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Analytical Study of Resistance Drift Phenomena on $(PANI)_xMoO_3$ Hybrid Thin Films as Gas Sensors

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Polyaniline (PANI)-intercalated MoO_3 ($(PANI)_xMoO_3$), which is a conventional layered organic/MoO_3 hybrid, as a gas sensor has a resistance drift problem, which should be solved in order to realize practical applicable gas sensing devices. In this analytical study, XPS studies reveal that the resistance drift is caused by adsorbing and desorbing oxygen molecules from the atmosphere. The adsorption of enough oxygen molecules by annealing in air at a higher temperature than operating temperature can reduce the resistance drift phenomena.

Organic–inorganic nanohybrids composed of organic-guests and layered inorganic-hosts have attracted much attention for their unique structures and specifically, combination of the different properties of organic guests and inorganic hosts.[1–10] In cases of ion-exchangeable layered inorganic hosts, the organic components are embedded into the interlayers of inorganic host frameworks and organic and inorganic layers stack alternately at a nanometer scale when the inorganic host materials are dropped into the organic components solutions, i.e., simple hybridization process.

Layered organic–inorganic nanohybrids composed of a semiconductive MoO_3 host and various organic guests can be used as gas sensing materials for detecting volatile organic compounds (VOCs), specifically, aldehyde gases.[11] The detection of VOCs is judged from their characteristic increase or decrease in resistance responses. The mechanism of target gas detection is an increase or decrease of effective carrier electrons in the semiconductive MoO_3 hosts. The density of carrier electrons in MoO_3 layers are changed by VOC molecules diffusing into the MoO_3 interlayers and adsorbing onto MoO_3 layer frameworks or interlayer organic guests.[11,12] VOC sensors require high sensitivity and stability. We have previously reported that polyaniline (PANI)-intercalated MoO_3, e.g. $(PANI)_xMoO_3$ hybrid, exhibits excellent resistance increase in response to exposure to formaldehyde and acetaldehyde of several tens of ppb at 40–60 °C, which is the same level as the regulation values against indoor air quality.[13] However, the present hybrids have a problem with resistance base line drift. The conductivity of conventional semiconductive-type gas sensors usually changes over long-term operation as a result of factors such as grain growth and poisoning by several species in the atmosphere.[14–22] In the case of $(PANI)_xMoO_3$, the drift mechanism should be different because they are operated at lower temperature than conventional semiconductive-type sensors. However, the drift of $(PANI)_xMoO_3$ could be caused mainly by adsorbing and desorbing contaminant gas, i.e. moisture and other unknown causes. In order to develop a driftless $(PANI)_xMoO_3$ sensor, it is important to elucidate the mechanism of the resistance drift. In the present study, we have investigated the drift mechanisms of $(PANI)_xMoO_3$ thin films.

Experimental

Preparation of $(PANI)_xMoO_3$ Thin Films. The $(PANI)_x$-MoO_3 thin film elements were synthesized in accordance with our previous reports:[13,23] 1) deposition of MoO_3 thin films by chemical vapor deposition (CVD) on a silicon substrate with a $LaAlO_3$ buffer layer and a platinum comb-type electrode; 2) insertion of sodium ions into MoO_3 interlayers by reduction. MoO_3 is reduced by sodium dithionite to form $[Na(H_2O)_2]_xMoO_3$, consisting of anionic MoO_3 layered frameworks and interlayer sodium cations; 3) intercalation of PANI into MoO_3 interlayers by ion exchange. MoO_3 thin films were prepared by the pyrolysis of hexacarbonylmolybdenum in oxygen atmosphere by CVD.[24,25] The deposition experiments were performed under the following conditions: the total pressure was 110 Pa with an oxygen flow rate of $50\,mL\,min^{-1}$, 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 dithionite and sodium molybdate dihydrate for 20 s to reduce the MoO_3 and to insert ion-exchangeable sodium ions between the MoO_3 sheets.[26] Aniline (16.4 mmol) was added to 15.4 mL of 1.0 M HCl aqueous solution. 1 mL of $(NH_4)_2S_2O_8$ (0.22 mmol) aqueous solution was added to the resulting aniline hydrochloride solution and then stirred magnetically while bubbling with nitrogen for 30 min. The PANI aqueous suspensions were filtrated twice through an Advantec PTFE membrane filter having 0.50 µm pore size in order to remove insoluble PANI. The Na^+-accommodated MoO_3 films were soaked in the solution for 30 s to ion-exchange Na^+ for soluble PANI. The resulting hybrid films were washed with distilled water quickly and then dried in vacuo. The formation of $(PANI)_xMoO_3$ was confirmed by XRD measurements. The characterization of the $(PANI)_xMoO_3$ hybrid have been reported in our previous papers.[27,28]

Resistance Measurements. The resistance of the $(PANI)_x$-MoO_3 thin films was measured by a standard two wire method using a platinum comb-type electrode and gold wires. The temperature of the thin films was controlled by a box-type or flow-type chamber.

