Influence of Molecular Orientation on Electrical Conductivity in Copper Phthalocyanine Thin Films

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Abstract

Control the orientation of molecular stacking in copper phthalocyanine (CuPc) thin films were tried by applying an electric field during vacuum deposition. The results of the absorption spectra and X-ray diffraction suggest that the electric field changes the molecular configuration in the CuPc thin films. The vertical resistivity of the film grown under the electric field was smaller than that of film grown without electric field.

Introduction

Metallophthalocyanines (MPc) have attracted a great deal of research interest for many years due to their excellent properties such as high thermal and chemical stability, high photoconductivity and excellent semiconducting behavior. These researches cover quite wide fields, such as liquid crystals, molecular rectifying devices, organic field-effect transistors, light-emitting diodes, molecular wires, and molecular switches.[1] As it is well known that highly ordered MPc films are very important for high performance of electronic devices based on organic materials, it is essential to develop new growing techniques to grow high quality organic films for high performance. Copper phthalocyanine (CuPc) is one of the metallophthalocyanines, which shows a high photoconductivity in visible region. Many studies have been reported on applications of CuPc films to photoreceptors in electrophotography, solar cells, etc. It is also desirable to prepare highly ordered CuPc films for those applications. Two types of cuPc layers, thin films and CuPc pigment dispersed layers, are usually used for device applications.

Figure 1 shows the chemical structure of the CuPc molecule. It is know that there are several crystal forms in CuPc, on of which, α fomr, is shown in Fig. 2. We prepared CuPc thin films by vacuum deposition and tried to control the molecular orientation in the films by applying an electric field during the vacuum deposition. This paper describes the experimental results on the electrical properties of CuPc thin films vacuum deposited under applying an electric field.

Experimental

Applying an Electric Field Perpendicular to the Substrate by Using an Electret

Copper phthalocyanine (CuPc) thin films, 0.5-1.5 μm in thickness, were grown by vacuum vapor deposition on ITO glass substrates or Corning7059 glass substrates. Two kinds of CuPc films were prepared under the same conditions with or without applying an electric field during the vacuum deposition. One was grown by the conventional vacuum deposition with resistance heating, which means any electric field was not applied during vacuum deposition. The other was also grown by the vacuum deposition, but an electric field was applied to the growing films during vacuum deposition. The electric field was introduced in the space of film growth by using an electret of Teflon sheet placed between the substrate and the substrate holder (Fig. 3). The electric field was applied perpendicular to the growing film in this case.

In order to examine the crystal structure, X-ray diffraction analysis was carried out and absorption spectra were measured on the CuPc thin films. Electrical resistivities of CuPc thin films, perpendicular to (vertical resistivity) and parallel to (parallel resistivity) the film plane were measured. For that purpose, an Au electrode was deposited on the CuPc thin film deposited on the ITO glass and the vertical resistivity was measured. For the parallel resistivity measurements, a pair of gap electrodes of Au were deposited on the CuPc thin films vacuum deposited on the Corning 7059 glass substrate.

Applying an Electric Field Parallel to the Substrate by Using a Pair of Gap Electrodes

The application of an electric field parallel to the growing films was carried out as follows. First, a pair of Au gap electrodes (3 mm in width, 8 mm in length, and the spacing: 1 mm) were deposited on the Corning7059 glass substrate as shown in Fig. 4. Then, a DC voltage of 1kV was applied to the electrodes and the vacuum deposition of CuPc was carried out.

The substrate temperature was changed in the range from room temperature to 150°C. The thicknesses of CuPc thin films prepared in this experiment were about 0.5-1.5 µm. The crystal structure of the films was analyzed, and the resistivity of the films parallel to the film place were also measured.

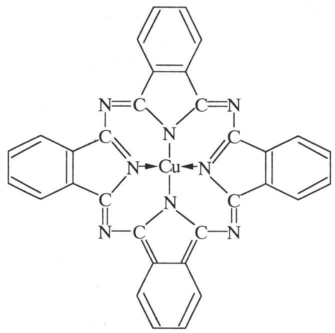

Figure 1. Chemical structure of CuPc molecule.

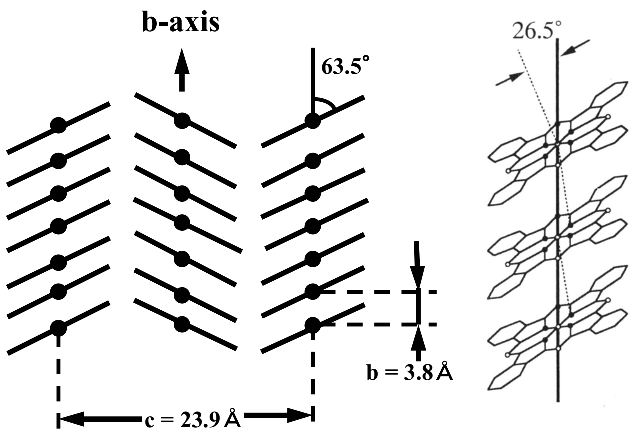

Figure 2. Molecular configuration of α-type CuPc.

