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Metallo-phthalocyanines(MPCs) are very sensitive to toxic molecules such as electron affinitive NO₂ gas and also chemically and thermally stable since lots of MPCs have been studied for the potential chemical gas sensors for NO₂ using their electrical conductivity. In this study, thin films of octa-dodecyloxy copper-phthalocyanine were prepared by Langmuir-Blodgett(LB) method and characterized by using UV/Vis absorption spectroscopy, and ellipsometry. It was found that the proper transfer surface pressure for the film deposition was 25mN/m and the limiting area per molecule was 112 Å²/molecule. The film thickness of one layer was 64 Å. Current-voltage(I-V) characteristics of these films were investigated as a function of film thickness.

Keywords: Langmuir-Blodgett method, phthalocyanine, current-voltage characteristics, NO₂ gas sensor

INTRODUCTION

Langmuir-Blodgett(LB) method has the advantages in aligning the molecular orientations and easy control of thickness compared to the other methods such as PVD, and CVD^[1]. Phthalocyanines(Pcs) are well-known organic semiconducting materials having thermal, mechanical and chemical stabilities^{[2],[3]}. Lots of Pcs have

been studied for the potential chemical gas sensors for NO₂ using their electrical conductivity. In order to use phthalocyanine as a gas sensor material, phthalocyanine must have high sensitivity and selectivity with respect to the gas. Sensitivity of phthalocyanine films is dependent on film thickness, temperature, gas concentration and film morphology, etc.^[4]. In this paper, the basic experimental results on the fabrication of CuPc LB films, as a function of film thickness, temperature and/or gas concentration on current-voltage characteristics are discussed.

EXPERIMENTAL DETAILS

Materials and π -A isotherm

In this study, octa-dodecyloxy CuPc(CuPc(OR)₈ (C₁₂₈H₂₁₈O₈N₈Cu, molecular weight =2050.664) molecule was used as a gas sensing material. A structure of the CuPc(OR)₈ molecule is shown in Fig. 1. The π -A isotherm of CuPc(OR)₈ Langmuir film was measured using Kuhn-type LB trough(NIMA 611), where purified water(18.3M Ω · cm) was used as the subphase.

Film Deposition

A chloroform(CH₃Cl) was used as a solvent for CuPc(OR)₈ with a concentration of 0.5×10^{-3} mol/ℓ. Microscope-slide glass, quartz, and silicon wafer were used for I-V, UV/vis absorption spectroscopic, and ellipsometric measurements, respectively as a substrate. The CuPc(OR)₈ LB film was formed with Y-type.

Measurements

A thickness of the 1, 3, 5, and 7 layered CuPc(OR)₈ LB films was measured by spectroscopic ellipsometer(Plasmos SD-2100). The UV/Vis absorption spectra of CuPc(OR)₈ LB films were measured with HP 8452 diode array spectrophotometer. A change in electrical conductance was measured with the films exposed to NO₂ gas. Current-voltage (I-V) characteristics of the film in plane was measured using Keithley 238 electrometer. Voltage was applied from 0 to 10V in an interval of 1V. Aluminium electrode was vacuum- deposited at a pressure of 10⁻⁵ Torr for electrical measurement.

RESULTS AND DISCUSSION

π -A Isotherm

Figure 2 shows the typical π -A isotherm of the CuPc(OR)₈. A limiting area per

molecule is about 112\AA^2 , and the proper transfer pressure for film deposition is in the range of the 20 to 40 mN/m. In this study, the surface pressure of 25mN/m was chosen for the film deposition.

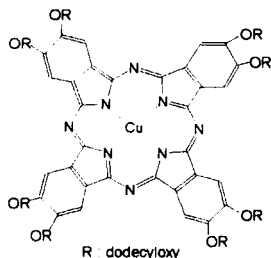


FIGURE 1 Molecular structure of the CuPc(OR)₈

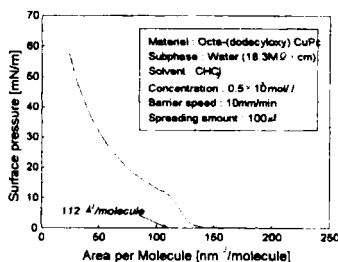


FIGURE 2 π -A isotherm of the CuPc(OR)₈.

Conformation of Film Deposition

There are several ways of confirming the film depositions such as the transfer ratio, electrical and optical properties, thickness measurement and so on. Figure 3 shows UV/Vis absorption spectra of CuPc(OR)₈ LB films as a function of number of layer. The intensity of several peaks increases linearly as the number of layer increases. As shown figure 4, which indicates that the film are well-deposited at molecular level. The average thickness of one layer of CuPc(OR)₈ LB film is about 64Å, which seems to be thicker than the previously reported value.^[3]

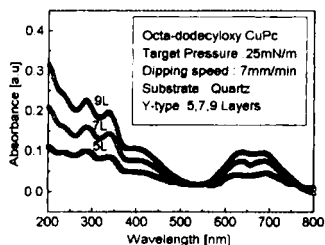


FIGURE 3 UV/Vis absorption spectra of CuPc(OR)₈ LB films.

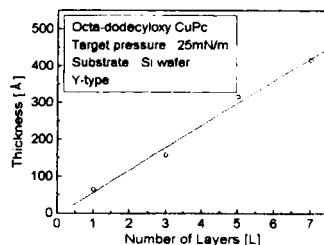


FIGURE 4 Thickness measurements by ellipsometry of CuPc(OR)₈ LB films.

NO₂ Gas Detection Characteristics

Figure 5 shows the electrical conductance variation of the 35 layered CuPc(OR)₈ LB films when the films are exposed to the 200ppm NO₂ gas. There is an increase of conductance by 7 times compared to that of gas-free states. Figure 6 shows the NO₂ gas sensitivity characteristics of CuPc(OR)₈ LB films as a function

of a number of layer. It was observed that the sensitivity increased as the film thickness increased. This may be due to the increase of the contact area between electrode and LB films as the film thickness increases.

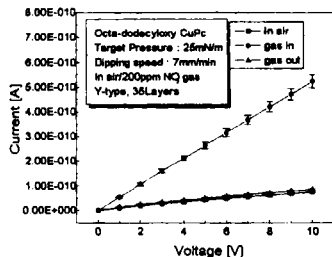


FIGURE 5 Current-Voltage characteristics of the CuPc(OR)_8 LB film of 35 layers.

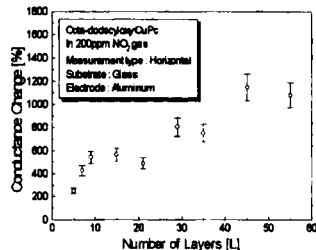


FIGURE 6 NO_2 gas sensitivity characteristics of CuPc(OR)_8 LB films as a function of number of layers.

CONCLUSIONS

The following conclusions have been obtained from the experiments with the CuPc(OR)_8 LB films being exposed to NO_2 gas at room temperature.

1. It was confirmed that CuPc(OR)_8 LB films were prepared well at molecular level.
2. It was found that there is an increase in electrical conductance of CuPc(OR)_8 films exposed to NO_2 gas by 7 times.
3. As the film thickness increases, the sensitivity of the CuPc(OR)_8 LB film to NO_2 gas increases.

Acknowledgments

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