The scanning probe microscopy of the structural, elastic and conductive properties of two-component phthalocyanines

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Abstract. Thin films of two-component H₂Pc, PdPc, PbPc, CuPc phthalocyanines were studied by scanning probe microscopy methods. Young's modulus values of the phthalocyanines films were measured, which made it possible to optimize the regimes for studying soft phthalocyanine films and to select suitable probes with proper stiffness and the magnitude of the force acting onto the surface. For all films, the electric field induced reversible local conductivity switching effect was studied. It is shown that under room conditions it is possible to reversibly change the value of the local conductivity of a copper phthalocyanine film approximately by an order of magnitude. When conducting the experiment under vacuum conditions, a significant weakening of this effect occurs. It has been established that for a CuPc film, a pressure of 20 mbar is the lower boundary value for creating regions of increased conductivity. The observed effect is explained by the penetration of OH⁻ ions (from the surface adsorbed water film) into the phthalocyanine film with the subsequent formation of oxygen-containing complexes that increase conductivity.

1. Introduction

One of the first mentions of phthalocyanine in the scientific literature is associated with the synthesis of phthalimide. Today, metal phthalocyanines (MPc, where M is a metal atom) are among the most interesting organic compounds. Metal phthalocyanines are organic materials that: (i) exhibit high catalytic activity, (ii) are resistant to solvents, (iii) can change the conductivity under the applied voltage, (iv) can be in thermal and chemical stability with various substrates [1]. Due to these properties, films based on MPc are widely used in the development of thin-film organic transistors [2] and light-emitting devices [3]. There are prospects for the possible use of MPc films as a medium for recording and storing information [4]. It is known that applying a voltage pulse can switch the conductivity of the phthalocyanine film [4]. It should be noted that the conductivity of MPc films can strongly depend on the penetration into the film of oxygen atoms (and OH⁻ groups) from the environment and adsorbed water film on the surface [5, 6]. Oxygen can be incorporated into the phthalocyanine molecule, which affects the electrical properties of phthalocyanine [5, 6]. It should be noted that an organic field-effect transistor based on a combination of PbPc and CuPc layers was constructed, which also showed high photosensitivity in the near IR region [7].

It is worth noting that many polymeric materials are "soft" materials, which imposes restrictions on the possibility of their research by contact methods. In addition, the most of the measured values for these materials were obtained from "macroscopic" areas, so they are averaged values. In this paper, atomic-force microscopy (AFM) will be used to study the conductive properties of phthalocyanine films. AFM allows measuring the physical properties of various materials with the
nanoscale resolution. It should be noted that it is difficult to investigate soft materials using standard AFM methods, since during the scanning process undesirable modification and scratching of the films under study may occur. However, the use of specialized AFM methods, minimizing the force of impact on the surface, allows one to perform such research. Today, AFM methods are already used to study the surface of thin organic films [8, 9] and, as expected, will continue to be actively used to carry out local spatial diagnostics of MPC films with high spatial resolution.

The purpose of this work is to optimize the AFM methods for the “non-destructive” study of local conductive and elastic (Young's modulus) properties of PdPc, H₂Pc, PbPc and CuPc films, as well as to determine the effect of adsorbed oxygen on the conductivity of phthalocyanine films in room atmosphere and vacuum conditions.

2. Samples

First, a thin conducting ITO layer (0.3 µm) was deposited on the glass substrate. Then, films of a conjugated silicon-containing polymer were deposited on the ITO surface using a spraying method. The surface of the obtained films was mirror-smooth and retained fairly good adhesion to the ITO film. After the polymer film was dried, a CuPc film (with thicknesses d=10, 30, 60 and 100 nm) was applied on its surface by vacuum (p~10⁻⁴ Torr) thermal sublimation. PbPc films (d=50 nm) and PbPc (d=50 nm) were deposited by thermal evaporation method. All films had a mirror-smooth surface and a uniform dark blue color [10].

Probe measurements were carried out using a scanning probe microscope «NTegra-Aura» (NTMDT, Russia). This microscope allows measurements in vacuum conditions (p_vac~10⁻² mbar) and ultralow currents (0.03-100 pA) detection. In this work, NSG01 and CSG11/Pt probes (NTMDT) with characteristic stiffness coefficients of 5 N/m and 0.1 N/m, respectively, were used. To measure the Young's modulus of CuPc films, the “Peak-Force Tapping” method was used with auto-tuning the feedback parameters regime “ScanAsyst” (BRUKER). The probes used were Tap525a (BRUKER), the pressure force on the sample ranged from 0.5 to 400 nN. These measurements were made on a «Multimode-8» (BRUKER) microscope.

