Effect of applied electric field on growth morphology of copper phthalocyanine thin films

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Abstract. The effect of electric field on the initial stages of copper phthalocyanine adsorption on the SiO\(_2\) substrate was studied experimentally. The external electric field was applied during thermo-vacuum evaporation of CuPc. Using atomic-force microscopy and scanning electron microscopy, it was found that in the presence of an electric field, the film morphology changes. Instead of randomly oriented elongated crystallites, new form bend-shaped ones are formed on the substrate surface. The paper provides an explanation of the experimentally observed effect of the electric field on the structure of the growing film.

1. Introduction

The metallophthalocyanines (MPcs) are widely used in organic electronics as active layers in solar cells, organic light-emitting diodes (OLED), organic field–effect transistors (OFET) and for other applications [1–4]. The effectiveness of such devices depends strongly on the structure of the CuPc film consisting of one-dimensional domains. These domains, formed as a result of self-alignment of MPC molecules, possess highly anisotropic properties. Thus, the charge carrier mobility along the domain axis is two orders higher than that in thin film [5]. A film consisting of domains mostly oriented perpendicularly to the substrate surface can be used for solar cell device manufacturing, while that with in-plane orientation would be suitable for field-effect transistors manufacturing. Thus, the proper co-alignment of the domains in CuPc films is necessary to improve efficiency of the organic devices. Different factors may be used to control the domain alignment during growth process, such as electric or magnetic field, or mechanical motion of the substrate [2].

The sensitivity of CuPc film morphology to the presence of electric field is explained by the anisotropic polarizability of flat CuPc molecule, the in-plane component being approximately six times higher than the perpendicular one [6]. This effect was observed experimentally earlier in the works [7-9]. The novelty of this paper is that here we study the initial stages of CuPc film growth in the electric field, the formation of single crystallites.

2. Experimental details

For CuPc deposition oxidized silicon wafer with previously deposited interdigitated gold electrodes was used as a substrate. The oxidized silicon wafer was prepared by thermal oxidation of Si(100) n-10\(^{17}\). The oxide width was approximately 0,5 \(\mu\)m. The electrodes consist of 500 finger pairs, each finger was 5 \(\mu\)m wide. The inter-electrode gap was also 5 \(\mu\)m. The average electrode height was estimated by atomic force microscopy (AFM) as 120\(\pm\)20 nm. The application of +500V to one of the electrodes and grounding the other one during the growth process generated the in-plane electric field.
of $\sim 10^4$ V/cm in between the electrodes. The initial relief of the gold electrodes was determined using scanning tunneling microscope (STM) on high-vacuum GPI–300 microscope developed at the Prokhorov General Physics Institute (Moscow) with a new vacuum module developed and manufactured in the Ioffe Institute (St. Petersburg).

Copper phthalocyanine powder (CuPc) was prepared in Saint-Petersburg State Institute of Technology by template synthesis (at 180°–190° for 2 h) upon melting of phthalonitrile with copper acetate, reprecipitation from sulfuric acid, followed by sequential purification with boiling distilled water and organic solvents. The purity was controlled using silica gel thin-layer chromatography. The absence of impurity absorption lines in the IR region and the coincidence of the absorption spectrum with etalon one indicated the high purity of the powder. CuPc was deposited by thermo-vacuum evaporation under residual pressure $5 \cdot 10^{-4}$ Pa on the substrate kept at 150°C. The effusion cell with the powder, whose temperature was maintained at 450°C, was located at a distance of 15 cm from the substrate. The evaporation process lasted 60 min, with 0.2–0.4 nm/min average growth rate.

Atomic-force microscope (AFM) and scanning electron microscope (SEM) were used to study the morphology of the grown CuPc films. The AFM topography were obtained in tapping mode on the “NTegra-Aura” (NT-MDT, Moscow, Russia) with NSG11 (NTMDT) probes with a tip radius of about 10 nm. The probe oscillation frequency ranged from 100 to 150 kHz. SEM micrographs were taken using a JSM-7100F (JEOL Ltd., Tokyo, Japan).

