Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Anomalous Changes in Electric Conductivity of Cu-Phthalocyanine Observed During Evaporation Process

Shin'ichi Kawato [a], Kouichi Hayashi [a], Toshihisa Horiuchi [a] & Kazumi Matsushige [a]

[a] Department of Electronic Science and Engineering, Faculty of Engineering Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto, 606-01, JAPAN

Version of record first published: 04 Oct 2006.

To cite this article: Shin'ichi Kawato , Kouichi Hayashi , Toshihisa Horiuchi & Kazumi Matsushige (1996): Anomalous Changes in Electric Conductivity of Cu-Phthalocyanine Observed During Evaporation Process, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 247-256

To link to this article: http://dx.doi.org/10.1080/10587259608040340

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 247–256
Reprints available directly from the publisher
Photocopying permitted by license only

ANOMALOUS CHANGES IN ELECTRIC CONDUCTIVITY OF Cu-PHTHALOCYANINE OBSERVED DURING EVAPORATION PROCESS

SHIN'ICHI KAWATO, KOUICHI HAYASHI, TOSHIHISA HORIUCHI AND KAZUMI MATSUSHIGE
Department of Electronic Science and Engineering, Faculty of Engineering
Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-01 JAPAN

Abstract The *in-situ* measurement of lateral electric conductivity of copper phthalocyanine was conducted during a vacuum evaporation process. The conductivity was found to change anomalously at the first stage of film growth. With increasing thickness, it increased abruptly from about 2 nm in film thickness, and showed a sharp peak at about 7 nm. Even if the evaporation rate or the sample purity was varied, the similar behavior was observed. Possible reasons for this anomalous phenomenon are discussed from the structural changes and molecular motion occurring during the growth process of the evaporation films.

INTRODUCTION

In these years, many functional molecules have drawn a great interest from their superior electronic, photonic and other interesting properties, and have been extensively investigated from the view points of application. In order to realize such the electro-optic devices utilizing their maximum functional abilities, however, it is necessary to arrange the each molecules as we desire and to control their structures and properties at thin film states. Accordingly it is recognized that the precise understanding of the structures and various properties of such thin films especially

during a growth process is essential.

In the present work, we used copper phthalocyanine (CuPc), one of such functional organic materials. CuPc is a typical p-type organic semiconductor, and well known to exhibit photoconductivity and high sensitivity to electron acceptor gases[1,2], and so its photonic and electronic properties at a film state have been extensively investigated[3,4,5]. However, the *in-situ* observation of dark conductivity during evaporation has never been conducted, and the details of the conduction mechanisms in the ultra-thin films have not been elucidated yet.

In these years, on the other hand, we have studied crystalline structures and molecular orientation in CuPc film during an evaporation process, by using a total X-ray diffraction and fluorescence measurement system combined with a vacuum evaporation apparatus, and found that the CuPc molecules start to crystallize over an amorphous-like layer in the case of glass substrate. Some details were reported elsewhere[6].

In order to investigate how the electric conduction is affected by such structural changes in the CuPc films, we performed here the *in-situ* measurement of dark conductivity during an evaporation process and analyzed the dependency of electric conductivity on film thickness.

EXPERIMENTALS

CuPc powder was purchased from Tokyo Chemical Co. Ltd., and the purified sample was prepared by a train sublimation technique. Before the evaporation the sample was further cleaned by heating under vacuum condition at about 600 K for several hours. Film thickness and evaporation rate were monitored by a quartz oscillation. The density of CuPc film was assumed to be 1.62 g/cm^3, which is the density of α-type CuPc crystal. The sample evaporation was conducted at several different conditions with keeping the rates at the same pressure of 10^{-5} Pa.

