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# Field-Effect Transistors for Gas Sensing

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## Abstract

This chapter reviews gas-sensitive field-effect transistors (FETs) for gas sensing. Although various types of gas sensors have been reported, this review focuses on FET-based sensors such as catalytic-gate FETs, solid electrolyte-based FETs, suspended-gate FETs, and nanomaterial-based FETs. For recognition of analytes in the gas phase, the combination of cross-reactive gas sensor arrays with pattern recognition methods is promising. Cross-reactive sensor arrays consist of gas sensors that have broad and differential sensitivity. Signals from the cross-reactive sensor array are processed using pattern recognition methods. Reports of FET-based sensor arrays combined with pattern recognition methods are briefly reviewed.

**Keywords:** gas-sensitive field-effect transistor, gas sensor, cross-reactive sensor array, pattern recognition method

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## 1. Introduction

The importance and demand for sensing gases, vapors, and volatile organic compounds (VOCs) have been increasing in fields such as diagnostics [1–4], environmental monitoring for industrial, agricultural, home safety, and so on [4, 5]. Various types of gas sensors and sensor arrays have been researched and developed [6–8], including field-effect transistor (FET)-based sensors. Following the report of pioneering work on catalytic-gate FETs, research on FET-based gas sensors has been extended to various types of gas-sensitive FETs. In this chapter, catalytic-gate FETs, suspended-gate FETs (SGFETs), and solid electrolyte-based FETs are introduced. Gas-sensitive FETs based on nanomaterials such as carbon nanotubes (CNTs), nanowires (NWs), graphene, and transition metal chalcogenides have also been investigated because the high surface-to-volume ratios of nanomaterials are attractive for improving sensor properties [5, 9]. These nanomaterial-based FETs are also reviewed.

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For recognition of gaseous and volatile analytes from sensing results, two main methods have been used [3]. The conventional recognition method uses selective sensors with specific receptors designed for selective interaction with target analytes [3, 6]. Another recognition method uses a combination of cross-reactive sensor arrays and pattern recognition methods [3, 6–8, 10]. These cross-reactive sensor arrays consist of gas sensors that are responsive to a broad range of analytes and have differential sensitivities. To date, various gas sensors have been applied in sensor arrays [6, 8], including gas-sensitive FETs. In this chapter, research on the combination of FET-based sensor arrays and pattern recognition methods is briefly reviewed.

## 2. Gas-sensitive FETs and field-effect devices combined with catalytic metal gates

Catalytic-gate FETs are one of types of gas-sensitive FETs. In 1975, Lundström et al. first reported a Pd-gate FET sensitive to hydrogen [11, 12]. Pioneering research on catalytic-gate FETs opened up the field of FET-based gas sensors and other gas-sensitive field-effect devices such as capacitor-based [13–17] and Schottky diode-based sensors [18, 19]. Catalytic-gate field-effect devices feature a nanoscale layer of catalytic metals, such as palladium and platinum, as a gate electrode on insulating layers in a metal-insulator-semiconductor (MIS) structure [20]. **Figure 1** shows reported schematic illustrations of this structure and the threshold voltage shift of a Pd-gate FET that is sensitive to hydrogen [21]. In initial reports of catalytic-gate FETs, Pd as a catalytic-gate electrode was deposited onto the insulating layer of the MIS structure of the FET [11, 12, 21]. **Figure 2** shows changes observed in the threshold voltage [11] on hydrogen introduction to Pd-gate FETs. The gas-sensitive mechanisms of catalytic-gate FETs and catalytic-gate field-effect devices have been described in earlier reviews [20, 21].

Porous metal gates in catalytic-gate field-effect devices have allowed for important progress in  $\text{NH}_3$  sensing [20, 22]. **Figure 3** shows reported TEM observations of 3- and 7-nm-thick Pt layers evaporated onto  $\text{SiO}_2$ . These thin Pt layers consist of discontinuous metals [22]. The choice of catalytic materials, the structure of the catalytic layer, and the operating temperature affect the sensitivity and selectivity of catalytic-gate field-effect devices [14, 15, 20]. Furthermore, the type of insulating materials used in the MIS structure also influences the responsive properties of gas-sensitive field-effect devices [16].

