

## Effect of the Electric Field on Ordering of Copper Phthalocyanine Films at the Molecular and Nano-scale

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(Received 16 July 2014; published online 29 August 2014)

Thin films of copper phthalocyanine (CuPc) have been prepared by vacuum thermal evaporation in the absence and in the presence of an applied electric field during film growth. It was found that both the film structure and its electrical properties were noticeably modified by the external field. Namely, molecular stacks become more ordered and conductivity of the films deposited under an external field was substantially increased as compared to the reference film. We discuss that although the CuPc molecules have small dipole moment in the ground state, nevertheless the induced dipole moment by the applied electric field can essentially promote orientation of molecular stacks in the film.

**Keywords:** Thin films, Copper phthalocyanine, Orientation of molecules, Electrical properties, Vacuum thermal evaporation.

PACS numbers: 73.61. – r, 81.07.Nb, 68.55.am

### 1. INTRODUCTION

Recently, self-organization at the molecular level of an organic matter has been a subject of the intense research work [1-3]. The possibility of formation of organic thin films with new electrical and optical properties is a hot and increasingly attracting topic for researchers.

There is an approach how to facilitate self-organization of organic molecules which consists in an application of additional external control over the molecule [4-7]. Various factors such as temperature [4,6], type of the substrate [7] can significantly improve organization of molecular nanostructures. Recently, due to substantial development of vacuum technology, it was possible to use additional factors stimulating self-organization through applied electric and magnetic fields [8-11]. The effect of self-organization of different phthalocyanine molecules in films with application of an electric field during their growth [12,14,15] and annealing [16] has been shown in recent works [12-16]. According to these works, application of an electric field leads to the formation of aggregates of phthalocyanines and their alignment along the field due to induced electric dipole moment of a molecule [13,16]. The authors of these articles emphasize that the molecules, for example, copper phthalocyanine (CuPc), are able to organization under an electric field and assume that the ordering of the molecules takes place within the aggregates. However, no evidence on the film anisotropy through electrical and optical properties has been shown. In this paper, we have obtained thin films of CuPc under applied electric field and explored their electrical properties compared with properties of similar films grown without application of an electric field. We have grown both amorphous and crystalline structure of the films on the same substrate and studied their electrical characteristics.

### 2. EXPERIMENTAL

CuPc powder (98%) was purchased from Sigma Aldrich. Films of CuPc have been prepared by vacuum thermal evaporation (VTE) technique. Deposition was carried out on modernized installation VUP- 5M with thermal evaporation system at the final pressure inside the chamber of about  $10^{-4}$  Pa. Film thickness and deposition rate was controlled by the quartz microbalance. The average thickness of the films was 100–150 nm. The deposition rate was about 0.05 nm/s.

Ceramic and glass plates coated with a couple of comb-like gold electrodes were used as substrates. Gold electrodes were prepared by lithographic method. The period of the electrode grating was 20 nm. We used a substrate with two gratings on the same surface of ceramic (glass) plates. During the deposition, an electrical potential was applied to one of the gratings, while the other one remained as the reference. Therefore, two CuPc films of equal thickness were prepared in a single process on the same substrate. The difference between the obtained film was due to the fact that one of them was grown by application of an electric field. The applied electric field during deposition of the films was 25 kV/cm. This electric field was selected since it provided the most stable and reproduced result.

Before film deposition, the substrates were cleaned in isopropanol using an ultrasonic bath, followed by washing in distilled water and drying with nitrogen.

Depending on the substrate temperature, the film deposition resulted in films of amorphous or crystalline form of CuPc. Room temperature yielded an amorphous form of phthalocyanine, whereas the substrate temperature of 200 °C yielded β-crystalline form of CuPc [17-19].

Measurements of current-voltage characteristics of the films were carried out using the device HP 4140B.

Measurements were conducted at room temperature and ambient conditions. Voltage has been applied across the comb-like gold electrodes on ceramic substrates. The electrical measurements have been performed in the dark and under illumination conditions, with a halogen lamp ( $\sim 100$  mW/cm $^2$ ) as the light source.