The measuring system employed is shown in Figure 1. An optically flat SiO_2 glass was used as the substrate. For *in-situ* conductivity measurements, an interdigitated gold electrode were deposited on it, whose gap width was 100 μm. Before the evaporation, its surface was cleaned by heating the substrate up to 450 K

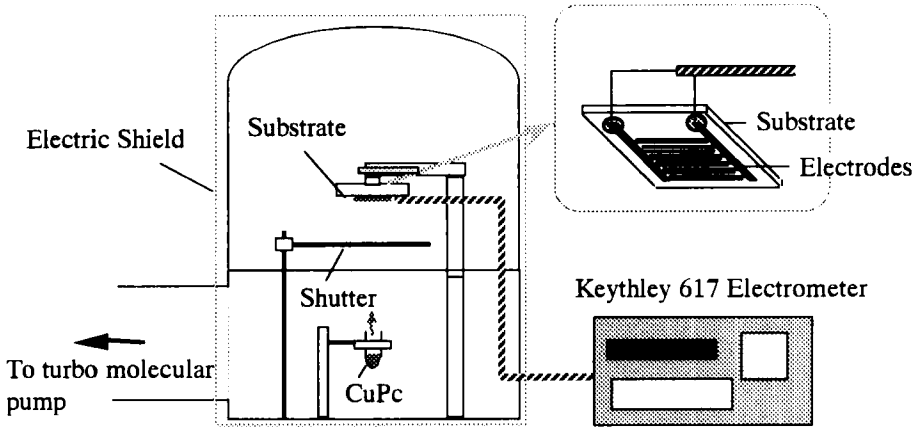


FIGURE 1 The system of evaporation

under vacuum condition. The evaporation was started after the substrate was cooled to room temperature.

Electrical conductivity measurements were performed by applying the voltage of 100 V between the electrodes, therefore the electric field between the electrodes was 10 KV/cm. The current was measured with Keythley 617 high impedance electrometer.

RESULTS AND DISCUSSION

First, purified CuPc sample was tested. Figure 2 shows one example of the time variations of observed value of current and film thickness. Although the film thickness monitored with a quartz oscillation crystal revealed almost a monotonous increase after opening an evaporation shutter, the current did not immediately increase and was in an extremely low level up to about 2 nm in film thickness, and then began to increase sharply. After the current shows the peak at about 7 nm, it decreased. Although this kind of the peak formation in the current-time(film thickness) relation has not been reported, similar behavior was always observed in this study, even when non purified CuPc sample was used, or the evaporation rate was changed between 0.2 to 40 nm/min, though the values of measured currents varied considerably at each experiments. Any

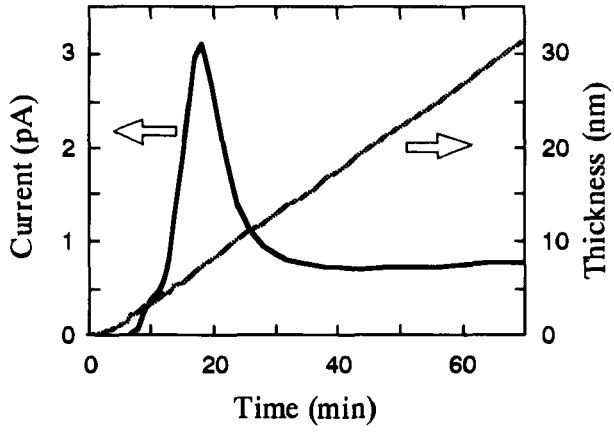


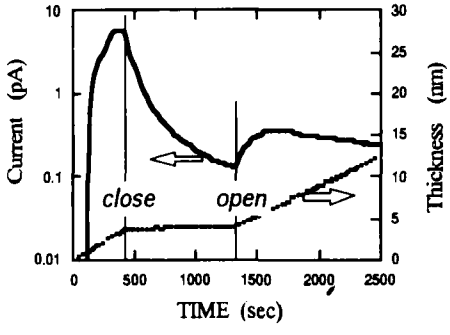
FIGURE 2 The typical time variation of electric current and film thickness

systematic dependency of the value on evaporation rates was not observed in these experiments. Interestingly, for all experiments with using purified CuPc sample, the observed conductivity was higher than the cases using non purified CuPc under the same evaporation rate. This fact suggests that impurities included in non purified sample disturb in some degree to the increase in the lateral electric conductivity in the film, or carrier generation.

