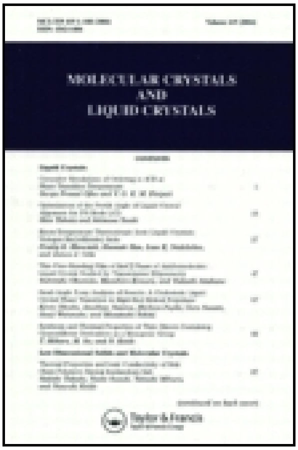

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No_2 Gas-Detection Characteristics of the CuTBP And Li_2Pc Langmuir-Blodgett Films

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Abstract The NO_2 gas-detection characteristics were investigated using the functional organic Langmuir-Blodgett(LB) films of copper-tetra-tert-butylphthalocyanines (CuTBP) and dilithium phthalocyanines(Li_2Pc). Optimum conditions for a film deposition were obtained through a study of π-A isotherms and a status of deposited-film was confirmed by electrical and optical methods such as thickness measurement using ellipsometry. A response of the LB films to the NO_2 gas was measured by a change in the electrical conductance when the films are exposed to the gases. The CuTBP LB film shows the bigger change in the electrical conductance than the Li_2Pc LB film when they are exposed to the NO_2 gases. The CuTBP and Li_2Pc LB films recover to the original state when the gas is evacuated.

INTRODUCTION

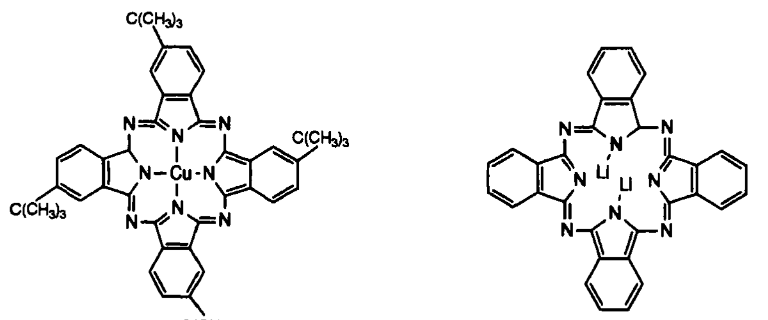
It is expected that a molecular-electronic devices could be developed near future using the organic materials. A manufacture of the ultra-thin film is necessary for these devices to be developed. It is, however, being recognized a limitation of miniaturization of the inorganic devices normally based on silicon. There is a growing interest and study for a manufacture of the organic devices to overcome the limitation of the inorganic ones using different techniques.[1] The Langmuir-Blodgett(LB) technique has the advantage in aligning the molecular orientations and easy control of thickness compared to the other methods such as physical-vapor deposition(PVD) and chemical-vapor deposition(CVD).[2] A basic concept of the LB technique is transferring the monolayer which is well-oriented on the subphase to the solid substrate.

Phthalocyanines are well-known organic semiconducting materials not only in the stability of thermal and chemical aspects but also in the optical and electrical sensitivities to the gases.[3] Thus, it is being used in various electrical and electronic devices. It is, especially, under investigation for a potential application as the gas sensor, because it is very sensitive to the NO_X gases.[4,5] Our research group has synthesized several phthalocyanine derivatives, such as copper-tetra-tert-butylphthalocyanine (CuTBP), dilithium phthalocyanine (Li_2Pc), and tetra-3-hexadecyl-sulphamoyl-copperphthalocyanine(HDSM-CuPc). In this paper, the NO_2 gas-detection characteristics of the CuTBP and Li_2Pc LB films are discussed by measuring the electrical conductance at room temperature.[6,7]

EXPERIMENTAL DETAILS

Materials and π-A isotherm

In this study, CuTBP($C_{48}H_{48}CuN_8$, M.W.=800.51) and Li_2Pc($C_{32}H_{16}N_8Li_2$, M.W.=526.41) molecules which are phthalocyanine derivatives are used. Here, M.W. refers a molecular weight. A structure of the CuTBP and Li_2Pc molecule is, respectively, shown in Fig. 1(a) and (b). Optimum conditions of manufacturing the LB films were mostly determined by a study of surface pressure-area (π-A) isotherms. The π-A isotherms were measured using the moving-wall type LB deposition apparatus(NL-LB-240S-MWA). And purified water(~18MΩ · cm) was used as the subphase.



