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Structure and Properties Due to NO_2 Gas in Copper Phthalocyanine Films Prepared by Oblique Vacuum Evaporation Method

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1. Introduction

Phthalocyanine (Pc) dyes [1] have been attracting much interest for developing many kinds of electronic and optical devices. Many studies using various Pc derivatives have been reported for organic solar cells, field effect transistors, organic light emitting diodes, gas sensors, secondary batteries, etc. Certain conducting polymers [2] have achieved limited success in electronic nose applications, and phthalocyanines and porphyrins have attracted interest as organic sensors [3-7].

In this study, copper phthalocyanine (CuPc) thin films were fabricated using an oblique vacuum evaporation method [8] and the structure and properties due to NO_2 gas exposure were investigated. The structure and properties were evaluated by the measurements of atomic force microscopy (AFM), attenuated total reflection (ATR) and current vs. voltage characteristics.

2. Experimental Details

Figure 1 shows the chemical structure of CuPc molecule used in this work. CuPc films were fabricated by an oblique vacuum evaporation method. The oblique angle θ_o was defined as the inclination angle of the vertical line of the substrate to the evaporation source. That is, $\theta_o = 0°$ is a conventional evaporation method. For the AFM and ATR measurements, the CuPc thin films with the thickness of 15 nm were deposited on the Ag-evaporated glass substrates. For the electrical measurement of current vs. voltage characteristics, Ag electrodes were evaporated on glass substrates with the gap between the electrodes of about 20 mm and the gap length of about 20 μm and Cu thin films with the thickness of about 15 nm were deposited on the substrates with Ag gap electrodes.

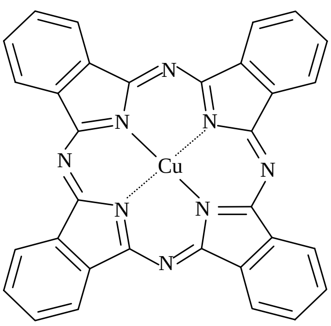
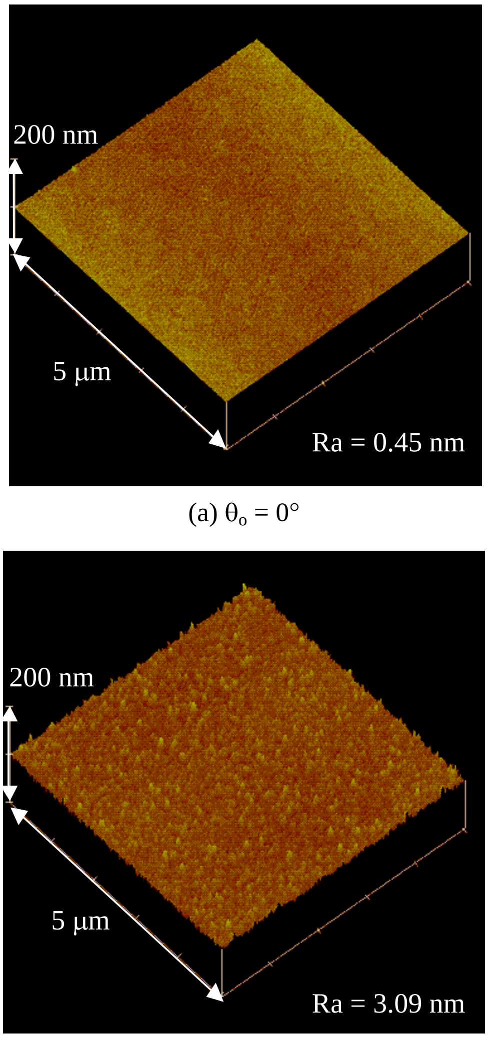


Fig.1. Chemical structure of CuPc molecule.

3. Results and Discussion

Figure 2 show the AFM images of the CuPc thin films on Ag. (a) and (b) indicate the results for the samples prepared at $\theta_o = 0°$ and 80°, respectively. The surface roughness Ra of the CuPc films was found to increase markedly with the increase of the oblique angle.