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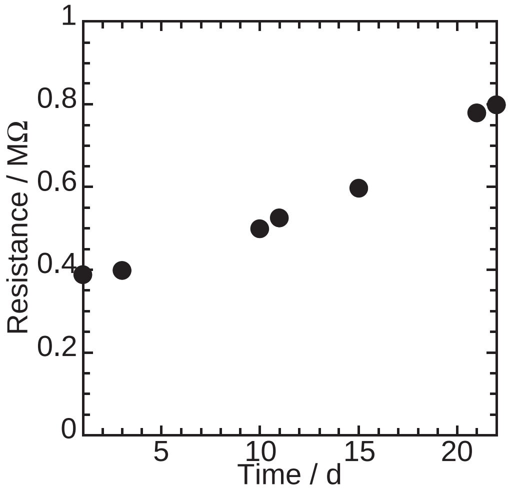

Figure 1. Resistive profiles of the (PANI)$_x$MoO$_3$ thin film at 40 °C in room air.

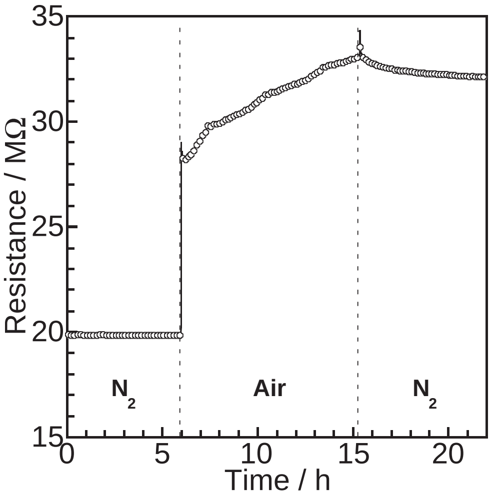

Figure 2. Resistive profiles of the (PANI)$_x$MoO$_3$ thin films at 35 °C in nitrogen and air.

XPS Analysis. The X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ULVAC PHI1800 XPS apparatus equipped with Al Kα radiation. The settings were 11.75 eV pass energy and 0.1 eV step size. The binding energies were calibrated by the C 1s peak at 284.6 eV.

Results and Discussion

Resistance Drift of the (PANI)$_x$MoO$_3$ Thin Films. Figure 1 shows the resistance profiles of (PANI)$_x$MoO$_3$ thin film in room air at 40 °C over approximately one month. Before each measurement, the thin film was heated at 100 °C for 5 h to clean the surface of the thin film. The resistance was corrected after 4.5 h since the film temperature was cooled to 40 °C. The resistance of the thin film after the temporary heating at 100 °C is always lower than that just before heating, so that the temporary heating should be actually effective for cleaning the thin film and releasing the adsorbed moisture. However, the resistance of the (PANI)$_x$MoO$_3$ thin film increased over a long time scale as shown in Figure 1.

To investigate oxygen effects, we tried to heat the (PANI)$_x$-MoO$_3$ thin film in nitrogen at 100 °C for 2 h, then cooled to 35 °C in nitrogen. When the resistance of the (PANI)$_x$MoO$_3$ thin film is measured at 35 °C in nitrogen, it is very stable and does not show a resistance drift for several hours as shown in Figure 2. However, the resistance of the (PANI)$_x$MoO$_3$ thin film increases drastically when it is exposed to air, as shown in Figure 2. The increase of the resistance in air is not observed after the carrier gas is changed to nitrogen again. The resistance increases again when the carrier gas is changed to air or oxygen. It is, therefore, plausible that the resistance drift of (PANI)$_x$MoO$_3$ is caused by oxygen.

