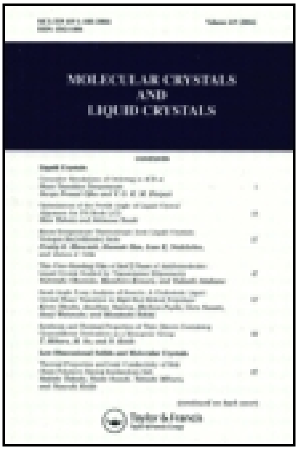

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Surface Properties of Metallophthalocyanine LB Films and their Sensing Applications

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Surface Properties of Metallophthalocyanine LB Films and their Sensing Applications

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Multilayer thin films of H_2Pc and CuPc were coated on QCM by the LB method as to be used as NO_2 sensing materials. The mechanism of NO_2 desorption on both Pc sensing films was investigated using XPS and FTIR.

Keywords: phthalocyanine(Pc); Langmuir-Blodgett(LB) film; NO_2

INTRODUCTION

Extremely toxic nitrogen dioxide(NO_2) has become a serious atmospheric pollutant owing to the increase in the number of automobiles and factories. Therefore, a number of studies on gas sensors for NO_2 have been carried out[1]. In this study, we focused on the piezoelectric quartz crystal microbalance(QCM) coated with metallophthalocyanine(MPc) sensing materials. When the mass of the coated QCM changes upon adsorption of target molecules, the resonant frequency downshifts of QCM occur, indicative of the amount of adsorbed NO_2 molecules. In our previous report on quartz resonator sensor systems coated with MPcs Langmuir - Blodgett(LB) films, the adsorption sites of the sensing films were excluded[2]. In this work, characterization of sensing membrane were studied with XRD, ellipsometry, AFM. The mechanism of NO_2 desorption on the sensing membranes was investigated with XPS and FTIR.

EXPERIMENTAL

The schematic procedures to obtain several kinds of Pcs, the procedure of LB film fabrication[2], and the parameters for X-ray diffraction[3] were described in our previous reports. For the purpose of determining the thickness of LB films, ellipsometry of Rudolph/Auto(II) with the specific wave length of 633 nm and AFM of AutoProbe M5(Park Scientific Instruments, USA) were used. The X-ray photoelectronic spectroscopy(XPS) measurements were carried out with the monochromatized AlK X-ray source(hν=1486.6 eV). In the FTIR experiments, 260 layers of CuPc LB film were deposited onto silicon wafers. The same film sample was studied for three times; the initial pure state, NO_2-exposed state, and the state recovered with pure N_2 pursing. A schematic diagram of the gas sensing apparatus and the experimental procedure in detail were shown in our previous paper[2].

RESULTS AND DISCUSSION

The lattice spacings of H_2Pc and CuPc LB films measured from the thin film XRD spectra were found to be 21.8Å for H_2Pc and 22.7Å for CuPc. The results from the resonant frequency measurement (9 MHz QCM) before and after the deposition of 20-layer-LB film 10737 Hz for H_2Pc and 5300Hz for CuPc reveal that the deposited amount of H_2Pc was almost twice as much as CuPc. Ellipsomety measurement was done for 4, 6, and 10 layers of H_2Pc and CuPc LB films coated on silicon wafers. The film thickness was compared for H_2Pc and CuPc in Figure 1. At each number of strokes, the H_2Pc[4] film was much thicker than the CuPc film. Also, we could obtain the same evidences from the AFM average height data.

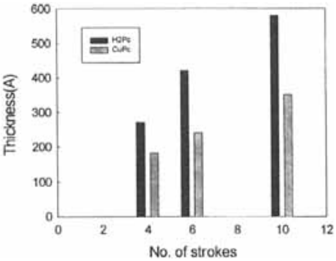
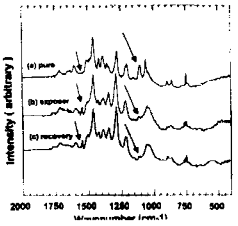


FIGURE 1. Thickness of Pcs LB film measured by ellipsometry vs. No. of strokes

The NO_2 adsorption sites were still not identified to be the central metal site and ether group in the side chains on each Pc molecule. To obtain more detailed understanding of the NO_2 sensing mechanism, we undertook an investigation of the XPS spectra of a 30-layer CuPc LB film on a silicon wafer. The characteristic Cu2p(1/2) and Cu2p(3/2) peaks corresponded to the binding energy values of 956.09 eV and 936.13 eV, respectively, before NO_2 adsorption. However, they were after NO_2 adsorption. These peak shifts of Cu2p(1/2) and Cu2p(3/2) can be related to the environments of the atoms[5].

The structure of the MPc membrane was confirmed by FTIR, as shown in Figure 2. When the sensing membrane was exposed to NO_2, the peak at 1111cm^{-1} corresponding to the ether group disappeared, but a peak indicative of the ether group complexed with NO_2 sprang out at 1540 cm^{-1}. From these results, therefore, it can be concluded that the ether group was desorbed of NO_2 and was not recovered by pursing with pure N_2. We have reported that

H_2Pc has an excellent sensing ability among the other Pc derivatives we tested[2]. In Figure 3, the normalized frequency change(Hz ratio with respect to the amount of CuPc transferred) as a function of the NO_2 concentration is shown.



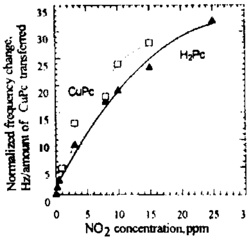


FIGURE 2. FTIR spectra of 260-layer CuPc LB film

FIGURE 3. Normalized frequency change of H_2Pc and CuPc

CONCLUSION

The XPS, NMR, and FTIR results describe that the sensing sites of the NO_2 gas were the core metal site and side chain(ether group), and the side of MPcs were not recovered by carrier gas purging. Both films showed significant frequency changes in the ppm scale under the air-based sensing condition.

Acknowledgments

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