Fig. 4

Fig.5

Fig.6(a)

Fig. 6(b)

Fig.7(a)

Fig.7(b)

Fig.7(c)

Fig. 8

Fig. 9

Fig. 10