Investigation of the Resistance Drift Phenomena by XPS Analysis. The Mo in the MoO$_3$ layers of the (PANI)$_x$MoO$_3$ thin film is partially reduced to Mo^{5+}, and interlayer PANI bears it as a counter cation to the negatively charged MoO$_3$ layers. In other words, interlayer organic components, PANI, donate their electrons to the MoO$_3$ layers, and then the MoO$_3$ hosts possess electroconductive ability. The drift is considered to arise as follows: 1) oxidation of Mo^{5+} to Mo^{6+} and/or 2) absorption or desorption of oxygen. To investigate the resistance drift phenomena, XPS measurements were carried out. We used two kinds of thin films, one was annealed at 100 °C for 1 h in nitrogen, and the other was annealed at 100 °C for 5 days in oxygen. During the annealing processes, the resistances of the thin films were measured. The initial resistances of the two thin films in nitrogen were approximately the same value, 11.7 MΩ. The resistance of thin film annealed in nitrogen did not fluctuate. However, the resistance of the thin film annealed in oxygen increased over 120 MΩ. After annealing, these thin films were removed from the heating apparatuses and then set in the XPS apparatus.

Figure 3 shows Mo 3d spectra of XPS profiles on both kinds of (PANI)$_x$MoO$_3$ thin films. In the range of Mo 3d spectra, the large Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ doublet peaks appear at 232.7 and 235.8 eV, respectively, indicating that Mo^{6+} species are the principal ingredients of Mo, as shown in Figure 3.[29,30] In addition to the Mo^{6+} species, both the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ doublet peaks have weak shoulders at lower binding energy, 231.3 and 234.4 eV, respectively. These shoulders can be due to Mo^{5+} species.[30] The atomic ratio of Mo^{6+}:Mo^{5+} can be calculated by the area of Mo 3d peaks of each species. Relative contents of Mo^{5+} species of (PANI)$_x$MoO$_3$ thin films annealed in nitrogen or oxygen atmospheres are approximately 7% in either case. It should be pointed out that the atomic ratio of Mo^{6+}:Mo^{5+} does not show a significant change even after heating in oxygen. These results prove that the oxidation of Mo of the (PANI)$_x$MoO$_3$ thin films has not occurred in the above conditions. Therefore, the oxidation of Mo is not the reason of the resistance drift problem.

In the range of the O 1s core level, non-symmetric broad O 1s peaks appear, as shown in Figure 4. As a result of fitting, dominant peaks at 530.5 and 532.5 eV are attributed to the MoO$_3$ host and the SiO$_2$ on the substrate, respectively.[29–31] Moreover, a remnant peak at 531.9 eV is observed, which is ascribed to adsorbed oxygen onto the MoO$_3$ layers.[29] In the case of the thin film annealed in nitrogen, a weak adsorbed oxygen O 1s peak is observed, as shown in Figure 4a. Interestingly, dramatic changes in the components took place for the oxygen annealed thin film, as shown in Figure 4b. The electroconductiveness of the (PANI)$_x$MoO$_3$ thin films is domi-

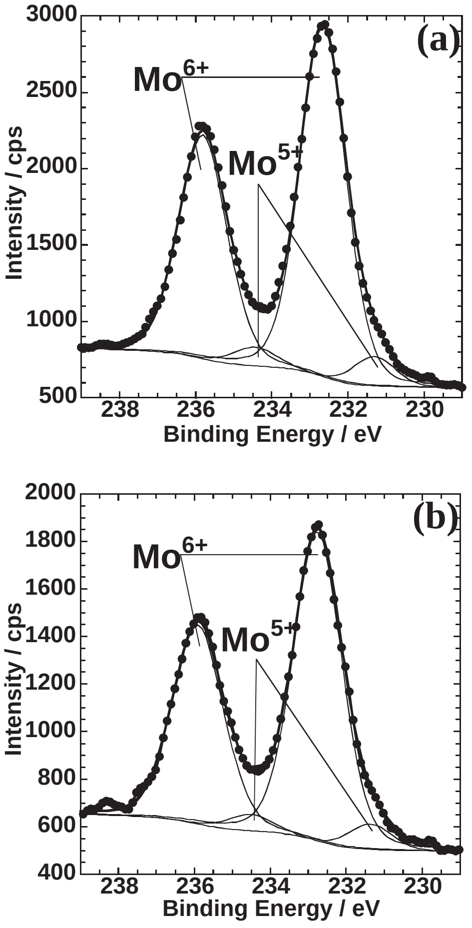

Figure 3. XPS Mo 3d core level spectra of $(PANI)_xMoO_3$ thin films which were annealed at 100 °C into (a) N_2 and (b) O_2 atmospheres before the measurements.