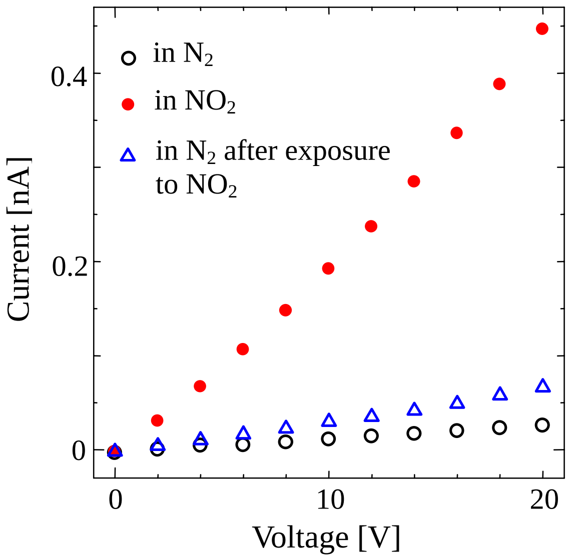


(a) $\theta_o = 0°$

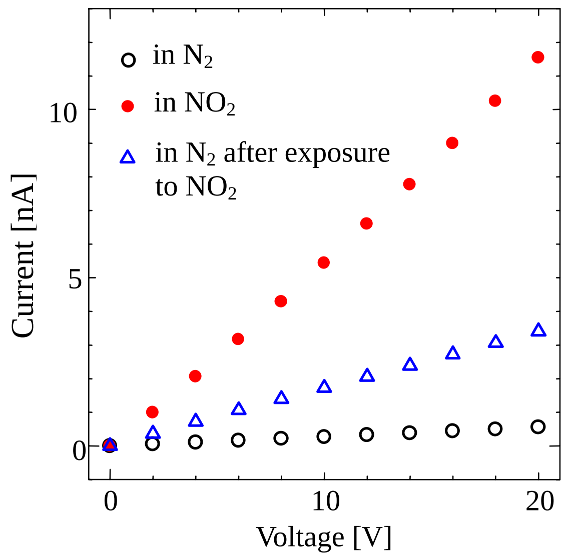
(b) $\theta_o = 80°$

Fig. 2. AFM images of CuPc thin films on Ag thin films prepared at the different oblique angle θ_o.

Figure 3 shows the current vs. voltage characteristics of CuPc thin films. (a) and (b) indicate the results for the samples prepared at θ_o = 0° and 80°. The open circles represent the result initially measured in N_2 gas. The closed circles represent the result measured in 10 ppm NO_2 gas after exposure to 10 ppm NO_2 gas. The triangles represent the result measured in N_2 after exposure to 10 ppm NO_2 gas. It was found that the current considerably increased after exposure to 10 ppm NO_2 gas. The increase in current for the sample prepared at θ_o = 80° is also found to be much larger than that for the sample prepared at θ_o = 0°. It was considered that the results were strongly related with the structure of the CuPc thin films.



(a) θ_o = 0°



(b) θ_o = 80°

Fig. 3. Current vs. voltage characteristics of CuPc thin films in N_2, in 10 ppm NO_2, and in N_2 after exposure to NO_2.

The current response to 10 ppm NO_2 gas for the CuPc thin film prepared at θ_o = 80° is shown in Fig. 4. The response and recovery times were not so fast. The applied voltage was 10 V. It was thought that sensitivity for the sample prepared at θ_o = 80° is better than that for the sample prepared at θ_o = 0°.

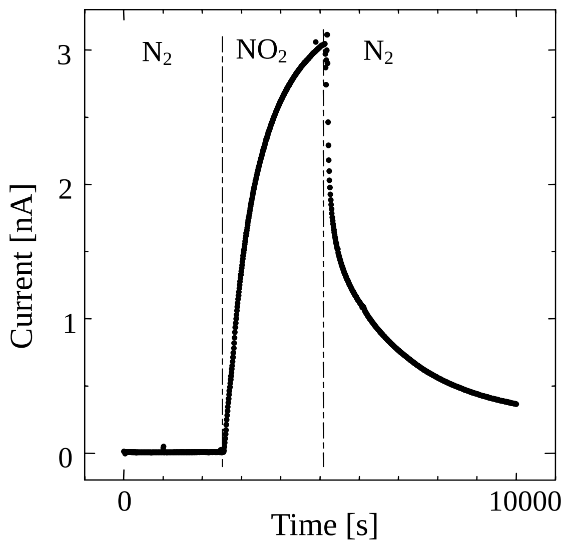


Fig. 4. Current response to 10 ppm NO_2 gas for the CuPc thin film prepared at θ_o = 80°. The applied voltage was 10 V.

The ATR properties were also measured for the CuPC thin films prepared at θ_o = 0° and 80°. It was found that the resonance curves shifted to the higher incident angle due to NO_2 gas exposure. From the ATR curves, the complex dielectric constants of the CuPc thin films were also evaluated.

4. Conclusions

CuPc thin films were prepared by the oblique vacuum evaporation method and the structure and properties were investigated. It was found that the structure and properties were considerably changed by the oblique angle of the vacuum evaporation. The properties due to NO_2 gas exposure were also markedly changed. The results in this work are useful for the development of sensing devices.

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