3. Experimental results and discussion

Figures 1a, 1b, 1c show the AFM topography of H₂Pc, PbPc, PdPc films, respectively. The value of roughness (RMS) for these films is: RMS(H₂Pc)= 18 nm, RMS(PbPc)=8 nm, RMS(PdPc)=4 nm. The measured large roughness values may indicate that the thermal evaporation method used in this work is not optimal for creating smooth H₂Pc, PbPc, PdPc phthalocyanine films. For practical applications, it is necessary to obtain smooth films of phthalocyanines with a roughness comparable to the roughness of the substrate.

![Figure 1. The AFM topography of films: (a) H₂Pc (RMS=18 nm), (b) PbPc (RMS=8 nm), (c) PdPc (RMS=4 nm).](image-url)

Figure 2 shows the AFM topography of a 10 nm thick CuPc film (see Figure 2a) and that of ITO substrate (inset in Figure 2a). It can be seen that the relief of CuPc film follows the surface relief of the ITO substrate. The roughness values for these films are: RMS(CuPc)= 2.8 nm and RMS(ITO)= 2.3
nm. The relief of CuPc films with 30, 50 and 100 nm thickness also follows the surface relief of the ITO substrate, and their roughness slightly changed in the range of 3-3.5 nm. Thus, among the films studied, smooth and homogeneous CuPc films are of the greatest interest and importance for potential applications.

Figure 2. (a) The AFM topography of 10 nm thick CuPc film, inset – substrate ITO, (b) the current map I(x,y), obtained simultaneously with the topography data (Figure 2a) under forevacuum conditions p<sub>res</sub> > 20 mbar.

It was established experimentally that the pressure on the CuPc film during scanning in the AFM contact mode leads to irreversible modifications of the surface relief. This was manifested in the formation of grooves after scanning, comparable to the thickness of the film (see Figure 3a and inset). In addition, the deformed region had a conductivity similar to that of the ITO substrate (see Figure 3b and inset), so it can be assumed that the CuPc film from this area was pressed out by a probe to the edges of the scanning area.

Figure 3. (a) AFM topography after scanning the middle part with a force of 400 nN, inset - profile taken along the dashed line, (b) the current map I(x,y), obtained simultaneously with the topography data (Figure 3a), inset - averaged current profile.

As a result, the further accurate measuring of the CuPc conductivity maps without “destroying” the film surface became difficult. Therefore, in this work, the perspective method of “Peak-ForceTapping” [11] was applied, which allows minimizing the pressure force acting on the soft sample. Using this method, the Young modulus (E) of CuPc films was also measured. The characteristic value of the measured Young's modulus was E ≈ 3±0.5 GPa. This value is comparable to the values previously measured for copper phthalocyanines, which makes it possible to characterize the sample as “soft”. It is worth noting that the specific values of the elastic moduli of phthalocyanine films depend on the presence of pores and can vary greatly for different growth methods of Pc films. The measured values of the Young's modulus were used to optimize the method of studying
phthalocyanine films and selecting probes with appropriate stiffness as well as selecting optimal values of forces acting on the surface.

Measurements of conductivity values and characteristic values of flowing currents on a conductive ITO substrate and a CuPc film were performed. On the ITO substrate, a current-voltage characteristic was measured, which showed a linear (metallic) character. On the CuPc film, the rectifying (diode) character of the I–V characteristic was observed. The polarity of the forward branch of the current-voltage characteristic indicates that the CuPc film has p-type conductivity. The obtained I–V characteristics were reproduced with repeated repetition of the experiment. This made it possible to determine the characteristic voltages (in the range from 1 to 2 volts) that can be applied to the CuPc films to accurately measure the conductivity currents without modifying the conductive properties of the films (no switching of conductivity regime).

