Eurasian ChemTech Journal 11 (2009) 45-49

On Physical Vapor Deposition of Organic Semiconductor CuPc Thin Films in High Gravity

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Abstract

Thin organic films of *p*-type semiconductor copper phthalocyanine (CuPc, $C_{32}H_{16}N_8Cu$) deposited by vacuum evaporation on glass substrates at different gravity conditions, from 50 g to –50 g (g – denotes the terrestrial gravity acceleration) in a centrifugal machine, were investigated. Thickness distribution of the film deposited was determined by measurement of absorbance using a scanning light beam probe. An anisotropic distribution of the film was observed in the direction of source and substrate rotation. The anisotropy is associated with centrifugal motion of the source-substrate system. In a direction perpendicular to the rotation, the deposition distribution was isotropic and obeyed, in principle, the theoretical approach which requires a maximum deposition in the centre of the sample. The experimentally observed influence of the acceleration on the deposition rate of the CuPc films on the substrate was simulated.

Introduction

Organic semiconductor devices are attracting extensive interest for their potential applications. Organic materials have a large variety of structures and properties that depend on processing conditions. In [1,2] properties of heterojunctions on the base of copper phthalocyanine was described. Copper phthalocyanine thin films deposited by physical vapor transport at microgravity were more homogeneous, smoother and denser than those made at unit gravity conditions [3-5]. At the same time centrifugal materials processing had given many interesting results for different materials [6]. Centrifugal processing of organic semiconductors was considered because of their large molecular weights and week van der Waal's intermolecular bonding. At high-gravity conditions we expect the centrifugal force to influence the deposition process, structure and properties of the resulting film.

Copper phthalocyanine (CuPc) is one of the well-studied organic photosensitive semiconductors [7]. It has high absorption coefficient in wide spectrum and high photo-electromagnetic sensitivity at low intensities of radiation. It is possible simply to deposit thin CuPc films by vacuum sublimation. Purification of CuPc is simple and technology is economical as the sublimation occurs at relatively low temperatures (400-600°C). Recrystallization of CuPc is attained from organic solutions at room temperature.

It is known that, at least, seven crystalline polymorph states of CuPc exist: α, β, γ, *R*, δ, ε *etc*. The α-CuPc form is a metastable one at $T = 165°C$ and can be converted thermally or with solution to the β-form. The α and the β forms are the most frequently encountered states of CuPc. The fabrication of CuPc films were in β-form because thermal sublimation was used for film deposition. The structure that

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Printed in Kazakhstan

characterizes the β-form is a monoclinic crystal $P2_1/a$ with a = 19.407 Å, b = 4.79 Å, c = 14.628 Å and β = 120.93 Å [3]. It has a band gap of about 1.6 eV and a conductivity of 5×10^{-13} Ω^{-1} cm at T = 300 K [8,9]. The molecular weight of the CuPc molecule is 576 a.m.u. Sublimation temperatures varies from 400°C at a pressure of 10^{-4} Pa to 580°C at 10^{-4} Pa [10].

In [11] the electrical conductivity of films composed of two photosensitive organic semiconductors, poly-N-epoxypropylcarbazole (PEPC) and CuPc were investigated, which had been deposited from solution at different gravity conditions from 1 g to 1107 g. An increase in conductivity and a decrease in activation energy with increased acceleration were found. In [12] a new experimental PVT chamber was constructed and used to deposit CuPc thin films at different acceleration, from –50 g to 50 g. It was found that integral optical absorption increased with increasing acceleration during film growth. Moreover, the peaks shifted to lower wavelengths values as the acceleration was increased. Different morphologies were found under different conditions. X-ray diffraction indicated that the centrifugal force caused the crystals constituting the films to be strained. This paper continues the work done in [12] and presents experimental and theoretical results on investigation of the differential optical properties of CuPc films deposited from vapor at high gravity conditions in a centrifugal machine.

Experimental

In our experiments industrially produced CuPc ($C_{32}H_{16}N_8Cu$) was used. Figure 1 shows the molecular structure of a *p*-type organic semiconductor CuPc molecule [3-5,7].

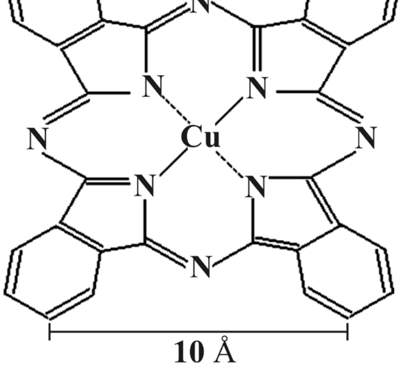

Fig. 1. Molecular structure of CuPc.

Figure 2 shows schematic diagram of the chamber, which was installed inside the rotating drum that constitutes the high gravity experimental facility described elsewhere [13]. The drum was 1.06 m in diameter and 0.97 m in length.