(a) (b)

FIGURE 1 Molecular structures of the (a) CuTBP and (b) Li_2Pc.

Film Depositions

A xylene($C_6H_4(CH_3)_2$) was used as a solvent for CuTBP. And the spreading solution of the Li_2Pc was made with a concentration of 10^{-3} mol/l by mixing chloroform and aceton(1:1 volume ratio). Quartz plate, silicon wafer and microscope glass slide substrate were, respectvely, used for a UV/visible absorption measurement, thickness measurement by spectroscopic ellipsometry, and a gas-detection experiment. Aluminium electrodes were vaccum-deposited at a pressure of 10^{-5} Torr for a measurement of the electrical capacitance and conductance. The CuTBP and Li_2Pc LB films were made with a formation of Y-type and Z-type, respectively.

Measurements

The thickness of the different number of layers was measured by spectroscopic ellipsometry (ellipsometer: Rudolf S2000). The electrical capacitance of the LB film was measured using the LCR meter(EDC-1620). Gas-detection characteristics of the 5-layered LB films were performed using home-made experimental system. A change in the electrical conductance along the vertical direction was measured with the films exposed to 200 ppm of the NO_2 gases. The LB films are situated in the chamber filled with the NO_2 gases. Current-voltage(I-V) characteristics of the films along the lateral direction were measured using the Keithly 238 electrometer. Voltage was applied from 0 to 10V in an interval of 1V (See Figure 2).

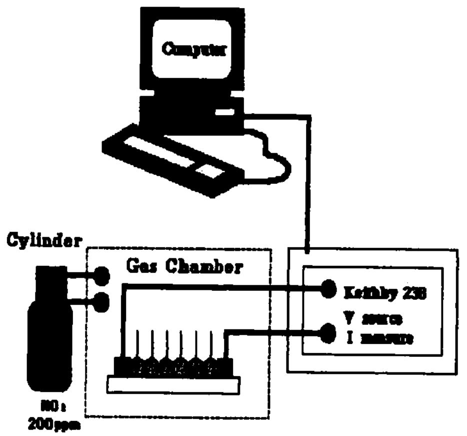


FIGURE 2 Schematic diagram of the current-voltage measurement circuit.

RESULTS AND DISCUSSION

The π-A isotherms tell us the optimum conditions of film deposition. Figure 3 shows the typical π-A isotherms of the CuTBP and Li_2Pc molecules. A limiting area of the CuTBP and Li_2Pc molecule is, respectively, around 72 $Å^2$ and 14 $Å^2$. The proper surface pressures for the film depositions of the CuTBP and Li_2Pc are, respectively, in the range of 20~40mN/m and 30~35mN/m. These results are in agreement with the reported ones.[8] A summerized optimum conditions for the film deposition of each specimen are shown in table I.

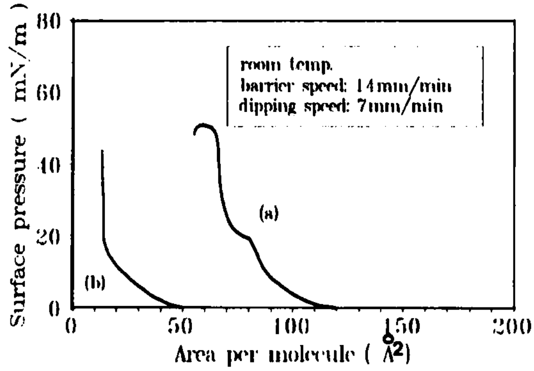


FIGURE 3 Typical π-A isotherms of the (a) CuTBP (b) Li_2Pc molecules.

TABLE I Deposition conditions of the CuTBP and Li_2Pc LB films.