For estimation of possible oxide charging, Kelvin-probe measurements using DCP11 (NTMDT) probes with a tip radius of about 70 nm on the “NTegra-Aura” were done. The distance between the tip and the surface was approximately 50 nm. Measurements were performed in atmospheric conditions, the humidity level was about 20%.

3. Results
The AFM images of CuPc crystallites grown on the oxidized silicon substrate are shown in Fig.1: (i)- in the inter electrode gap (Fig.1a) and (ii)- aside the electrodes (Fig. 1b).
Figure 1. AFM images of CuPc crystallites grown on oxidized silicon substrates under (a) and without (b) external electric field. The sections shown in panels (c) and (d) are made between the black arrows on panels (a) and (b), respectively.

The shown images represent different parts of the same sample; at that the growth conditions were identical, except for the electric field. The mean height of the crystallites was estimated from height profiles (fig. 1(c) and 1(d)) of the images 1(a) и 1(b), respectively. According to these data, the height of the crystallites grown under the electric field is three times larger compared to those grown without the electric field. This explains the seeming difference in amount of deposited CuPc between Fig.1a and Fig.1b.

The morphology of the forming CuPc crystallites also differs in inter electrode gap and aside the electrodes. In the gap short bend-shaped crystallites grows (Figs. 1a, c) while elongated ribbon-shaped crystallites are formed aside the electrodes (Figs. 1b, d). The latter form is typical for thermo-vacuum evaporation process on SiO₂ substrates maintained at 150°C [10].

Figure 2a shows the SEM micrograph of the inter-gap area, presenting a top view of the crystallites, formed in the presence of electric field more distinctively. The direction of applied electric field (between the gold electrodes) is marked by black arrow. The image does not reveal the expected preferred orientation of the crystallites in the applied electric field. Most of the formed crystallites are bend-shaped.

To get more information on the effect of the electric field of the substrate on the morphology of forming CuPc crystallites, we analyzed the form of those, growing over the gold electrode (Fig. 2b). The image in the insert of Fig. 2b was obtained by STM before the CuPc deposition. It shows that the initial gold surfaces consist of separate granules, approximately 100nm in both lateral directions. Over these metal granules, CuPc crystallites having prevalently bend-shape form grow. Some prolonged crystallites sticking out of the surface are also formed on the metal surface.
Observation of similar bend-shaped crystallites on both metal and inter-gap area surfaces, where the origins of electric field were different, is unexpected. The electric field is generated perpendicularly over metal surfaces. For the inter-electrode area the external electric field was assumed to be parallel to the substrate surface. Since the orthogonally orientated electric fields affect on CuPc molecules in a different way, crystallites of different types are expected to be found on the studied surfaces. To explain the observed crystallite similarity, we supposed that in the inter-gap SiO$_2$ area the normal component of electric field was non-zero. Such a non-zero component could be generated by local charges in the SiO$_2$ dielectric layer. The field injection of a charge into the SiO$_2$ thin film had been observed earlier with 5·10$^6$ V/cm electric field and at room temperature [11].

To check whether the charge injection took place during the CuPc deposition and to estimate the perpendicular component of electric field in the gap, a test experiment at ambient conditions at room temperature (RT) was performed. The voltage of 50V was applied to the interdigitated gold electrodes for 10 minutes. Then the residual potential distribution was probed by Kelvin–probe method (KPM) in 5 – 7 minutes after the voltage switch-off (see Fig.3). The observed charge accumulation was affected by the air moisture in the test experiment. The water, absorbed on the surface contributes to charge dissipation and thus reduces the magnitude of the surface potential.

Simple calculations allow us to estimate the corresponding value of z–component of the electric field related to the charge injection in the test experiment. $E_z = \Delta \phi / d \approx 0.1V/50nm=2 \cdot 10^4 V/cm$, where $\Delta \phi$ – potential difference and $d$ – distance between the tip and the surface. It is reasonable to assume that in vacuum conditions, when the substrate temperature was higher than the RT and equal to 150°C and the applied voltage was ten times higher than that in the test, the perpendicular component of the electric field could achieve the value of 10$^6$ V/cm that is equal to the in-plane component. Thus, the resulting electric field is parallel to the substrate surface only in the center of the inter-electrode gap, and is directed at ~45° near the electrodes.
Figure 3. Residual potential distribution in inter-electrode gap obtained by KPM after switching off the 50V applied for 10 min.

