The Investigation of The Electrical Properties of A Newly Synthesized Phthalocyanine Thin Film and The Effect of The Preparation Conditions

Yasemin Aktaş, Pınar Şen*, Fatih Dumludağ, Ahmet Altındal, Metin Özer*, Mustafa Bulut* and Özer Bekaroğlu*

> Marmara University, Departmant of physics, Göztepe, Istanbul, aktasy@yahoo.fr * Marmara University, Department of chemistry, Göztepe, Istanbul

Abstract. A detailed study of the effect of the film preparation conditions on the d.c and a.c conductivity of a newly synthesized trinuclear phthalocyanine (CuPc) thin film was investigated. Thin films have been prepared by different methods (seamering and airbrush) at different substrate temperatures and derivative were carried out at the temperatures between 290 K and 420 K. We find that the experimental data are described by thermally activated conductivity dependence on temperature. The frequency dependence of the conductivity follow a universal power law ' ω^{s} ' for all compounds. The comparison of the experimentally determined s values and the temperature dependence of the ac conductivity with the prediction of CBH model suggest that the obtained results are in agreement with the prediction of the CBH model for all films.

Keywords: Phthalocyanine; Activation energy; Correlated barrier hopping

INTRODUCTION

Metal phthalocyanines (MPcs) compounds are of great interest in various applications including chemical sensing, photovoltaic cells and other optoelectronic devices[1-6].

Thin films of Copper phthalocyanine have shown interesting electronic properties that can be used in photovoltaic applications, light-emitting diodes and gas sensing devises [7,8]. CuPc compound has features of thermo-stability, high sensitivity and rapid response-recovery times in the detection of oxidizing gas [9]. It is well known that the preparation conditions of the MPc film effects their electronic properties. Although, many recent report have been published on the conduction properties of the Pc film but very little work have been appeared on the effect of the substrate temperature on the electrical properties of the Pc films. In the present work, a new trinuclear copper phthalocyanine has been synthesized. Thin films of the metallophthalocyanine compounds have been prepared by two different methods on interdijital transducer. The d.c and a.c conductivity behavior of the air brush and seamering coated films of these compounds were studied for different substrate temperatures between 295 K and 393 K.

EXPERIMENTAL

Figure 1 shows the schema of the molecular structure of Pc used.

Trinuclear phthalocyanine derivative has been prepared from 4,4',4"-[1,3,5-triazine-2,4,6triltris(thio)]tri-phthalonitrile, 4,5-bis(hexylthio)phthalonitrile, CuCl and ürea was ground well in a ball-mill and placed in a flask. The reaction was heated and stirred at 195°C under argon for 12 h. After cooling to room temperature, it was refluxed in hot ethanol and then filtered. The procedure was repeated two times. The dark green product was washed with hot water, hot methanol, hot ethanol and dried in vacum.

Ten finger interdigital gold electrodes with 100 μ m gap were deposited photolithographically on precleaned glass substrate. Prior to vacuum evaporation glass substrates were thoroughly cleaned by ultrasonically. Thin films of compound were obtained by air brush and seamering chloroform solutions of the product over the electrode arrays to obtain devices suitable for electrical measurements. A home made chamber was used to allow electrical characteristics to be measured over a wide temperature range. d.c conductivity measurements were performed by using a Keithley 617 electrometer, a.c conductivity measurements were carried out with a Keithley 3330 LCZ meter in the frequency range 40 Hz.- 100 kHz. in the same range of temperature (between 290 K and 420 K).

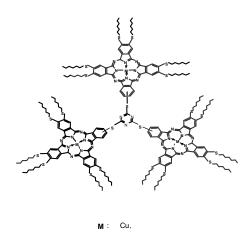


FIGURE 1. Schema of the molecular structure.

RESULTS AND DISCUSSION

All films have demonstrated hysteresis effect at low temperature. The figure 2 shows the I-V characteristic of the films at 295 K which prepared at 295 K substrate temperature for different preparation method.

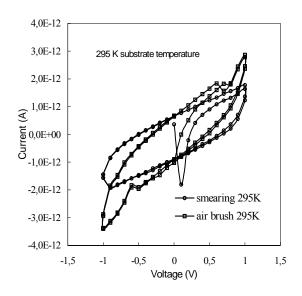


FIGURE 2. The I-V characteristic of the film at 295 K for different preparation methods

When the temperature elevated the hysteresis effect was disappered. We can see this on Fig. 3.

The Fig. 3 shows the I-V characteristic of the films at 387 K which prepared at 295 K substrate temperature for different preparation method.

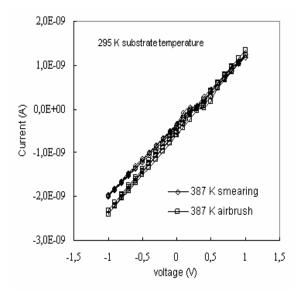


FIGURE 3. The I-V characteristic of the film at 387 K for different preparation methods

Same type of behaviour were observed for all fims. The effect of the temperature on dc conductivity of the films were also investigated.