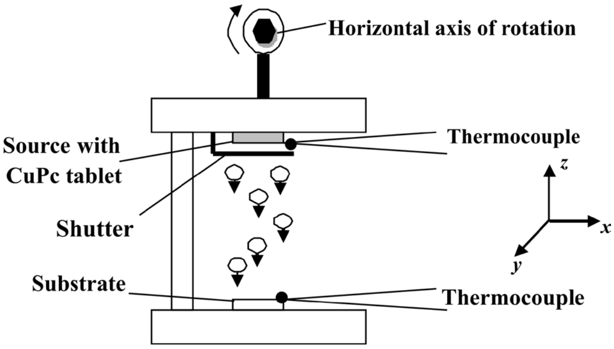

Fig. 2. Schematic representation of the physical vapor transport chamber for thin film vapor deposition in high gravity. Position of the heater and substrate shown for positive acceleration. For negative acceleration the heater and substrate should be reciprocally exchanged.

In this apparatus 100 g was attained at a rotation speed of 495 rpm with substrate located approximately 365 mm away from the rotational axis. In the PVT chamber the distance between the heater and substrate was 4 cm. The substrate was a BK-7 glass plate, 4 cm in diameter and 2 mm thick. A circular CuPc tablet 3 cm in diameter was used as a sublimation source. During deposition, rotary and turbo pumps were used to evacuate the chamber up to 0.3-0.4 Pa. The temperature of the heater and the substrate were 570 and 50-70°C, respectively. The deposition had duration of 2-2.5 hours at acceleration of –50 and 50 g. Figure 3 shows schematic diagram of the sample.

Absorbance of the films was investigated by conventional experimental equipment. For estimation

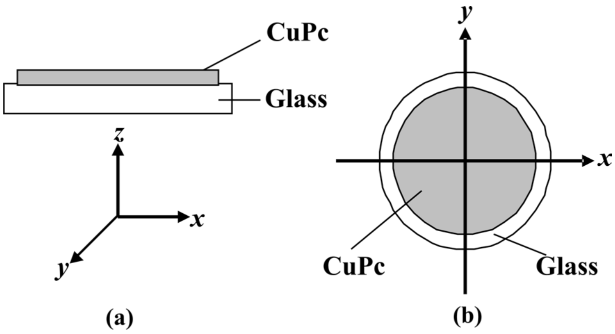

Fig. 3. Schematic diagram of the sample: (a) Side view (b) Top view.

of CuPc thickness at different places of the film, the absorbance distributions were measured and then calculations were made by using Lambert-Buger formula [14]:

$$I = I_0\exp(-\alpha x) \qquad (1)$$

where I_0 and I are beam inlet and outlet sample illuminating light intensities respectively, α is the absorbance coefficient and x is the thickness of the film. For CuPc $a = 0.7\times10^7$ m^{-1} at wavelength $\lambda = 632.8$ nm [15] was taken.

For investigation of differential optical properties the surface of the CuPc thin films was scanned by a filament lamp beam probe having a diameter of 3 mm. Approximately 10% of the incoming light was reflected from the glass surface so that the light's intensity at the inlet was reduced by 10%. This was taken into account when calculations were carried out for determining the thickness. The CuPc films thickness was 15-100 nm for the samples deposited from –50 g to 50 g respectively.

Results and Discussion

Figure 4a shows the position of source, substrate distance (*H*) between source and substrate and distance (*L*) between the center of substrate and the point where the thickness was calculated. Figure 4b shows the experimentally obtained relative distribution l/l_0 (l is the thickness of the film, l_0 is the thickness of film in the center of substrate at $L = 0$) of CuPc film deposition at 50 g on a glass substrate in two directions: parallel and perpendicular to the centrifugal motion, *x*-axis and *y*-axis directions in Figs. 2 and 3 respectively. In the centre of the substrate the film's thickness was equal to 100 nm. It is seen that maximum thickness of the film is observed at the centre of the sample in perpendicular direction, while in parallel direction the maximum shifted to the end of the sample. Location of the maximum with respect to the centre of the CuPc film is opposite to the centrifugal motion of the substrate. Obviously the observed shift of the maximum is due to the centrifugal motion of the substrate that happen during movement of the CuPc molecules from the source to the substrate. It may be considered as an anisotropic distribution of the CuPc film deposited at high gravity conditions.

Figure 4c shows a relative l/l_0 distribution of CuPc film deposition at 20g on a glass substrate in two directions: parallel and perpendicular to the centrifugal motion, *x*-axis and *y*-axis directions in Figs. 2 and 3 respectively. In the centre of the substrate the film's thickness was equal to 70 nm. As in the previous case the maximum thickness of the film is observed in the centre of the sample in the perpendicular direction. In the parallel direction the maximum shifted a little from the centre of the CuPc film. Comparison of the results showed in Figs. 4b and 4c shows that the value of the maxima shift is proportional to the value of gravity acceleration.

