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Syntheses of the Substituted Aluminumfluoro Phthaloyanines and their Application to NO_2 Gas Sensing

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1. Introduction

Metallo-phthalocyanines (MPcs) have been applied to NO_2 gas sensors for long time. However, there are still many problems for practical applications: the sensing mechanism is not yet clarified in detail and the long-term stability and reproducibility are not achieved. We have reported that the gas-sensing characteristics can be improved through a modification of the film microstructure for copper phthalocyanine (CuPc) and alminumfluoro phthalocyanine (AlPcF) thin films.[1]

It is expected that the gas sensing properties of organic semiconductors could be improved by molecular engineering, *i.e.,* the molecular structure can be modified through chemosynthesis to fit the physico-chemical properties to the gas sensing application needs.[2] In the case of AlFPc, substitution of the Pc macrocyle seems to be one of the most promising ways of tuning the sensor response of organic semiconductors.

2. Experimental

The thin films were deposited by a sublimation method on the mica substrates in the vacuum of 10^{-5} Pa. The source material was sublimed at 380-500℃ and the substrates were kept at room temperature. The film thickness was monitored by a quarts oscillator. Finally, the 20-finger interdigitated gold electrodes were vacuum evaporated onto the films to measure the electrical conductivity in NO_2 ambience diluted by N_2 gas and N_2 reference gas.

The source materials were characterized crystallographucally by using the spectrophotometer and the X-ray diffractometer. The conductive current of the films was measured by using the electrometer under the dc bias of 10 V. Gas sensitivity of the sensor elements was estimated by an increase of the current (ΔI) in the interest gas ambience. The operation temperature was kept at 120℃ and the gas flow rate was 300cc /min.

In this report, the syntheses of the substituted aluminumfluoro phthalocyanines are described and the NO_2 gas sensing characteristics of their sublimed thin films are discussed based on the molecular structures.

3. Results and discussion

Syntheses and physical properties of the source materials

Three novel substituted aluminumfluoro phthalocyanines (AlFPcRn), namely aluminumfluoro tetra-*t*-butyl-phthalocyanine [AlFPR$_4$, R=-C(CH$_3$)$_3$], aluminumfluoro octa-methyl-phthalocyanine [AlFPcR$_8$, R=-CH$_3$] and aluminumfluoro oxyhexylene-diethyl malonate -phthalocyanine [AlFPcR, R=-O(CH$_2$)$_6$CH(COOC$_2$H$_5$)$_2$] were synthesized by using $AlCl_3$ as Al source and HF acid as F source through condensation of the phthalonitrile (4,5-dimethyl phthalonitrile for AlFPR$_8$, 4-*t*-butyl-phthalonitrile for AlFPR$_4$, 4-oxyhexylene-diethyl malonate -phthalonitrile and o-phthalonitrile for AlFPcR).

The volatility and solubility of AlFPcR$_4$ could be attributed to the characteristics of the t-butyl radical which occupies a vast space to weaken the interaction between the Pc macrocyles. Methyls in AlFPcR$_8$ are too small to change the volatility and solubility noticeably. As for AlFPcR, the high vaporization temperature stems from its high molecular weight and its solubility may result from the flexible substituent.

The NO_2 gas sensing characteristics

Compared to AlFPc films, all the AlFPcRn films have lower sensitivity but the response and recovery of AlFPcR films are faster than AlFPc films. Of the three substituted Pc derivatives, the AlFPcR shows the highest sensitivity and the fastest response/recovery whereas AlFPcR$_8$ exhibits the lowest sensitivity and the slowest response/recovery. It is clear that the gas sensing characteristics of AlFPcRn are strongly influenced by the substituents: the mono-substituted MPc shows better response/recovery reproducibility than the unsubstituted counterpart but the sensitivity and recovery of the tetra- and octa-substitutied phthalocyanines are worse than simple AlFPc.

