Layered Hybrid Thin Film of Molybdenum Trioxide with Poly(2,5-dimethylaniline) for Gas Sensor Sensitive to VOC Gases in ppm Level

Toshio Itoh,* Ichiro Matsubara, Woosuck Shin, and Noriya Izu
National Institute of Advanced Industrial Science and Technology (AIST),
Shimo-Shidami, Moriyama-ku, Nagoya 463-8560

(Received September 6, 2006; CL-061031; E-mail: itoh-toshio@aist.go.jp)

A layered organic/inorganic hybrid thin film consisting of MoO_3 with a double-methylated polyaniline derivative, poly(2,5-dimethylaniline), showed a distinctly increasing resistivity as a response to ppm levels of aldehydic gases, and its sensitivity to acetaldehyde is higher than that to formaldehyde, which can be explained by solubility parameter theory.

Layered organic–inorganic hybrids have attracted much attention as novel functional materials because of their unique structure involving various combinations of layered inorganic hosts and organic guests.[1] The intercalation of organic guests in layered inorganic host interlayers is a simple process. Layered inorganic hosts can be easily made to accommodate organic guests by ion exchange. Such hybrids have great potential for the development of excellent properties; i.e., as photofunctional materials,[2] electronic materials,[3] and gas sensors.

Alternately stacked organic–inorganic hybrids that consist of semiconductive MoO_3 sheets (host) and various organic components (guest) can be used as volatile organic compound (VOC)-sensing materials. Almost all organic/MoO_3 hybrid sensors show a distinct response to aldehydic gases, i.e., formaldehyde and acetaldehyde, whereas they show little or no response to other VOCs.[4] Organic/MoO_3 hybrids are among the promising candidates for formaldehyde sensing materials provided that the signals from formaldehyde and acetaldehyde can be separated. However, all the typical organic/MoO_3 hybrids ever prepared have a higher sensitivity to formaldehyde than to acetaldehyde. VOCs are detected by their characteristic resistive responses, which are caused by VOC diffusion into the hybrid interlayers and the adsorption onto the organic components or MoO_3 sheets. We have also reported that organic/MoO_3 hybrids have a great potential for selective VOC sensing, because the sensing properties of organic/MoO_3 hybrids can be controlled by modifying the interlayer organic components, which have the function of molecular recognition.[4] Therefore, it is expected that a new type of organic/MoO_3 hybrid, which has different organic components, can show a higher sensitivity to acetaldehyde than to formaldehyde. The exact concentrations of both formaldehyde and acetaldehyde can be obtained by the analysis of signals simultaneously supplied from the two types of hybrid. In the present study, we have investigated the VOC-sensing properties of a poly(2,5-dimethylaniline)/MoO_3 ($(PDMA)_xMoO_3$) hybrid thin film.

The procedure of synthesizing $(PDMA)_xMoO_3$ hybrid thin film is as follows: 1) deposition of MoO_3 thin films on a silicon substrate with a $LaAlO_3$ buffer layer and a gold comb-type electrode by chemical vapor deposition (CVD); 2) insertion of sodium ions into MoO_3 interlayers by reduction; 3) intercalation of organic components into MoO_3 interlayers by ion exchange. MoO_3 thin films were prepared by the pyrolysis of molybdenum hexacarbonyl in oxygen atmosphere by CVD.[5] The deposition experiments were performed under the following conditions: the total pressure was 110 Pa with an oxygen flow rate of 50 mL/min, the source temperature was 40 °C, the substrate temperature was 500 °C, and the deposition time was 15 min. The MoO_3 thin films were immersed into an aqueous solution of sodium hydrosulfite and sodium molybdate dehydrate for 20 s to reduce the MoO_3 and to insert ion-exchangeable sodium ions between the MoO_3 sheets.[6] Thus-obtained $[Na(H_2O)_2]_xMoO_3$ films then underwent an ion-exchange reaction. The 2,5-dimethylaniline (16.4 mmol) was added to 15 mL of distilled water with 1.5 mL of 12 M aqueous HCl. Sodium persulfate (0.22 mmol) as a polymerization initiator was added to 2,5-dimethylaniline hydrochloride solution and was stirred magnetically while bubbling with nitrogen for 30 min. After being stirred, $[Na(H_2O)_2]_xMoO_3$ films were soaked in a PDMA suspension for 30 s to ion-exchange Na^+ for soluble PDMA. The resulting hybrid films were washed quickly with distilled water and then dried at 90 °C for 30 min in air.

Figure 1 shows X-ray diffraction (XRD) patterns of the MoO_3, $[Na(H_2O)_2]_xMoO_3$, and $(PDMA)_xMoO_3$ hybrid thin films. The series of $(0k0)$ XRD peaks for each film show a characteristic high periodic regularity. Moreover, all the XRD patterns show only $(0k0)$ peaks, indicating that $(PDMA)_xMoO_3$ hybrid grains are regularly oriented along the face of the substrate. The interlayer distances of MoO_3, $[Na(H_2O)_2]_xMoO_3$, and $(PDMA)_xMoO_3$ hybrid are 0.69, 0.94, and 1.37 nm, as revealed by the $(0k0)$ peaks, respectively. These results indicate that the interlayer distances depend on the size of interlayer cations.

The VOC-sensing properties of the $(PDMA)_xMoO_3$ hybrid were determined experimentally using a flow apparatus. The $(PDMA)_xMoO_3$ hybrid thin film was placed in homeothermic chamber, and the resistance of the thin film was measured directly through the gold comb-type electrode. The target VOC concentrations were precisely controlled using the flow system with a mass flow controller. The total flow rate was maintained

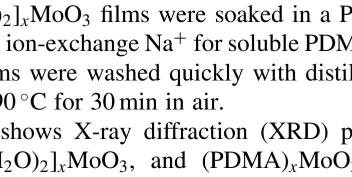

Figure 1. X-ray diffraction patterns of (a) MoO_3, (b) $[Na(H_2O)_2]_xMoO_3$, and (c) $(PDMA)_xMoO_3$ hybrid thin films, measured at ca. 20 °C.