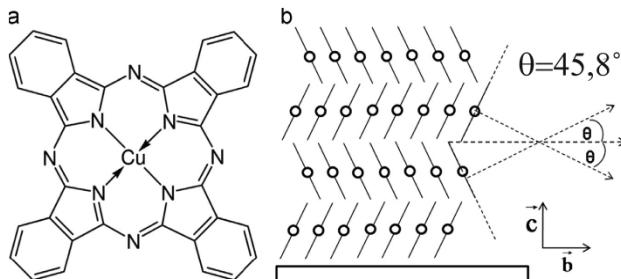
Film morphology was investigated using an AFM microscope NanoScopeIIa (produced by Digital Instruments, Veeco Metrology Group, USA) and SEM microscope JEOL 6400.

Quantum-chemical calculations of the electronic structure of CuPc molecule and its change in the applied electric field and in aggregates were performed using Gaussian and HyperChem packages.

### 3. RESULTS AND DISCUSSION

#### 3.1 The formation of amorphous and $\beta$ - forms of CuPc on ceramics.

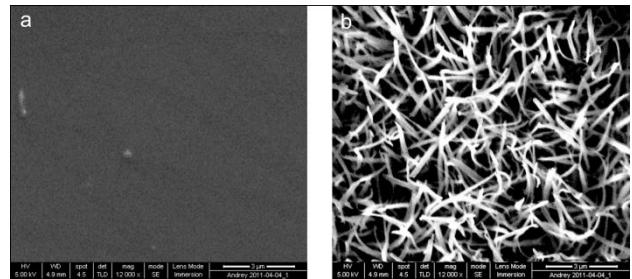
The structural formula of a CuPc molecule is shown in Fig. 2 (a). The molecule has a planar structure, which, when deposited at room temperature, forms one dimensional  $\beta$ -polymorph stacks of CuPc as shown in Fig. 2(b) [20,21]. The stacking axis is known as the b-axis of the crystal which shows strong  $\pi$ -coupling between neighboring molecules [20]. CuPc being a symmetric and planar molecule has a negligible dipole moment.



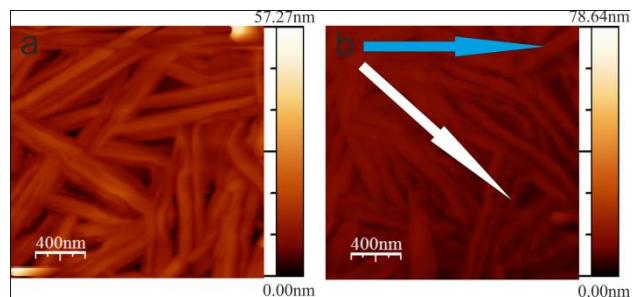
**Fig. 2 –(a)** Structural formula of CuPc molecule. **(b)** A schematic representation of molecular stacking in CuPc thin film on substrate. CuPc molecules form crystals of  $\beta$ -phase when evaporated onto substrate at 200°C temperature. CuPc molecular planes makes 45.8° angle with the crystal b-axis, while the c-axis is normal to the substrate.

In order to get reproducible results for the growth of both amorphous and  $\beta$ -phase of CuPc films at room temperature and 200 °C, respectively, we used a slow deposition rate (0.05 nm/s). Fig.3 shows SEM images of the CuPc film surfaces on glass substrates. It should be noted that the microstructure of the film surfaces deposited onto glass and ceramic substrates are similar, hence we show film surface images on the glass substrate only. The obtained structures correlate well with results obtained elsewhere [17-19]. Namely, deposition of CuPc onto substrates being at room temperature leads to formation of continuous amorphous films (Fig.3a), while deposition onto the heated to 200 °C substrates leads to formation of molecular aggregates (Fig.3b). In the latter case there is no continuous film on the substrate. Instead, there are clusters of randomly interwoven crystallites of the  $\beta$ -phase which

resemble a cotton wool. The studies showed that these crystallites have a form of nanorods with diameter of 80-150 nm and length of up to 5  $\mu$ m. It should be noted that we did not find substantial difference in characteristic size of nanorods and their displacement on the surface of the both types of substrates.



**Fig. 3 –** SEM image of the CuPc film surfaces deposited on glass substrate: a) substrate at room temperature, b) substrate heated to 200°C.