The results of the dc conductivity for indicated substrate temperatures are shown in figure 4.

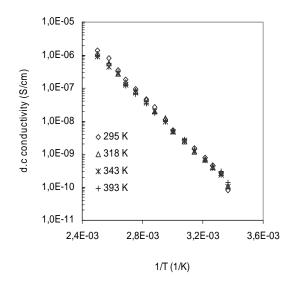


FIGURE 4. temperature dependence of the dc conductivity of the films for different substrate temperatures.

It can be seen from Fig.4 that the experimantal data are described by thermally activated conductivity dependence on temperature.

The variation of the measured dc conductivity for the CuPc films exhibit a dependence exponentially on temperature. The value of thermal energy of electrical conduction calculated from the slopes of the ln $\sigma_{d,c}$ vs 1 / T graphs, decreased with the increase of substrate temperature.

The values of the activation energy of the films, have been calculated from the slope of the Fig. 4, by using equation 1.

$$\sigma_{dc} = \sigma_0 \exp(-\frac{E_A}{kT})$$
(1)

where σ is the conductivity at *T* temperature, *E* is the activation energy, *k* is the Boltzman constant and σ_0 is the pre-exponential factor.

The values of activation energies for different substrate temperatures and different preparation methods are determined in Table 1.

It seen from table 1 that as the activation energy is small than 1 for all films.

When the conductivity of the compounds is measure by ac technique, we observed that the frequency of the conductivity follow a universal power law, ω^s fort all coumpounds. The results obtained from the frequency dependence of the measured ac conductivity for the indicated substrate temperature showed that frequency exponent s is definitely a function of temperature for all samples and shows a general tendency to increase with decreasing temperature. This behavior of s values is an indication of hopping conduction.

TABLE 1. activation energy of CuPc for different preparation conditions and substrate temperature

Substrate temperature (K)	Seamering	Air brush
295	0.79	0.76
318	0.76	0.78
343	0.80	0.97
393	0.62	0.78

Figure 5 and 6 show the temperature dependence of the ac conductivity of the films at 393 K substrate temperature.

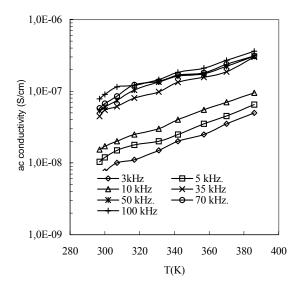


FIGURE 5. temperature dependence of the ac conductivity of the films which prepared at 393 K substrate temperature with smearing for different frequency.

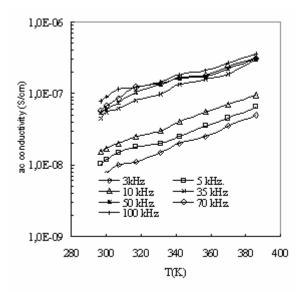


FIGURE 6. temperature dependence of the ac conductivity of the films which prepared at 393 K substrate temperature with air brush for different frequency.

The results obtained from the Fig.5 and Fig. 6 showed that for hight frequency ac conductivity of the air brush film shows a highter conductivity then smearing film.

Linear relationship was obtained between the measured ac conductivity and the temperature at constant frequencies for all films investigated. The comparison of the experimentally determined s values and the temperature dependence of the ac conductivity with the prediction of correlated barrier hopping (CBH) model suggest that the obtained results are in agreement with the prediction of the CBH model for all films.

REFERENCES

- 1. D. Lelievre, M. A. Petit, J. Simon, *Liq. Cryst.* 4 (1989) 707.
- N. Kobayashi, Curr. Opin. Solid State Matter. Sci. 4 (1999) 345.
- D. K. Rittenberg, K. I. Sugiyra, Y. Sakata, S. Mikami, A. J. Epstein, J. S. Miller, *Adv. Mater.* 12 (2000) 126.
- A. Altındal, Z. Z. Öztürk, S. Dabak, Ö. Bekaroğlu, Sens. and Actuators B 77 (2001) 389.
- 5. J. M. Lupton, Appl. Phys. Letters 81 (2002) 2478.
- M. O. Liu, C. H. Tai, W. Y. Wang, J. R. Chen, A. T. Hu, T. H. Wei, J. Organomet. *Chem.* 689 (2004)1078.
- S.T. Lee, Y.M. Wang, X.Y. Hou, C.W. Tang, *Appl. Phys. Lett.* 74(5) (1999) 670
- 8. J.D. Wright, Prog. Surf. Sci. 31 (1989) 1.
- 9. Y.L. Lee, W.C. Tsai, C.H. Chang, Y.M. Yang, *Appl.Surface* Sci. 172 (2001)