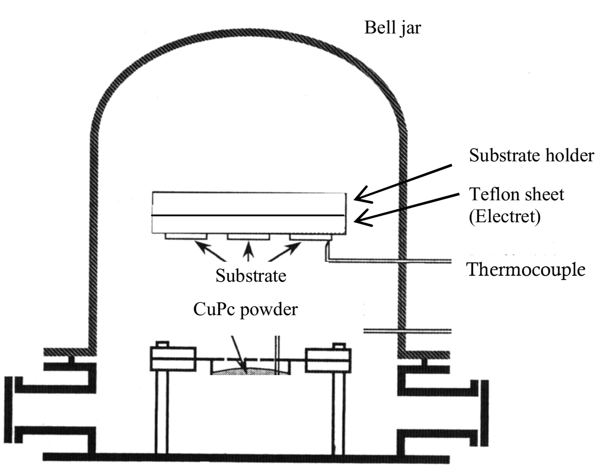

Figure 3. Vacuum deposition apparatus with Teflon electret sheet.

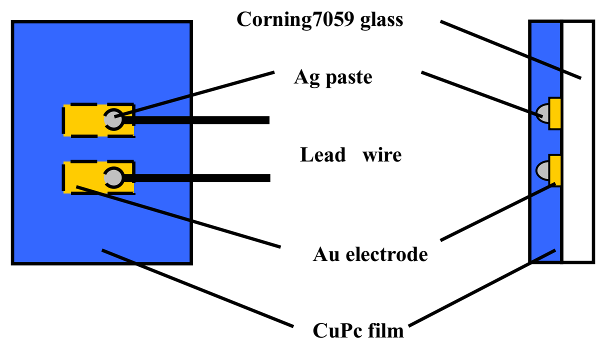

Figure 4. A pair of Au electrode configuration for applying electric field parallel to the film plane during vacuum deposition.

Results and Discussion

Figure 5 shows the optical absorption spectra of the CuPc films, vacuum deposited without and with applying an electric field perpendicular to the growing film during the vacuum deposition. It was found that the absorption peaks were enhanced in the both ranges of 300-400 nm and 600-800 nm for the CuPc film grown with applying electric field during vacuum deposition.

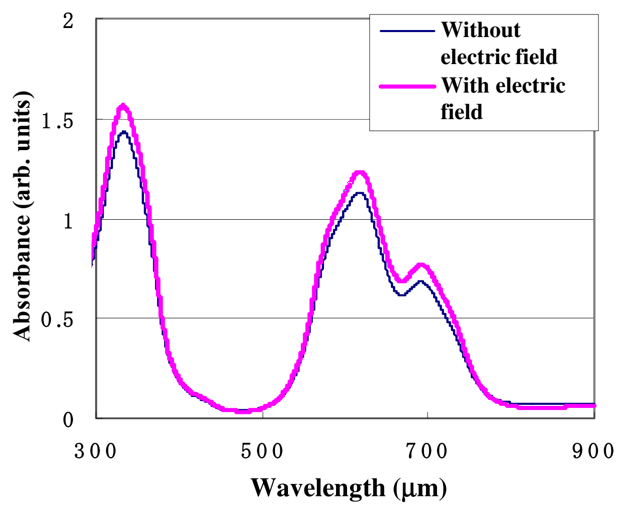

Figure 5. Optical absorption spectra of CuPc thin films

Ji et al. grew CuPc films by vacuum deposition under applying a magnetic field and they reported that the application of magnetic field improved the molecularb orientation.[2] The absorption peaks were enhanced in the both ranges of 400-500 nm and 600-1100 nm for the CuPc film grown with applying magnetic field during vacuum deposition in their result. Our result is in good agreement with their result, and suggests that an electric field can bring about changes in the molecule stacking orientation as the magnetic field.

The b-axis of the CuPc molecules is oriented perpendicular to the substrate surface and the a-axis of the CuPc molecules is oriented parallel to the substrate surface.

Figure 6 shows the X-ray diffraction pattern of the CuPc film vacuum deposited without electric field. The peak appeared at $2\theta = 27.5°$. Layer spacing of 3.24 Å was obtained from the result according to the Bragg equation. Figure 7 shows X-ray diffraction pattern of the CuPc film vacuum deposited with electric field. The peak appeared at $2\theta = 27.6°$. This result indicates that the layer spacing decreased from 3.24 Å to 3.23 Å in the direction of b-axis by applying an electric filed during vacuum deposition. This distance is almost equal to the distance between molecules. The result suggests that the intermolecular distance in the direction of b-axis was shorten by applying an electric field.