For operation at high temperatures, silicon carbide (SiC)-based FETs have been investigated. SiC is a wide-bandgap semiconductor, and can be used as a substrate for the MIS structure instead of the conventional Si substrate [17]. SiC can be used at high temperatures and harsh environments because of its chemical inertness [23–25]. SiC-based FETs have been applied to the sensing of CO [23],  $\text{NH}_3$  [23, 24],  $\text{NO}_2$  [24], and  $\text{SO}_2$  [25]. As with conventional catalytic-gate FETs using an Si substrate, the catalytic-gate material used in SiC-based FETs influences the sensitivity and selectivity of the sensor [25].

Catalytic-gate devices consisting of high-electron mobility transistors (HEMTs) have also been studied for operation at high temperature. For example, GaN/AlGaN heterostructures that exhibit two-dimensional electron gas (2DEG) induced by spontaneous and piezoelectric polarization at the interface of the heterostructure have been applied to a catalytic-gate HEMT

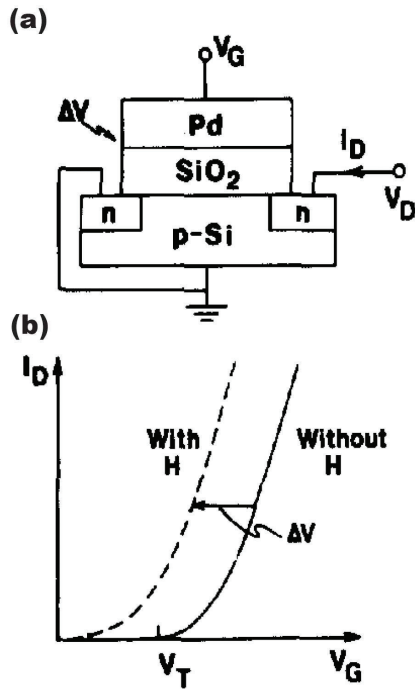


Figure 1. Schematic illustrations of the (a) structure and (b) threshold voltage shift of a Pd-gate FET sensitive to hydrogen. Reprinted with permission from Ref. [21]. Copyright 1993 Elsevier.

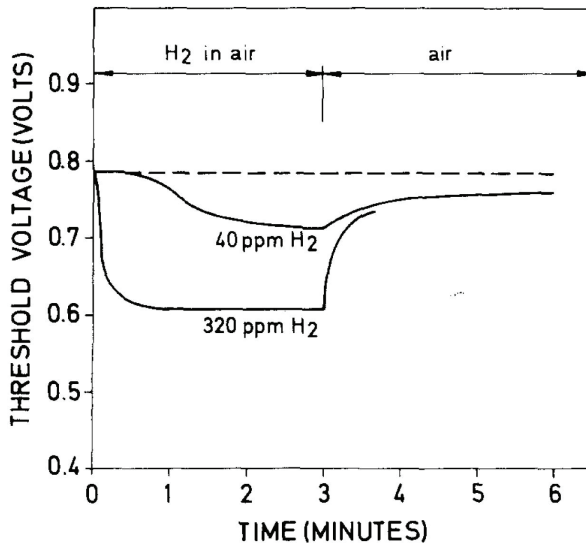
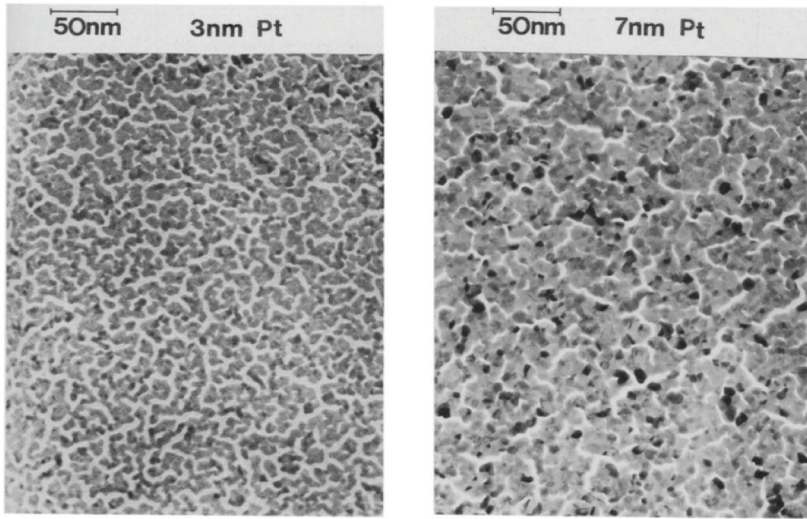