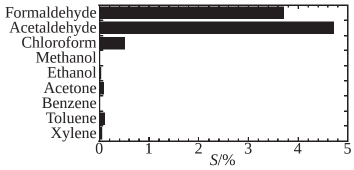

Figure 2. Magnitude of the sensitivity of the $(PDMA)_xMoO_3$ hybrid thin film to several types of VOCs (10 ppm) at 100 °C.

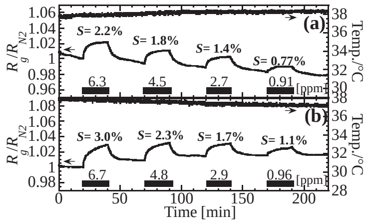

Figure 3. Normalized resistive profiles of the $(PDMA)_xMoO_3$ hybrid at approximately 40 °C. Target VOCs are (a) formaldehyde and (b) acetaldehyde. Bold lines with concentration values on the bottom of graphs indicate periods when VOCs flowed.

at 200 mL/min. After the pure nitrogen gas was passed through the chamber, the target VOC balanced with nitrogen flowed for 20 min, and then the gas flowing into the chamber was again changed to pure nitrogen gas. The sensitivity is defined as

$$S = \left(\frac{R_g}{R_{N_2}} - 1\right) \times 100 \tag{1}$$

where S, R_g, and R_{N_2} denote the sensitivity and the resistances of the thin film in the VOC and pure nitrogen gas just before VOCs flowed into the chamber, respectively.

The results of the sensitivity of the $(PDMA)_xMoO_3$ hybrid thin film to several types of VOCs (10 ppm) are summarized in Figure 2. The $(PDMA)_xMoO_3$ hybrid thin film shows a distinctly increasing resistive response to aldehydic gases. In contrast, there is little or no response to chloroform, alcohols, acetone, and aromatics. The $(PDMA)_xMoO_3$ hybrid thin film exhibits a similar selectivity to a typical organic/MoO_3 hybrid.

Figure 3 shows the dynamic response of the $(PDMA)_xMoO_3$ hybrid thin film to aldehydic gases with different concentrations. The drift of the baseline was caused by the change in temperature of the chamber. The observed increasing resistive response is caused by the absorption of aldehydic molecules into the $(PDMA)_xMoO_3$ hybrid interlayers. We have previously reported that the resistance of polyaniline/MoO_3 hybrids in response to VOCs in dry air is almost the same as that measured in nitrogen.[7] Semiconductive sensors generally show decreasing resistive response, if VOC molecules burn on the surface of the sensors. Therefore, a combustion mechanism is not likely to occur for MoO_3-based hybrid sensors. Moreover, the $(PDMA)_xMoO_3$ hybrid possesses a good reproducibility in its response, indicating that the hybrid can absorb and desorb aldehydic gases within several minutes. Noted that the $(PDMA)_xMoO_3$ hybrid thin film has a good potential for the detection of aldehydic gases with concentrations as low as 1 ppm.

The sensitivities of the $(PDMA)_xMoO_3$ hybrid thin film to aldehydic gases are shown in Figure 4. The S values are proportional to the concentrations of formaldehyde and acetaldehyde gases. Interestingly, it is clearly seen in Figure 4 that the sensitivity of the $(PDMA)_xMoO_3$ hybrid thin film to acetaldehyde is larger than that to formaldehyde, even though both formaldehyde and acetaldehyde belong to the same functional group, i.e., aldehyde. The transitional resistive response of organic/MoO_3 hybrids is caused by the diffusion of VOC molecules into the interlayers.[4] The difference in sensitivity to formaldehyde and acetaldehyde can be explained by the theory of the solubility parameter. The diffusion of VOC molecules in a polymer is improved when the solubility parameter values of the polymer and VOCs are close to each other.[8] The values of the solubility parameter for VOCs are based on their heat of vaporization.[8] The values for polymers are given by

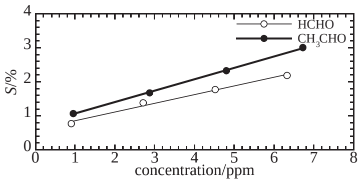

Figure 4. S values of the $(PDMA)_xMoO_3$ hybrid thin film exposed to aldehydic gases at approximately 40 °C.

$$\delta = \frac{\rho}{M} \times \sum F_i \tag{2}$$

where δ, ρ, M, and F_i denote the solubility parameter $[(MPa)^{1/2}]$, density, molecular weight per unit, and group molar attraction constants, respectively.[8,9] The solubility parameter of acetaldehyde has been reported to be 21.1 $(MPa)^{1/2}$.[8] The solubility parameters of polypyrrole and polyaniline, which are organic guests of typical MoO_3 hybrids,[4,7] are calculated to be 13.4 and 19.1 $(MPa)^{1/2}$, respectively, using Small's and Hoy's F_i constants.[8–10] On the other hand, the solubility parameter of PDMA is 21.0 $(MPa)^{1/2}$, indicating that acetaldehyde molecules diffuse extremely into the interlayer of the $(PDMA)_xMoO_3$ hybrid. Consequently, the PDMA is a suitable interlayer organic component of the organic/MoO_3 hybrid for obtaining a higher sensitivity to acetaldehyde than to formaldehyde.

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