	CuTBP	Li_2Pc
Barrier speed (mm/min)	14	14
Dipping speed (mm/min)	7	7
Surface pressure (mN/m)	25	30
Subphase temperature (℃)	room	room
pH	5.6	5.6

Confirmation of Film Deposition

There are several ways of confirming the film depositions such as the transfer ratio, electrical capacitance, mechanical and optical properties. Figure 4 shows the film thickness of the CuTBP and Li_2Pc LB films measured by spectroscopic ellipsometry. The thickness increases linearly as the number of layer increases, which indicates that the films are well-deposited. The average thickness of one layer of CuTBP LB film is about 17Å, which states that the molecules are oriented perpendicular to the substrate. The average thickness of one layer of Li_2Pc LB film is about 40Å, which implies the formation of multilayers rather than monolayer on the substrate.

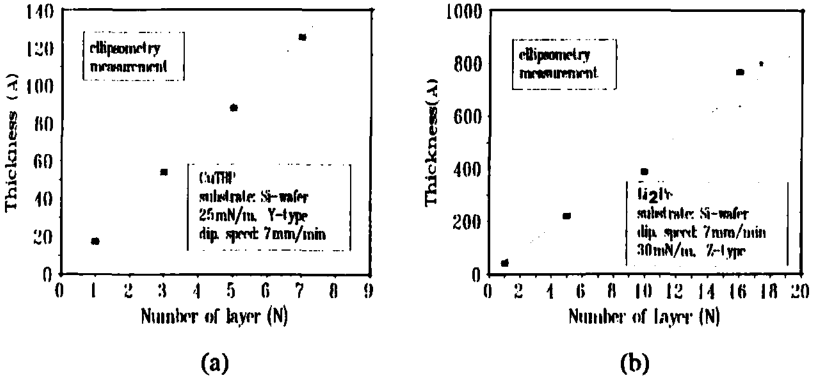


FIGURE 4 Thickness mesurements by ellipsometry depending on the number of layers of the (a) CuTBP and (b) Li$_2$Pc LB films.

Response to the NO$_2$ Gases

Figure 5 shows the electrical conductance variation of the 5 layered CuTBP and Li$_2$Pc LB films when the films are exposed to the NO$_2$ gases. Voltage was applied from 0 to 10V in an interval of 1V. Figure 5(a) and (b) show the conductance variations of the CuTBP and Li$_2$Pc LB films, respectively. There are increase of conductance by 40 and 10 times compared to that of gas-free states, respectively, when the films are exposed to the NO$_2$ gases. Thus, we can say that these films are sensitive to the NO$_2$ gases. And they also show that the films return to the original state when the gas is evacuated.

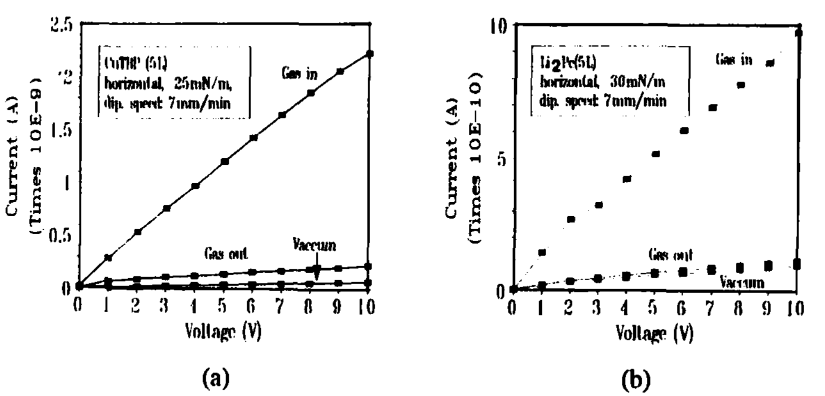


FIGURE 5 Current-Voltage characteristics of the (a) CuTBP and (b) Li$_2$Pc LB films comparing the gas-in and gas-out state.

CONCLUSIONS

The following conclusions have been obtained from the CuTBP and Li_2Pc LB films interacting with the 200 ppm of NO_2 gases at room temperature.

(1) The proper deposition conditions have been obtained through a study of π-A isotherms.

(2) We were able to confirm the status of the deposited films by thickness measurement using ellipsometry.

(3) When the LB films are exposed to the NO_2 gases, the phthalocyanine LB films show the reproducibility. Thus, the phthalocyanine LB films may be used as a NO_2 gas sensor.

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