Figure 2. Changes in the threshold voltage toward H<sub>2</sub> at different concentrations at 150°C. Reprinted with permission from Ref. [11]. Copyright 1975 American Institute of Physics.



**Figure 3.** Transmission electron micrographs of 3- and 7-nm thick porous Pt metal layers on  $\text{SiO}_2$ . Reprinted with permission from Ref. [22]. Copyright 1987 Elsevier.

as a gas sensor [26]. In this report, the GaN/AlGaN-based HEMT combined with a Pt gate electrode was operated at about  $400^\circ\text{C}$  for sensing of  $\text{H}_2$ , CO,  $\text{C}_2\text{H}_2$ , and  $\text{NO}_2$ .

### 3. Solid electrolyte-based FETs

Solid electrolytes can also be applied to FET-based sensors. For example, an FET-based oxygen sensor using yttria-stabilized zirconia (YSZ) as a solid electrolyte (**Figure 4**) has been reported [27]. In this sensor, a YSZ film was formed on an insulating layer consisting of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$ . Furthermore, a nanoscale layer of Pt was deposited on the YSZ film as a gate electrode. **Figure 5** shows responses of this sensor to oxygen and nitrogen (1 atm) [27]. At room temperature, a repeated stepwise response curve and a subsequent drift were observed. The response of the sensor showed a linear relationship against the partial pressure of oxygen in a logarithmic range between 0.01 and 1 atm. The sensitivity of the sensor to oxygen increased as the thickness of the Pt layer decreased.

To investigate the YSZ-based FET structure for use as an oxygen sensor, the crystalline structure and electrical properties were studied for a YSZ film deposited on a layer of  $\text{Si}_3\text{N}_4$  by RF sputtering [28]. In the capacitance-voltage curve, hysteresis was observed, and was considered to be caused by the movement of oxygen ions and/or electrons in the YSZ film. This resulted in an unstable response at room temperature as mentioned above. Therefore, to increase the stability and quicken the response of the oxygen sensor at room temperature, the solid electrolyte-based FET would need to incorporate an electrolyte with a high diffusion coefficient for oxygen ions [28].

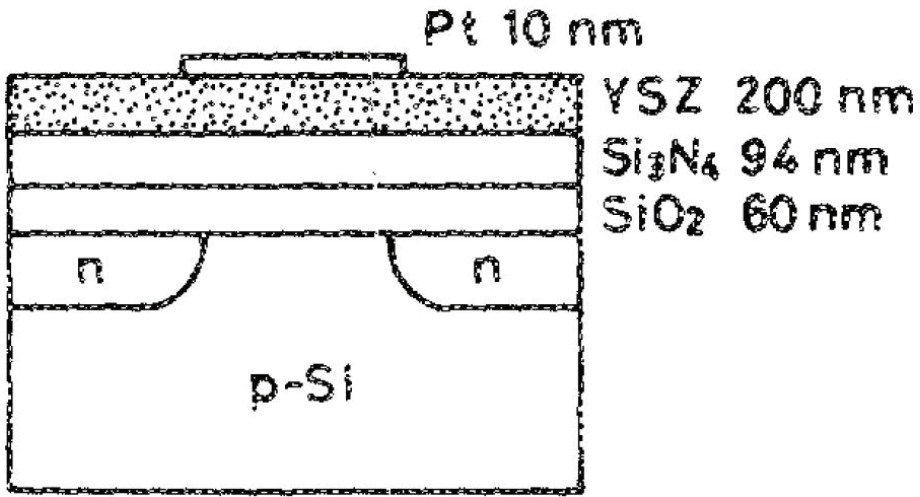


Figure 4. Schematic illustration of a YSZ-based FET. The YSZ-based FET is n-channel type and depletion-mode device. A nanoscale Pt layer is formed on a layer of YSZ. Reprinted with permission from Ref. [27]. Copyright 1988 American Institute of Physics.