The results seem to be attributed to the number and nature of the substituents which may change the physico-chemical properties. The gas sensing properties of the substituted MPcs are understandable in terms of the electron-donating effect and the steric effects of the substituents. As MPcs belong to p-type semiconductors and all the substituents are electron-donating groups which may increase the electron density resulting in a decrease in the number of carrier (hole), the sensitivity should decrease due to the substituents. On the other hand, the substituents are located in the peripheral rings and occupy a space to produce the steric effects which may have both the positive and negative influences on the gas sensing properties. The interstack distance and the Pc-Pc ring distance in the same stack seem to be enlarged by the steric effects, which may favor the diffusion rate. However, too many substituents in the Pc molecules can also occupy the NO_2 gas molecule pass way to hinder the interaction between NO_2 and Pc ring to cause the slow response and the incomplete recovery.

The improved sensing characteristics of AlFPcR seem to be ascribed, *inter alia*, to its asymmetric molecular structure. The asymmetrical distribution of the conjugated π system induced by the asymmetric molecular structure may take the intermolecular charge transfer process between NO_2 and the conjugated π system easier. In addition, the positive influence of steric effects of single substituent may exceed the negative influence.

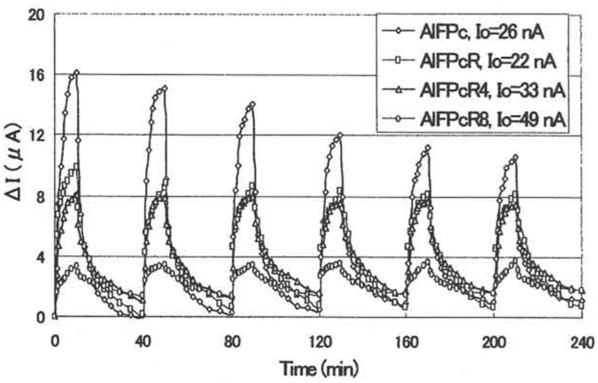

Fig. 1 Successive response/recovery of 6 nm films

The conductivity of all the 6 nm thick films (Fig. 1) and the 14 nm thick films of AlFPc and AlFPcR decreases whereas the conductivity of 14 nm films of $AlFPcR_4$ and $AlFPcR_8$ increase from one cycle to another during the initial cycles. The AlFPc film declines more apparently than its substituted counterparts. The decrease in the conductivity is clearly related to decrease in the adsorption sites of the film which could be ascribed to the NO_3^- poisoning effect.[3] The NO_3^- poisoning effect may arise from the transformation of MPc^+, NO_2^- to MPc^+, NO_3^-, which is formed irreversibly with O_2 absorbed in the film. As NO_3^- is more strongly bonded to MPc^+ than NO_2^-, it tends to localize the p-type charge carriers on MPc^+ and to reduce the number of free carriers. At the same time, the number of the adsorption sites available to NO_2 molecules decreases at each doping/dedoping cycle due to this poisoning.

Conductivity increase could be due to the inner adsorption effect. On each NO_2 doping, new adsorption sites inside the film can be reached by NO_2 molecules to produce higher and higher conductivity. The new availability of these sites could result from the molecular structure, microstructure and thickness of the film.

Increase or decrease in conductivity depends on both inner adsorption effect and NO_3^- poisoning effect. If MPc has no or less substituent (e.g. AlFPc or AlFPcR) or the film is very thin, the response/recovery behavior may be dominated by NO_3^- poisoning effect. For MPc with more substituents (e.g. $AlFPcR_4$ or $AlFPcR_8$) or thicker film, its sensing properties will be dominated by the inner adsorption effect.

4. Conclusion

The NO_2 gas sensing properties can be modified by the substituents through their electron-donating and steric effects. The sensing characteristics of MPcs can be improved by introducing only single substituent into the Pc molecule but too many substituents in the molecule decrease the sensitivity and deteriorate the gas response/recovery. The mono-substituted MPc provides the best combination of the gas sensing characteristics, *i.e.*, high sensitivity with good stability and reproducibility, for use in detecting and measuring low concentration (1 ppm) NO_2 gas.

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