**Fig. 4 –** AFM image of the CuPc film morphology deposited on ceramic substrate heated to 200°C: a) without electric field , b) with electric field (25 kV/cm). The blue arrow shows a direction of the electric field, the white arrow shows a direction of the CuPc nanowires

#### 3.2 The influence of the electric field on morphological properties

Fig. 4 shows the AFM morphology of films deposited with and without applied electric field at the temperature of the ceramic substrate of 200 °C.

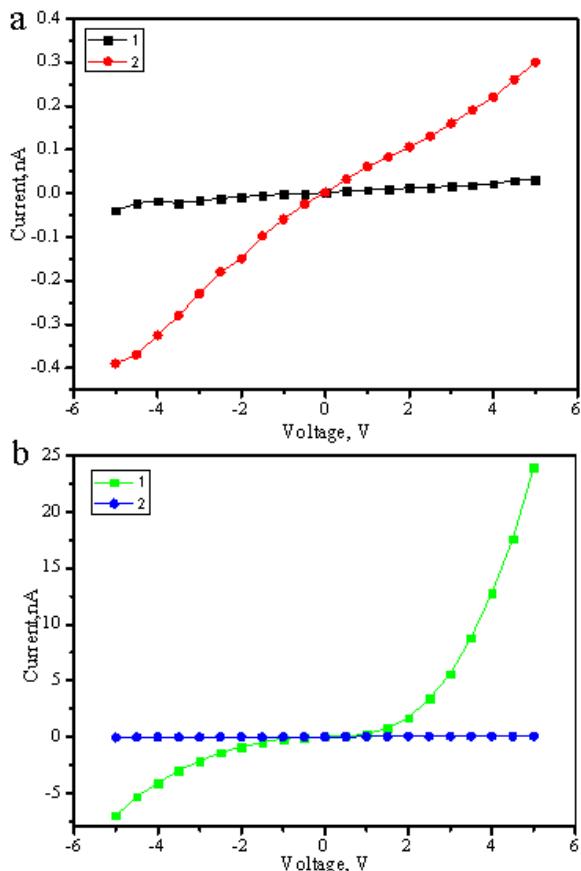
It has been found that despite of the high substrate temperature, there is a noticeable influence of the applied electric field on the film growth. Blue arrow in Fig.4.b indicates the direction of the applied electric field. It can be seen that there is a certain ordering in the film deposited at 200 °C. Moreover, the direction of preferred orientation of crystallites (white arrow) does not coincide with the direction of the applied field. Most of the crystallites try to sit at an angle of 40° in respect to the direction of the applied electric field.

Comparison of crystallites deposited under the electric field and without it showed that crystallites formed under the electric field are half thinner compared to the thickness of crystallites deposited without the electric field.

Deposition of CuPc under the electric field and without it at room temperature did not reveal significant difference in morphology between the two films. The both films have an amorphous structure which is similar to the structure shown in Fig. 3a. That is why we do not show here the morphology images of these films.

### 3.3 Electrical Properties

Figure 5 shows the current-voltage (*IV*) dependence of amorphous films and films of  $\beta$ - phase of CuPc aggregates. The same graph compares *IV* curves of the films deposited under the action of an electric field and without it in the dark.



**Fig. 5 –** *IV* characteristics of CuPc films deposited onto ceramic substrates: a) substrate at room temperature, b) substrate heated to 200°C; 1,2 – dark measurements for the samples prepared in the presence and absence of the applied electric field, respectively.

It has been found that the presence of an electric field during deposition affects the electrical properties of CuPc films. But our expectations concerning improvement of the electrical conductivity of the films deposited in an electric field as a result of the molecular ordering appeared not true in all cases. For example, Fig. 5a shows the *IV* characteristics of films deposited on a substrate at room temperature, which are structurally amorphous. From the curves it can be seen that the conductivity of films deposited in an electric field is worse than the same film deposited without the application of an electric field. The calculated values of resistance of the above films were 2000 MOhm in the case of application of an electric field and 500 MOhm for the film of the same thickness but grown without an electric field. It should be noted also that the electrical characteristics of amorphous CuPc films are linear within the range the applied bias.