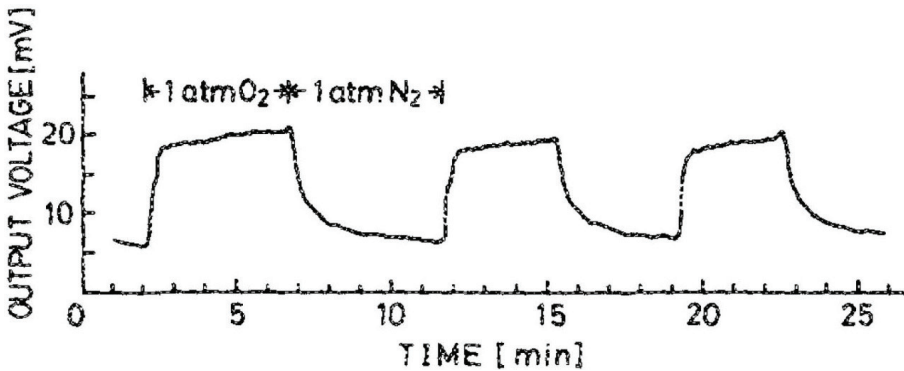
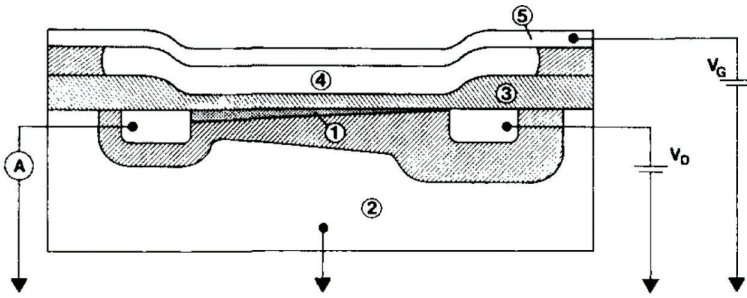


Figure 5. Responses at 20°C of a YSZ-based FET against O<sub>2</sub> and N<sub>2</sub>. Reprinted with permission from Ref. [27]. Copyright 1988 American Institute of Physics.

#### 4. Suspended-gate FETs

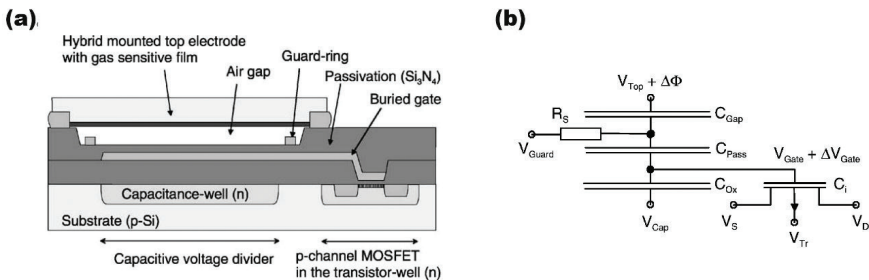
In 1983, Janata et al. reported an SGFET sensitive to dipolar molecules such as methanol and methylene chloride [29]. In the SGFET shown in Figure 6, fluid samples can penetrate into the gap between the insulating layer and the suspended metal mesh. Electrochemical surface modification using polypyrroles has been used to improve the selectivity of the SGFET [30]. This report described the preparation of SGFETs with differential selectivity by chemical modification with a polymer coating.