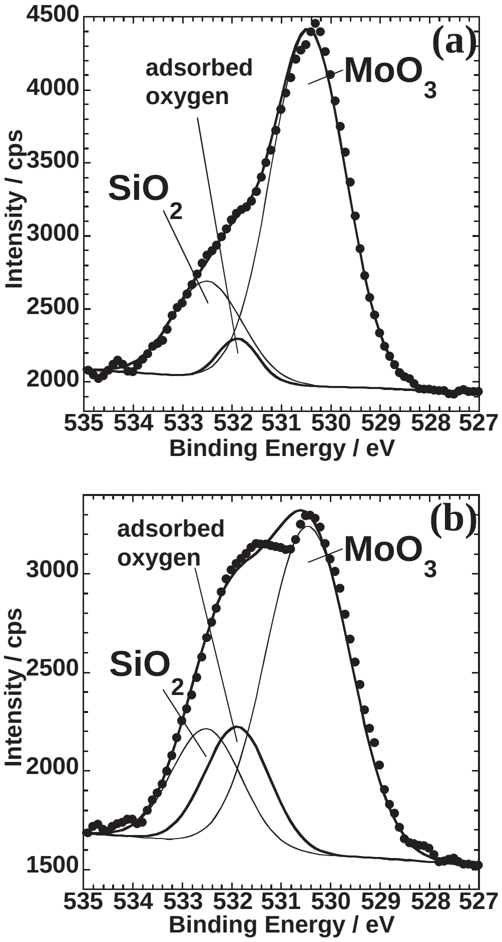

Figure 4. XPS O 1s core level spectra of the $(PANI)_x$-MoO_3 thin films which were annealed at 100 °C into (a) N_2 and (b) O_2 atmospheres before the measurements.

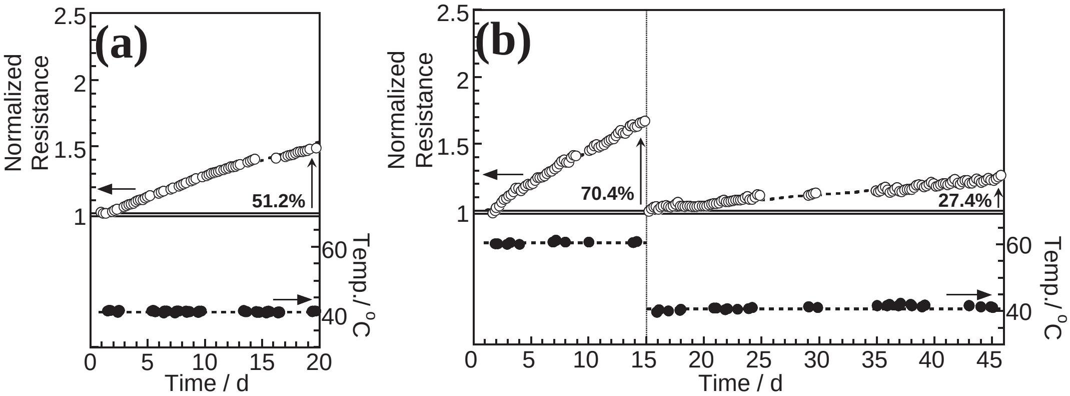

Figure 5. Normalized resistive profiles of the $(PANI)_xMoO_3$ thin films in dry air conditions. The heating chamber temperatures are (a) 40 °C, and (b) 60 °C and then cooled to 40 °C.

nated by the amount of carrier electron in the MoO_3 hosts. The carrier electrons tend to be trapped by the adsorbed oxygen molecules because of the high electronegativity of oxygen. In this case, the number of free electrons in the MoO_3 hosts is decreased. That is, the resistance increasing phenomenon obtained in Figure 2 is caused by negatively charged adsorbed oxygen molecules on MoO_3, as shown in Figure 4b. Consequently, the XPS results are in good agreement with the tendency of the resistive profiles in nitrogen and air conditions.

Effects of Aging. The resistance drift of the $(PANI)_xMoO_3$ thin film is mainly explained to be caused by adsorbing oxygen molecules, which could not be desorbed in the presence of air. Therefore, it is thought that adsorption of a sufficient quantity of oxygen should lead to the realization of resistance driftless $(PANI)_xMoO_3$ hybrid thin films.