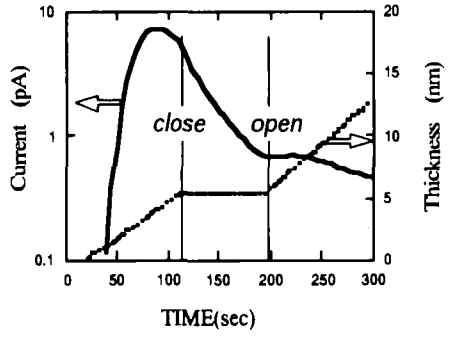
Further experiments were carried out in order to investigate the possible reasons for the observed singular time variations of electric currents. Since such the time variation can be thought to originate both from the lapse of time and from the increase of film thickness, in order to differentiate these two factors, the current variation was measured while stopping the increase of film thickness. In the experiment, the shutter was closed after the current value showed a peak, and reopened after a while.

Figure 3(a) shows the observed typical time variation of current and film thickness. While closing a shutter, in other words interrupting the absorption of the sample to the substrate, the current steeply decreased. Then when the shutter was reopened, it increased for a while and decreased gradually again.

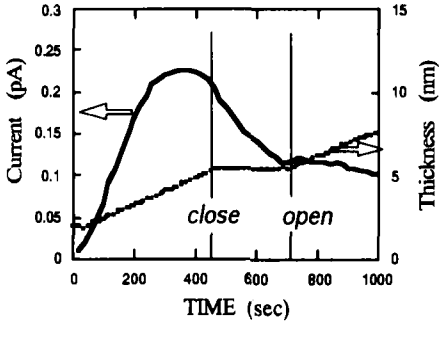
Similar experiments were performed by making the evaporation rate faster or using non purified CuPc, and different behaviors in the time variation were observed as shown in Figure 3(b,c,d). The speeds of the current decrease at the state of shutter close were lower as the evaporation rate was faster or as the purity of the sample was less



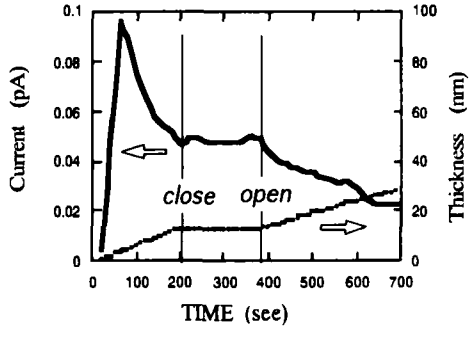
(a) using purified sample, rate was 0.4nm/min



(b) using purified sample, rate was 4nm/min



(c) using non purified sample, rate was 0.4nm/min



(d) using non purified sample, rate was 3nm/min

FIGURE 3 The time dependency of measured currents with shutter opened and re-opened during evaporation

pure. And the rates of the current increase after the shutter reopening were lower, too. When non purified samples were used and in addition the evaporation rate was fast enough, the current kept almost constant value while shutter was closed and then began to decrease again at reopening, as revealed in Figure 3(d). In this case the conductivity

seems to depend not only on time but on film thickness.

There are many reports on the formation mechanism of thin film in this CuPc. The most popular one may be the cluster growth mechanism, and so the lateral current variation at an initial film growth could be understood by a simple percolation theory. In this case the lateral conductivity increases rapidly at the early growth stage according with coalescence of clusters, and then would become almost constant value when this process is completed, by forming a continuously connected thin layer.

In contrast, the conductivity variation we observed here was quite different from the speculated one described above. Although the rapid increase at the early stage may be understandable by a percolation theory, the drastic decrease after the maximum can not be explained by such a simple theory, suggesting that other mechanisms should be incorporated with the observed conductivity variation. There are following two possible mechanisms for understanding this.