**Figure 6.** Schematic illustration of a suspended gate FET. Reprinted with permission from Ref. [29]. Copyright 1983 American Institute of Physics.

Improvement of fabrication processes is an important topic in SGFET research. Hybrid SGFETs prepared using an improved process and with diverse materials in the sensing layer have been reported [31]. In the fabrication process of hybrid SGFETs, the gate and body chip are prepared separately and then combined. This manufacturing technique has advantages over conventional methods because it allows for incorporation of a diverse range of sensitive materials in the structure. The flip-chip method has also been applied to the preparation of an SGFET for sensing ammonia [32]. In this report, a polyacrylic acid layer was formed on the gate structure by a spraying process.

The air gap in the gate structure of an SGFET causes undesirable effects on the sensing stability because of a lack of passivation, small W/L ratio, and a low gate capacity [33]. To overcome these drawbacks, research on SGFETs has been expanded to capacitively controlled FETs (CCFETs) [33] and floating-gate GasFETs (FGFETs) [34]. CCFETs contain an FET structure and a gas-sensitive capacitor with an air gap. FGFETs are a modification of CCFETs that use a floating gate for improved signal stability [34]. An FGFET with a hybrid-mounted gas-sensitive top electrode has been reported (**Figure 7a**) [34]. In this structure, the gas-sensitive capacitor and read-out transistor were integrated in one chip. **Figure 7b** shows the equivalent circuit diagram of the FGFET. The gate and the plate are electrically floating because they are isolated by the  $\text{SiO}_2$  layer. This FGFET was used for sensing  $\text{H}_2$  (500 ppm).



**Figure 7.** (a) Schematic illustration and (b) equivalent circuit diagram of a reported FGFET. Reprinted with permission from Ref. [34]. Copyright 2003 Elsevier.

Different FET-based sensors can be combined to extend the sensitivity range. For example, an SGFET responsive to high concentrations of  $H_2$  and a catalytic-gate FET with good sensitivity for low concentrations of  $H_2$  have been combined in one chip to increase the sensitivity range [35].

## 5. Nanomaterial-based FETs

FET-based gassensors have been expanded to sensors containing nanomaterials. Nanomaterial-based FETs have large surface-to-volume ratios, which contribute to high sensitivity and fast response and recovery times [3]. Nanomaterials allow for high-packing densities because of their intrinsic small dimensions [5]. This section briefly reviews FET-based gas sensors using nanomaterials such as CNTs, NWs, graphene, and transition metal chalcogenides.

### 5.1. CNT-based FETs

The fabrication of CNT-based FETs was first reported in 1998 [36, 37]. A typical CNT-based FET consists of a CNT, source and drain electrodes, insulating layer, and a substrate as the back gate [38]. Both individual CNTs and random networks of CNTs can be used to prepare CNT-based FETs. Chemical-gating effects of an individual single-walled CNT-based FET caused by exposure to gaseous  $NH_3$  or  $NO_2$  were reported in 2000 [39]. To date, CNT-based FETs have been applied to sensing  $H_2$  [40],  $CH_4$  [40],  $CO$  [40],  $CO_2$  [41],  $NO_2$  [40],  $NH_3$  [40],  $H_2S$  [40], alcohols [42], and breath samples [43].

To improve the sensitivity and selectivity of CNT-based FETs, they have been modified with nanoscale catalytic materials such as Pd [40, 44], Pt [40, 44], Rh [40], Au [40, 44], and Ag [44]. Furthermore, modifications with polymers [41], peptides [44], olfactory receptor proteins [45], and DNA [46, 47] have been reported.

### 5.2. NW-based FETs

#### 5.2.1. Gas-sensitive FETs using Si NWs

As a gas-sensitive FET using one-dimensional nanomaterials, an application of an Si NW-based FET for sensing  $NH_3$  was reported in 2006 [48]. After that, an FET-based sensor consisting of a highly ordered Si NW array on a bendable plastic substrate was prepared and applied to sensing  $NO_2$  at parts per billion levels [49]. Furthermore, Si NW-based sensors have been applied to sensing  $H_2$  [50].