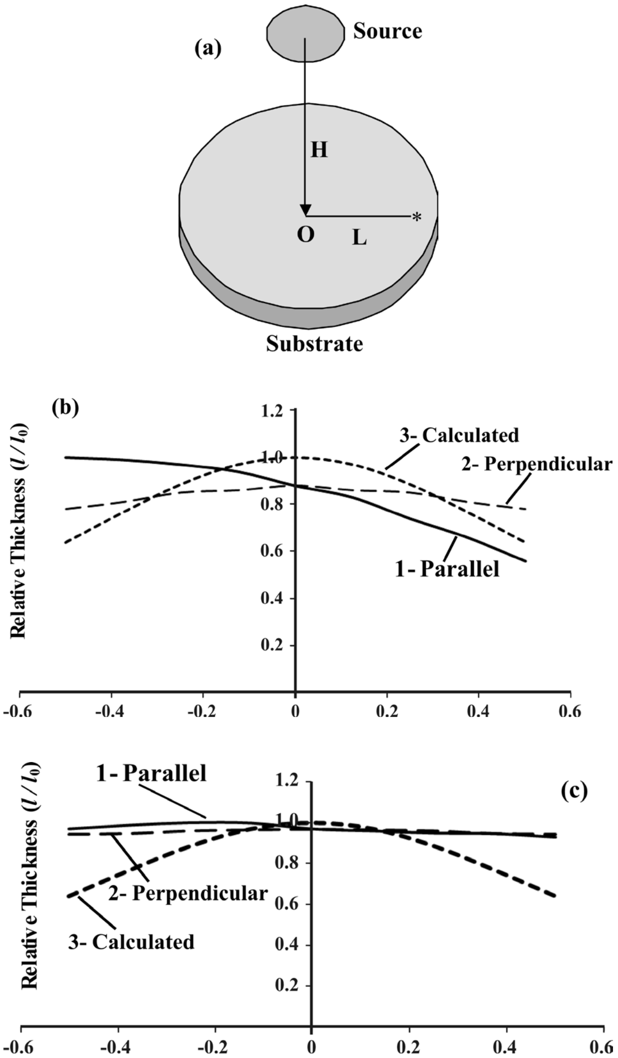

Fig. 4. (a) Shows the position of source, substrate and the Relative thickness of CuPc film deposited on the glass substrates; L is distance between the center of substrate and the point where the thickness is calculated, H is a distance between source and substrate. The l and l0 are the thickness of the film in the selected point and in the center of substrate, at L = 0: 1 and 2 – in the parallel and perpendicular directions to the centrifugal rotation respectively, 3 – calculated curve: a film deposited at 50 g, b film deposited at 20 g.

Deposition of the CuPc films at 1 g, in the centrifugal machine showed that films profiles in *x*-axis and *y*-axis directions was as shown in Figs. 4b and 4c for perpendicular direction (*y*-axis direction).

Probably the effect of some well-known pseudo forces (sometimes called inertial forces) is the reason for the anisotropic distribution of the CuPc film. In particular, Coriolis force which is proportional to the product of the normal to source surface velocity of the evaporated CuPc molecules and angular velocity of rotation may be in effect. As the temperature of the heater and pressure in the chamber were constant, the normal velocity probably would be constant as well. At the same time the anisotropic distribution of the CuPc film increases (Fig. 4) at higher acceleration of gravity or angular velocity, that is in the frame of Coriolis force effect in this case.

For theoretical estimations of a film thickness, deposited by vacuum evaporation usually two kinds of sources: a point source and a plane source [16] are described. If we take into consideration the sizes of source and substrate and the distance between them as comparable, it would be reasonable to use a plane source for calculation. For a plane source the thickness (*l*) of the deposited film is determined by the following expression [16]:

$$l = \frac{m\left\{\frac{1}{1+(L/H)^2}\right\}^2}{\pi\rho H^2} \qquad (2)$$

where *m* is total deposited mass, ρ is the density. The thickness (l_0) of the film in the centre of substrate, at $L = 0$ is equal to

$$l_0 = \frac{m}{\pi\rho H^2} \qquad (3)$$

and thus

$$\frac{l}{l_0} = \frac{1}{[1+(L/H)^2]^2} \qquad (4)$$

Calculated distributions of the CuPc thickness is shown in Figs. 4a and 4b. Comparison with experimental film profiles presented in Figs. 4a and 4b for the perpendicular directions show that the experimental profiles are more uniform. The reason probably is the small mean free path of the evaporated CuPc molecules under the pressure conditions in the centrifuge. Actually, the mean free path (λ) is determined from [16]:

$$\lambda = \frac{kT}{\sqrt{2\pi}\, Pd^2} \qquad (5)$$

where *k* is Boltzmann constant, *T* is absolute temperature, *P* is pressure, *d* is diameter of the molecule. Taking into account that CuPc molecules diameter is 10 Å we can obtain λ = 0.8 cm. As the value of λ is less than the distance between the source and substrate, the CuPc molecules undergoes a number of collisions when they move from source to the substrate.