4. Discussion

According to the experimental findings, bend-shaped crystallites mainly grow under the electric field. To analyze the form of this type of crystallites in detail, we have dissected one (framed in Fig.1a) in two orthogonal directions (white lines). The resulting sections are shown in Fig. 4: axial (X) and transverse (Y) directions. It is easy to estimate that the investigating crystallite is 250 nm in X, 150 nm in Y and 50–60 nm in Z directions. The X profile reproduces the bend-shaped form of the crystallite with flat gradient slopes. The additional tangent dotted lines also shown on X profile help to estimate that the crystallite axis is angled by approximately 35° to the substrate surface. A slight dip on Y section (Fig. 2a) allows us to conclude that the crystallite is comprised of two parallel ones, and the arrow indicates the junction point. The SEM micrograph shown in Fig.2a also demonstrates the twinned structure of crystallites.

Further we considered the factors affecting changing of CuPc film morphology in the electric field. The main one is the anisotropic polarizability of the flat copper phthalocyanine molecules, in-plane component of which is six times higher than the perpendicular one [6]. In the uniform electric field these molecules should orient themselves in such a way that the electric field vector lies in the plane of the molecule. Thus, on the initial stage of the deposition, the CuPc molecules should be adsorbed perpendicularly to the substrate surface in the normally directed electric field. Otherwise, in the case of an electric field parallel to the substrate surface, the molecules are expected to lie flat. Taking into account the possible inner structures of the CuPc crystallites [5], we can assume that for the electric field oriented parallel to the substrate surface, the angle between b-axis of the forming crystallite and the surface should be 63.5°(for α-type) and 56° (for β-type). In the normally oriented electric field, the molecules adsorb perpendicularly to the surface, and the angle between b-axis of the forming crystallite and the surface should be in the range of 0 – 26.5° (for α-type) or 0 – 44° (for β-type). This angle interval corresponds to different possible orientation of the crystallite, from lying on the surface (0°) to sticking out of the surface at 35°. According to the experimentally obtained value 35°, the latter orientation took place in our case. When the electric field decays with distance from the surface, one can expect the presence of bend-shaped crystallites with a possible inner structure shown in Fig.5.
The second factor affecting the morphology of CuPc film in electric field is macroscopic polarizability of the crystallites. The polarizability is determined by the inner structure of the forming crystallites, which depends on the growth conditions. At the settings similar to those of our experiment, CuPc molecules are arranged into α-type or β-type crystallites [12]. These 50 nm thick and up to several micrometers long crystallites, also called 1D wires (shown in fig.1b), consist of adjoining columnar molecular stacks. The CuPc molecular planes within a stack are parallel to each other and are inclined by 26.5° (for α-type) or 44° (for β-type) in respect to the stack axis (the b-axis). This structure appears energetically favorable, and hence all the known CuPc structure types are represented in molecular stacks formed by molecules lying in parallel, varying in angle between the molecule plane and the stack b-axis. The conductivity is several times higher along the b-axis than in the perpendicular direction. Consequently, the highest value of the macroscopic polarizability of the crystallite corresponds to the b-axis direction. Thus the preferable orientation of this crystallite is that with the maximal projection of b-axis on the direction of electric field. This corresponds to bend-shaped crystallites or those sticking out of the surface in case of electric field with non-zero component perpendicular to the substrate surface. The experiment findings confirm this conclusion.

5. Conclusion
We studied the effect of electric field applied during the growth process on the morphology of CuPc crystallites grown on SiO₂ substrate. The experimental results demonstrate that crystallites grown under electric field are mainly bend-shaped. The crystallites of such form were observed both on the gold electrode surface and in the inter-electrode gap area. We argue that they are most probably formed by the molecules oriented perpendicularly to the substrate surface. Such orientation takes place when the electric field is perpendicular to the substrate surface. The results of the Kelvin-probe experiment gave evidence that during the CuPc growth process the charge injection in SiO₂ layer took place and the resulting electric field in the inter-electrode gap was mostly directed perpendicularly to the substrate surface.

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