Figure 5 shows the normalized resistive profiles of the

Table 1. Resistance Drift Rate per 19 d 20 h at 40 °C on the (PANI)$_x$MoO$_3$ Thin Films

Preheating	Resistance drift rate per 19 d 20 h at 40 °C/%
No	51.2
60 °C for 14 days	17.5

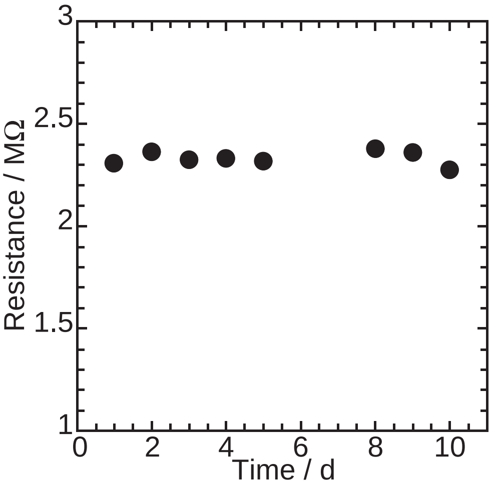

Figure 6. Resistive profiles of the (PANI)$_x$MoO$_3$ thin film at 40 °C in room air. The thin film was heated at 120 °C for approximately 1 month before this measurement.

(PANI)$_x$MoO$_3$ hybrid thin films in dry air. Here we have compared the drift phenomena for thin films with and without high temperature heating in air. For both the measurements, we used fresh thin films which were kept under dry air just after they were prepared. The resistance at 40 °C of the (PANI)$_x$MoO$_3$ thin film without annealing increased by 51.2% over 19 d 20 h, as shown in Figure 5a. The other (PANI)$_x$MoO$_3$ thin film was annealed at 60 °C for approximately 14 days and then cooled and kept at 40 °C. The resistance of the (PANI)$_x$MoO$_3$ thin film at 60 °C increased by 70.4% over approximately 14 days, indicating that oxygen adsorption is accelerated at 60 °C rather than at 40 °C. After heating at 60 °C, the resistance of the (PANI)$_x$MoO$_3$ thin film at 40 °C increased by 27.4% during approximately 31 days, as shown in Figure 5b. This value corresponds to 17.5% per 19 d 20 h, as shown in Table 1. The annealing at a high temperature in air appears to be effective in reducing resistance drift.

Figure 6 shows the resistive profiles of the (PANI)$_x$MoO$_3$ thin film, heated in air at 120 °C for approximately 1 month before measurement. Before each measurement, the thin film was heated at 120 °C for 10 min to clean the surface of the thin film. The resistance was corrected after 4.5 h since the thin film temperature was cooled to 40 °C. The resistance of (PANI)$_x$MoO$_3$ was increased by heating at 120 °C for approximately 1 month due to adsorbed oxygen molecules. The (PANI)$_x$MoO$_3$ thin film in Figure 6, however, possesses driftless resistance. Figure 7 shows the dynamic response of the thin film to 400 ppb formaldehyde gas. Although sensitiveness to formaldehyde is decreased as a result of extended heating at 120 °C to prepare drift-less material, the response is sufficient for application to detection devices.

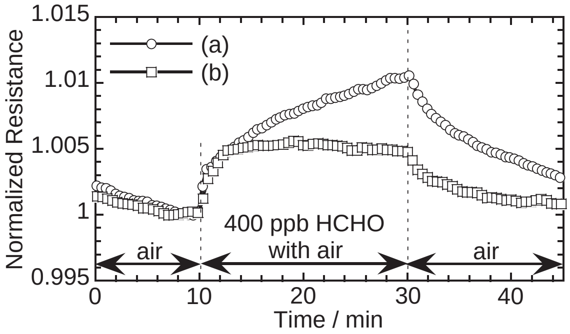

Figure 7. The dynamic responses of the (PANI)$_x$MoO$_3$ thin film to 400 ppb formaldehyde at 60 °C: (a) before and (b) after heating at 120 °C for approximately 1 month.

Conclusion

It is revealed that the adsorption and desorption of oxygen molecules into the (PANI)$_x$MoO$_3$ thin films produce a resistance drift. It is consequently explained that the adsorption of enough oxygen molecules by annealing in air at a higher temperature than an operating temperature can reduce the resistance drift phenomena of the (PANI)$_x$MoO$_3$ thin films.

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