Despite the potential of Si NW-based FETs for gas sensing, the sensitivity of bare Si NW-based FETs toward nonpolar volatile analytes is limited [51]. To overcome this, the native  $SiO_2$  layer on the surface of the Si NWs has been chemically modified with silane monolayers [51]. Silane monolayer-modified Si NW-based FETs have been used for sensing nonpolar VOCs [51] and exhaled breath samples [52]. Modification with nanoparticles [50] has also been used to improve the responses of Si nanomaterial-based FETs to target analytes. In addition, an Si nanoribbon-based FET functionalized with an organic compound that is reactive toward nerve agents at sub-ppm levels has been reported [53].

### 5.2.2. Gas-sensitive FETs using metal oxide NWs or compound semiconductor NWs

Metal oxide NWs such as  $\text{In}_2\text{O}_3$  [54, 55],  $\text{SnO}_2$  [56–58], and  $\alpha\text{-Fe}_2\text{O}_3$  [59] have also been applied to FET-based gas sensors. For example, an  $\text{In}_2\text{O}_3$  NW-based FET has been used for sensing  $\text{NO}_2$  and  $\text{NH}_3$  [54].

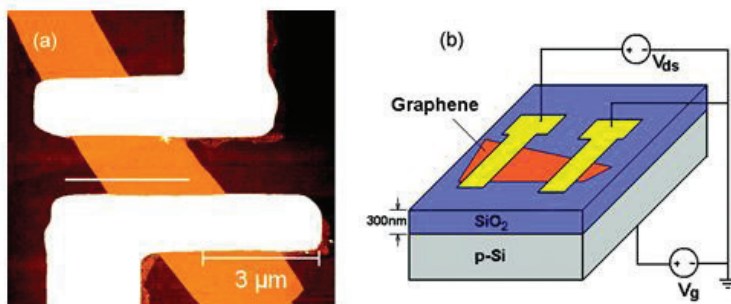
Surface modification of NWs with nanoparticles has been used to improve the sensitivity and selectivity of gas-sensitive metal oxide NW-based FETs. To date, Pd [56, 58], Pt [55], Ag [55], Au [55], ZnO [57], and NiO [57] nanoparticles have been used to improve the properties of metal oxide NW-based FETs for gas sensing. For example, Moskovis et al. reported modification of  $\text{SnO}_2$  NW-based FETs with Pd nanoparticles, and the application of this device to sensing  $\text{H}_2$  [58]. In this work, an unusual sensitivity to  $\text{H}_2$  in the charge depletion region of the device was reported [58]. This device was used for sensing a  $\text{H}_2$  concentration range from 10 to 2500 ppm [58].

Compound semiconductor NWs have also been applied in FET-based sensors [60, 61]. Gao and coworkers applied NWs of InAs, which is a III–V semiconductor, to fabrication of a gas-sensitive FET [60]. This FET-based sensor was responsive to several gases and alcoholic vapors [60].

### 5.3. 2D nanomaterial-based FETs

Because of their high surface-to-volume ratios in molecular-level interactions, two-dimensional nanomaterials are attractive for use in FET-based sensors [5, 62]. Applications of 2D nanomaterials such as graphene and transition metal chalcogenides to FET-type gas sensors have been studied.

Since the potential of graphene-based sensors for gas sensing was first reported [63], other studies have investigated gas sensing using graphene-based FETs [62, 64]. A reported graphene-based FET is shown in **Figure 8** [64]. **Figure 8a** shows an atomic force microscopy (AFM) image of the FET based on graphene. Schematic diagram of the back-gate-type FET is shown in **Figure 8b** [64]. In the structure, the FET consists of a graphene sample connected