First, the effects of impure oxidizing gases are considered. It is reported that the conductivity of CuPc thin film is sensitive to oxidizing gases on ppm order. If such

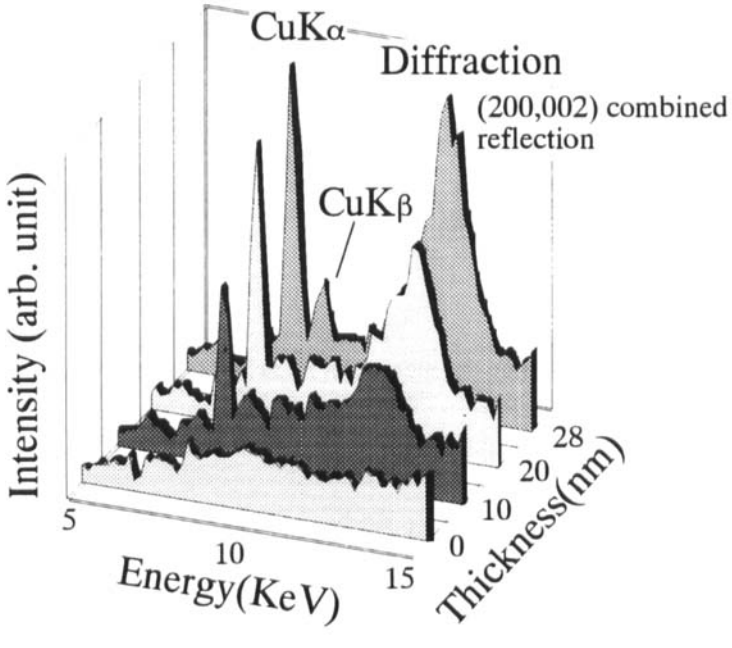


FIGURE 4 X-ray diffraction and fluorescence spectral changes with increasing film thickness

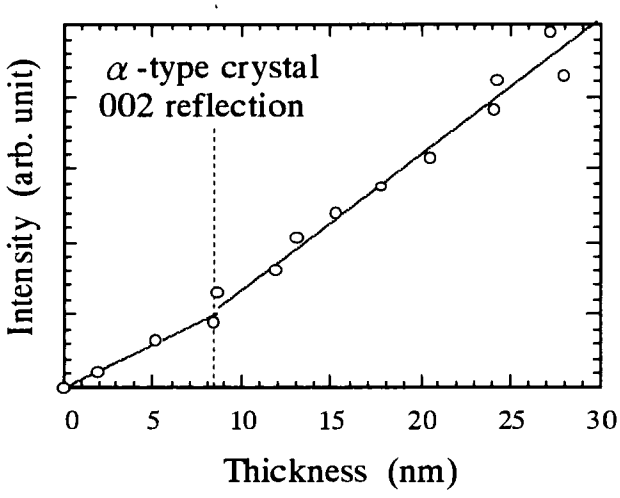


FIGURE 5 Thickness vaiation of intensity of 002 reflection from α -type crystal

gases were still released from a heated cell when an evaporation shutter was open, the first peak of the conductivity could happen. However in this case, the early variation of the conductivities during evaporation might depend mainly on time, so the thickness dependencies must vary when the rate was extensively changed. But in reality these changes were not observed. Likewise the time variation observed when the shutter was closed and reopened, could not be completely explained. And the gases still physisorbed on the surface of glass substrate before evaporation, may be considerable as the reason. Nevertheless it is not be able to explain all, either.

Next, the some structural changes at early stage of the film growth are considered. As showed in Figure 4 and 5, the results of *in-situ* TRXD measurements indicated that the diffraction intensity from the CuPc crystals formed in the evaporation film is rather weak in an early stage of film growth, 0～8 nm in film thickness, and then α -type CuPc crystals start to grow. This suggested that the structural changes from amorphous-like to more stable crystalline ones occur at about 8 nm in film thickness. Further details were reported elsewhere[6]. This value is almost consistent with the point where the early anomalous high conductivity was observed. So it is natural that this structural change is one of the most effective causes. In this case, however, there are the serious problems, why the lateral conductivity is higher at

amorphous-like state and why it becomes lower as crystals grow.