Table 1 shows resistivities, perpendicular to and parallel to the film plane, of the CuPc films grown under an electric field perpendicular to the growing film. The vertical resistivity of the film grown under the electric field was smaller than that of film grown without electric field.

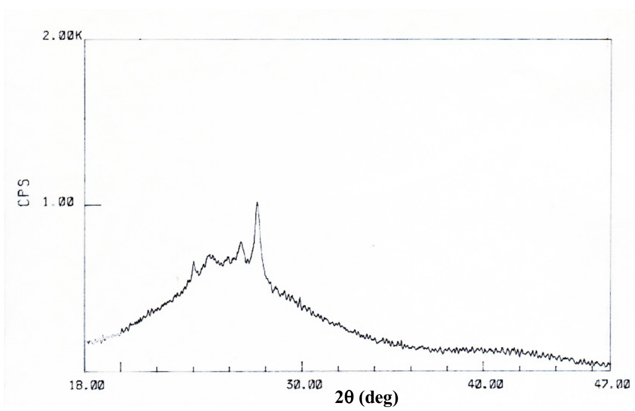

Figure 6. The X-ray diffraction pattern of CuPc film deposited without electric field.

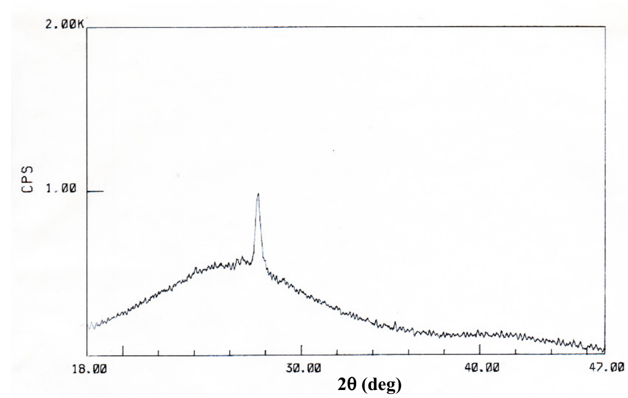

Figure 7. The X-ray diffraction pattern of CuPc film deposited with an electric field.

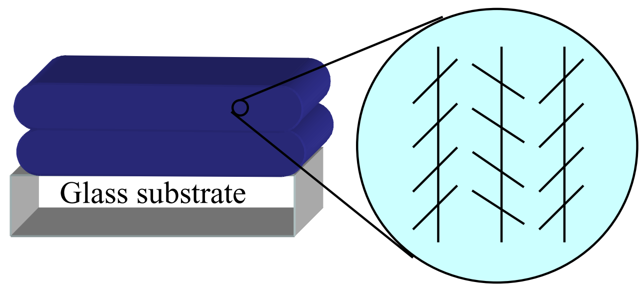

Figure 8. Molecular configuration in CuPc thin film.

Table 2 shows the resistivity, parallel to the film plane, of the film grown under an electric field parallel with the film plane for two choices of substrate temperature. The result shows the parallel resitivity of the film grown under the electric field decreased, and the effect of applying an electric field during vacuum deposition of CuPc film was enhanced by raising the substrate temperature during vacuum deposition. The CuPc molecules which reach the substrate do not lose their energy immediately at a high substrate temperature, making the molecular orientation more easily due to the applied field.

Table 1. Resistivities of the films grown under an electric field.

	Perpendicular to the substrates	**Parallel to the substrates**
Without electric field	2.4×10^8 Ωcm	4.3×10^7 Ωcm
With electric field	3.6×10^7 Ωcm	1.3×10^8 Ωcm

Table 2. Resistivites, parallel to the film plane, of the CuPc films deposited with an electric field parallel to the film plame during vacuum deposition.

	Substrate temperature 50 ^{o}C	Substrate temperature 150 ^{o}C
Without electric field	1.6×10^6 Ωcm	6.0×10^8 Ωcm
With electric field	1.0×10^6 Ωcm	2.0×10^8 Ωcm

The resistivities of both films grown with electric field and without electric field increased at the higher substrate temperature. This is because crystal grain of CuPc become large and the film becomes rough.

Conclusion

In summary, the use of electric field in controlling the molecule stacking orientation during vacuum deposition of CuPc film was shown in this study. The results of the absorption spectra and X-ray diffraction suggest that the electric field changes the molecular configuration in the CuPc thin films. The vertical resistivity of the film grown under the electric field perpendicular to the film plane was smaller than that of film grown without electric field. The effect of applying an electric field parallel to the film plane during vacuum deposition of CuPc film was enhanced by increasing substrate temperature.

References

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Biography

Toshikazu Tsuchiya is a student of the graduate school of science and engineering of Ibaraki University, Japan. He has been working on electronic properties of organic semiconductor thin films, and currently studying molecular orientation in copper phthalocyanine thin films. He is a member of The Society of Electrophotography of Japan and The Surface Finishing Society of Japan.