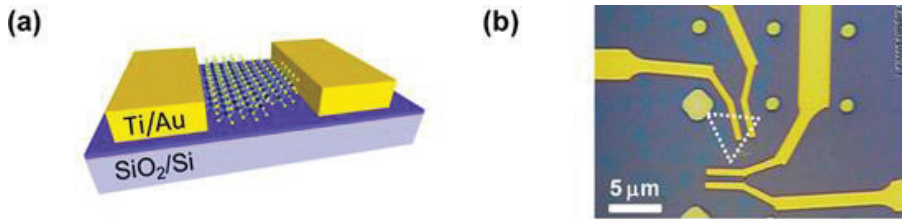


**Figure 8.** (a) AFM image and (b) schematic illustration of a graphene-based FET. Reprinted with permission from Ref. [64]. Copyright 2009 American Chemical Society.



with source and drain electrodes of Au/Cr, an SiO<sub>2</sub>-insulating layer, and a p-Si substrate as the back gate. In this report, the sensor was used for sensing NH<sub>3</sub> vapors [64].

As 2D nanomaterials, the transition metal chalcogenides MoS<sub>2</sub> [65], MoTe<sub>2</sub> [66], and WS<sub>2</sub> [67] have also been applied in FET-based gas sensors. **Figure 9a** shows a schematic illustration of a back-gate FET based on MoS<sub>2</sub> [5]. **Figure 9b** shows an optical image of MoS<sub>2</sub>-based FETs. In this FET, MoS<sub>2</sub> sheets were grown on an SiO<sub>2</sub>/Si substrate, with Ti/Au as the source and drain electrodes. This sensor was responsive to 20 ppb NO<sub>2</sub> and 1 ppm NH<sub>3</sub> [5].



**Figure 9.** (a) Schematic illustration and (b) optical image of a back-gate MoS<sub>2</sub> nanowire-based FET. Reprinted with permission from Ref. [5]. Copyright 2014 American Chemical Society.

## 6. Combination of gas sensors and pattern recognition methods

According to an earlier review [6], receptors in mammalian olfactory systems do not show highly selective responses against specific analytes. Pattern recognition methods are thought to be a dominant mode used in processing signals from the broad responses of the mammalian olfactory system [6].

Cross-reactive chemical sensor arrays combined with pattern recognition methods to mimic mammalian olfactory systems have been studied as an alternative sensor system to traditional sensing devices that use a “lock-and-key” design [6]. In intelligent sensor arrays using pattern recognition methods, complex patterns generated by nonspecific cross-reactive sensors are analyzed for classification and identification of analytes [3, 6–8]. Cross-reactive sensor arrays are constructed using sensors that are responsive to a broad range of analytes and have differential sensitivity [3, 6]. Conventional semiconductor processes can be applied to miniaturize FET-based sensors for the fabrication of cross-reactive sensor arrays.

Before data analysis, complex signals obtained from sensor arrays can be preprocessed and normalized for the application of appropriate computational methods [7, 8, 10]. After preprocessing and feature extraction, the selected method is performed. Currently, there is no general rule for the selection of computational methods. Therefore, computational methods must be appropriately selected on the nature of the data and the particular situation [7].

Various types of gas sensor arrays have been used with pattern recognition methods [6–8], including FET-based gas sensor arrays. For example, Lundström et al. reported combination

of catalytic-gate FET-based gas sensor arrays with pattern recognition methods [68, 69]. The signals from the FET-based sensor arrays were processed using conventional partial least-squares regression and an artificial neural network to predict the concentrations of individual gases [69]. Molecularly modified Si NW-based FET sensors have also been combined with an artificial neural network to recognize VOCs and estimate their concentrations [70].

## 7. Overview and outlook

For the introduction of gas-sensitive FETs, a broad overview of catalytic-gate FETs, solid electrolyte-based FETs, suspended-gate FETs, and nanomaterial-based FETs is given in this chapter. Arrays of these sensors can be combined with computational pattern recognition methods. As introduced, the combination of cross-reactive gas sensor arrays with pattern recognition methods is a promising method for the recognition of analytes in the gas phase. Cross-reactive sensor arrays should contain sensors that are responsive to a broad range of analytes and have differential sensitivity. Conventional semiconductor processes can be used for miniaturization of FET-based sensors. FET-based sensors may have advantages over other sensors used in device miniaturization of cross-reactive sensor arrays.

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