As mentioned above, the process of recording information can occur by changing the conductivity of the Pd film under the external bias. Our measurements show that to change the conductivity of the CuPc film (50 nm thick) it is necessary to apply voltages of more than 5 volts. In this work, experiments were performed on switching the conductivity of CuPc films by the application of large voltages of opposite sign. This allowed both to create areas of increased conductivity (without changing the thickness of the film) and return them to their original conductivity state. First, the area (marked with a dotted square in Figure 2a) was scanned with the positive voltage applied to the sample $U_{+}=+5V$. In the course of subsequent measuring of current maps I(x,y) it was observed, that the conductivity of this area has increased. So, the effect of conductivity switching to the “high conductivity state” was observed. Then, the middle part of this area has been scanned with the negative voltage applied $U_{-}=-5V$. It was observed (see Figure 2a), that after the negative voltage application the conductivity switched back to the original “low conductivity state”. The ratio of current density value in a “high conductivity state” ($j_{CuPc}$) to current density in a “low conductivity state” ($j_{CuPc}$) was measured $j_{CuPc}/j_{CuPc} \sim 8$. It should be noted that the value of the current in a “low conductivity state” is quite small and comparable with the device noise, which does not allow to measure $j_{CuPc}/j_{CuPc}$ with high accuracy. One can only assume that the conductivity of the film after switching increases by at least an order of magnitude.

It should be noted that these experiments were carried out at various residual pressure values in the SPM chamber (from $\sim 10^{-3}$ mBar to 1 Bar). It was found that reversible conductivity switching (see Figure 2) of CuPc films is possible only when the residual pressure exceeds a certain threshold value $p_{res}>p_n=20$ mbar. That is, under conditions of medium and high vacuum, this effect of conduction switching is absent. A possible explanation of the conductivity switching effect dependence on the experimental conditions can be as follows. On the surface of the film in atmospheric conditions there is a layer of adsorbed water. It is assumed that when a positive voltage is applied to the sample, OH ions from the surface water layer penetrate into the film, and when a negative voltage is applied, the opposite effect occurs, i.e. their removal from the film. These processes are manifested in the experiment as (i) conductivity switching to “high conductivity state” and (ii) the return of the film to its original “low conductivity state”. It should be noted that OH ions penetrating into the film can create oxygen-containing complexes in CuPc, which provide increased conductivity [5, 6]. The thickness of the water adsorbate layer can be reduced by pumping to high vacuum or by heating to high temperatures. We did not use high-temperature heating of phthalocyanine films, since it leads to their irreversible modification. Thus, the absence of conduction switching effect in vacuum conditions is due to a decrease of water adsorbate film thickness, which leads to a decrease of OH groups capable of penetrating into the film and modifying its conductivity.

Similar experiments on conduction switching were carried out for H$_2$Pc, PdPc, PbPc films. In H$_2$Pc films, the ratio of current densities values $j_{H2Pc}/j_{H2Pc} \sim 1.5$ was measured, i.e. in these films the conduction switching effect is weak. Apparently, this is due to the fact that metal-free phthalocyanine interacts weakly with oxygen [12]. In PdPc films, the effect of conduction switching of films was observed at any residual pressures down to $10^{-3}$ mBar. In the PbPc films, on the contrary, it was not possible to observe the conduction switching effect neither in forevacuum nor in atmospheric conditions.

\begin{equation}
\text{conductivity state} = \text{conductivity state} \times \text{conductivity state}
\end{equation}
conditions. This may be due to the structural features of PbPc. It is known that the central lead ion (Pb$^{2+}$) has the largest radius (1.2 Å), compared with the Pd and Cu atoms [12]. As a result, the PbPc molecule is not flat, and its central atom is shifted by 0.1 nm relative to the plane of the molecule [13]. To find out exactly how the structural features of PbPc can affect the conductivity, additional studies are planned.

4. Conclusion

In this work, the mechanical and conductive properties of CuPc, H$_2$Pc, PbPc, and PdPc films were studied using scanning probe microscopy. Among the studied samples, the CuPc film has the minimal roughness (~ 3 nm), and its relief follows the relief of the substrate. The characteristic value of the measured Young's modulus of CuPc film was $E \approx 3 \pm 0.5$ GPa. The measured values of the Young's modulus were used to optimize the method of studying phthalocyanine films and selecting probes with appropriate stiffness as well as selecting optimal values of forces acting on the surface. The effect of reversible conduction switching upon the application of significant positive voltage to phthalocyanine films was detected. The limit value of the residual pressure ($p_{res} \approx 20$ mbar) was found, above which ($p > p_{res}$) it was possible, and below which ($p < p_{res}$) it was not possible to switch the conductivity of CuPc films. This effect is explained by the penetration of OH$^-$ ions from the layer of water adsorbate into the CuPc film under the bias, followed by the formation of oxygen-containing complexes that provide enhanced conductivity.

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