Figure 5 shows the hhH evaporation at normal gravity conditions (1 g) may be simulated by the Langmuir expression [17]:

$$m_{eo} = 5.83\times10^{-2} P_e \sqrt{\frac{M}{T}} \ [\text{g/(cm}^2)\cdot(\text{sec})] \qquad (6)$$

where P_e is the equilibrium vapor pressure (in Torr), *T* is temperature, *M* is the molecular weight of the vapor species. If we assume that the P_e is affected by gravity acceleration (*G*) in the evaporation process, the expression for vapor pressure may be written in the following form:

$$P_e = P_{eo}\exp\left(-\frac{\Delta G}{Kg}\right) \qquad (7)$$

where $\Delta G = G - g$, *G* is negative acceleration, P_{eo} is pressure at 1 g, and *K* is proportionality coefficient (that can be determined from Fig. 6 empirically to be equal to 62). If we substitute Eq. 7 into Eq. 6, the normalized equation will be in the following form:

$$\frac{m_e}{m_{eo}} = \exp\left(-\frac{\Delta G}{Kg}\right) \qquad (8)$$

where m_e is the rate of thermal evaporation at high gravity (acceleration of *G*). If we consider that evaporation – deposition processes are correlated then Eq. 8 may be used for the description of deposition process, because there the obtained value shown in relative units. Figure 7 shows the normalized CuPc film deposition rate – negative acceleration relation-

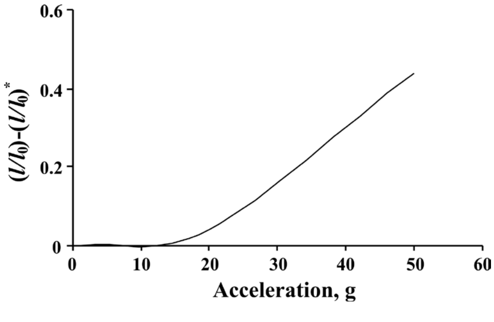

Fig. 5. Dependence of anisotropy of CuPc film distribution, as differences of relative thickness of two ends (l/l_0) and $(l/l_0)^*$ of the film, in parallel to centrifugal motion direction on acceleration.

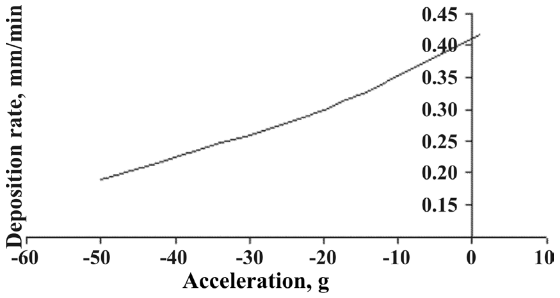

Fig. 6. Influence of negative acceleration on the CuPc film deposition rate.

ship, based on Eq. 8. It is seen that with increase of negative acceleration the deposition rate decreases.

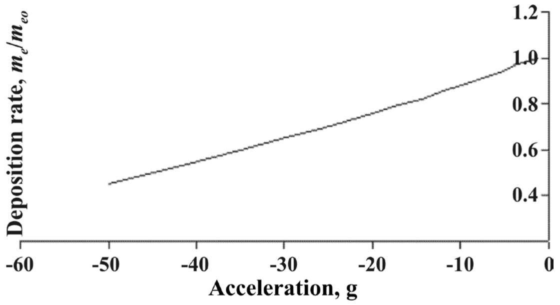

Fig. 7. Normalized the CuPc film deposition rate – negative acceleration relationship.

Conclusions

An investigation of thin organic films of *p*-type semiconductor copper phthalocyanine (CuPc) deposited by vacuum evaporation at different gravity conditions (from 50 g to –50 g) was made. The CuPc film surface was scanned by a light beam probe and differential absorbance of the sample was estimated. An anisotropic (asymmetrical) distribution was observed for the film deposited on the substrate in the direction of source and substrate rotation. In a direction perpendicular to the rotation, the deposition distribution was isotropic and obeyed, in principle the theoretical approach, *i.e.* maximum deposition in the centre of the sample. The experimentally observed influence of acceleration on the deposition rate of the CuPc films was simulated. The results obtained in this work may be useful in organic semiconductor thin film device technology and instrumentation.

Acknowledgments

The authors are thankful to National Engineering and Scientific Commission Pakistan for support of this work.

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Received 12 November 2008