CuPc evaporated thin films generally form the cluster structure and they are polycrystals. In this case, the hopping barriers between molecular units, between polycrystals, and between different clusters, will be the extensive barrier for the lateral electrical conduction. In contrast there are not such barriers in amorphous-like state, and moreover CuPc molecules may still migrate on substrate in that state. As a result the lateral electrical conductivity in amorphous-like state is relatively high. Then as film grows, the molecules begin to condense and form cluster structures, as shown in Figure 6. It is important that in this process the cluster structures form not on the amorphous-layer but rather inside of it, and this change of film growth is not generally

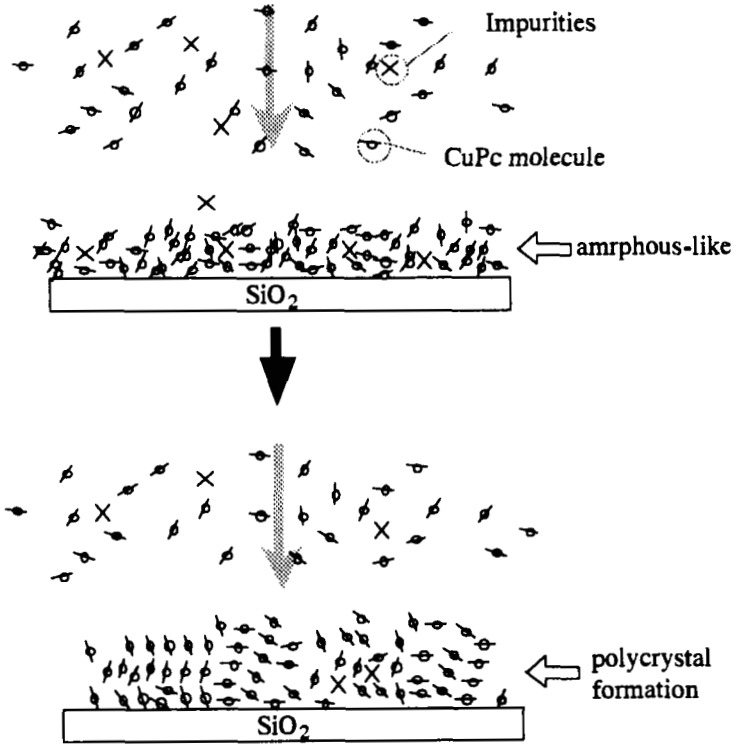


FIGURE 6 Structural change on the first stage of CuPc film growth

called layer-by-cluster type. Therefore the amorphous-like state gradually changes to polycrystals, the cluster structures. So the conductivity decreases. The changes of structures will occur with some relaxation time, and more supply of molecules will accelerate the changes. The impurities contained in non purified CuPc sample or the fast evaporation rate may form the amorphous-like state and disturb the changes in some ways. These hypotheses can explain our results rather reasonably.

The changes above mentioned is intrinsic. But in reality the observed variations may be concerned with both the structural change and the effects of oxidizing gases. For example, the conductivity of CuPc thin film may be more sensitive to such gases at the amorphous-like states. All the same, the conductivity variation of early stage of evaporation is concerned with structural change.

CONCLUSION

The variation of dark conductivity of CuPc thin film's growth during evaporation process was observed. The conductivity showed anomalous peak at early stage of film growth, 0～8 nm in film thickness. Using CuPc sample with different purity or the various rates of evaporation rate the similar behavior was observed. The time variation of the conductivity during interrupting the evaporation at the peak, seemed to be dependent on both evaporation rate and sample purity.

These results are understood by the structural changes occurring at early stage of film growth rather than a simple percolation theory, and this structural change is not caused by a simple layer-by-cluster type of film growth, probably a new type. However, further experiments ate needed to make clear. The measurements completely *in-situ*, under higher vacuum, with substrate temperature controlled, or with changing substrates are considerable.

REFERENCE

1. A. K. Hassan and R. D. Gould, Int. J. Electronics, 69, No.1, 11-17 (1990)
2. S. Dogo, J. -P. Germain, C. Maleysson and A. Pauly, Thin Solid Films, 219, 251-256 (1992)
3. R. D. Gould, Thin Solid Films, 125, 63-69 (1985)
4. R. D. Gould, J. Phys. D: Appl. Phys., 9, 1785-1790 (1986)
5. N. Minami and M. Asai, Jpn. J. Appl. Phys., 30, No.4A, L643-L646 (1991)

6. K. Hayashi, T. Horiuchi and K. Matsushige, Reports on Progress in Polymer Physics in Japan, 37, 295-298(1994)