Films obtained at 200°C showed the opposite effect. In this case, the poor conductivity of the films deposited

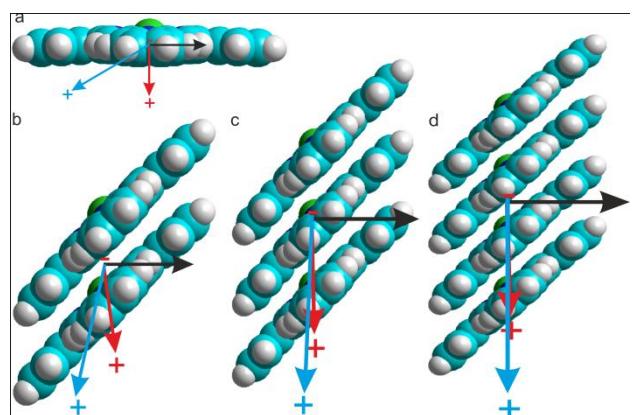
without an electric field has been revealed. *IV* characteristics are linear over the entire range of applied biases. In the case of the applied field during growth, the observed *IV* characteristics are close to the exponential dependence in the investigated range of applied bias and conductivity becomes much greater.

Our data allow us to argue assumptions made in the previous studies that the dipole moment of a single molecule is a determining factor in the interaction with the electric field. In this work, a direct sign of orientation of the molecules has been observed only for the  $\beta$ -phase of CuPc, which are grown at high substrate temperature. Otherwise, deposition of the molecules onto the substrate being at room temperature would result in better molecular orientation and film conductivity as compared with the film of the  $\beta$ -phase. However, we observed the opposite effect.

### 3.4 Quantum-chemical modeling and assumptions of the growth mechanisms.

Fig. 7 shows a single molecule and a stack of CuPc consisted of 2 to 4 molecules. Black arrow indicates the direction of an applied electric field. The red arrow indicates the direction of the own dipole moment of a single molecule or molecular aggregate. Blue arrow indicates the direction of the dipole moment induced by application of an external electric field.

Based on the performed simulation, it can be concluded that the increase in the number of molecules in the stack yields a significantly increased dipole moment. Moreover, the applied electric field induces more significant deflection of the induced dipole moment and at high applied fields the dipole moment is in the plane of the molecule. When the stack is as high as 4-5 molecules, the direction of the induced dipole moment becomes less sensitive to the direction of the applied field. Thus, the direction of the induced dipole moment in a stack of 4-5 molecules is almost the same as the direction of its own dipole moment.



**Fig. 7 –** Schematic view of (a) CuPc molecule and  $\beta$ -phase aggregates: (b) dimer, (c) trimer (d) tetramer. Black arrow shows the direction of the applied electric field, the red arrow shows the direction of the own dipole moment, the blue arrow shows the direction of the induced dipole moment.

The performed simulation of the electric field influence both on a separate molecule and on an aggregate suggests that in the case of deposition onto a

substrate being at room temperature (the formation of an amorphous form) an applied electric field leads to the formation of induced dipole moment of a single molecule. Since the molecules most likely sit on a substrate in such a manner that their surface is parallel to the substrate surface, the applied electric field induces the dipole moment in the plane of the molecule and it thus prevents the formation of even small molecular stacks such as dimers. In such a film the motion of charged particles is much more complicated, therefore a poor conductivity is observed.

In case of films deposited onto a heated substrate (crystallite form) molecular stacking prevails over separated molecules. Thus, molecular stack or aggregate forms first giving rise to increased dipole moment of the ensemble which is better controlled by an applied electric field. Simulations have showed that the larger the aggregate size the weaker effect of the applied electric field to change the direction of the induced dipole moment with respect to the own dipole moment. In this case, the electric field can only rotate the whole aggregate.

#### 4. CONCLUSIONS

Based on the above results we can conclude that the effect of the applied electric field on the growing film of CuPc is nontrivial. First, it was observed that the films grown under the applied electric field have better conductivity as compared with the films deposited without electric field influence which could evidence in favor of better orientation of molecular stacks along the applied electric field. Second, morphology of the films shows no perfect orientation of aggregates along the applied electric field. Such a controversial result can be explained by the fact that the molecular aggregates tend to arrange in the film not strictly parallel to the applied field direction, but at some angle which is a result of superposition of the induced and own dipole moments of the aggregate. Second, the change in conductivity of the films can be due to morphological changes of the aggregates themselves, for example, the change in density, film thickness, etc. These problems need to be studied in the future.

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