AFM Study of Ion Irradiated Metal Phthalocyanine Films

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1. Introduction

Metal phthalocyanine (PcM) thin films are nowadays proposed for use in electrical devices based on Schottky effect, electroluminescence, in field effect transistors, and resistive chemical sensors [1]. Although various approaches for their modification have been reported, such traditional for inorganic film processing technique as ion bombardment (including implantation, ion etching, plasma etc.) is still weakly extended to organic molecular crystals in comparison, e.g. with polymers [2]. Both theory and practice are less developed in this direction due to the known misgiving of the scientists employed in the technology of inorganic microstructures about attempting at a "dirty" organic material on the one hand, and a lack of interest among chemists in attracting new destructive methods enhancing the system complexity instead of, for instance, modification of a molecule by synthesis, on the other hand.

In this work we report some results on irradiation of copper hexadecachlorophthalocyanine (Cl*PcCu) thin films with carbon ions in a large dose interval. Ion beam implantation (gas and metal ions) into these films aimed at improvement of their gas sensing characteristics was previously considered in Ref. [3]. As shown, there are two contributions to the change of electrical and, hence, sensing properties of the actual PcM structure: appearance of new admixtures and carbonization of the layer. The first contribution can be divided into two types: metal particles, i.e. ions, complexes and clusters, and organic molecular shivers, which inevitably appear during the high energy ions deceleration. As Cl*PcCu is already highly carbonated material (32 atoms per molecule) and does not contain hydrogen which is able to give volatile compounds, we assume that carbon ions bombardment will help to identify the predominating type.

Roughly speaking, if such an implantation will mainly be responsible for the alteration of the Pc film properties, there is no more sense in varying, say, different metal ions, and thus the output parameters may simply be controlled by the conditions of irradiation process.

Most recently various scanning probe microscopy (SPM) techniques have been successfully applied to the study of structural and electrical effects in thin and ultra-thin PcM films (see, e.g. Ref. [4]). In the present work atomic force microscopy (AFM) was used for direct observation of structural changes occurring in Cl*PcCu film after ion bombardment.

2. Experimental

Commercially obtained Cl*PcCu powders (pigment Pc-green) were initially purified by sublimation. Thin polycrystalline films were grown using high vacuum evaporation technique (residual pressure less than 10^{-5} Torr) onto measuring substrata at 300 K. The substrate consisted of the alumina support and lithographically placed planar interdigital Ni-electrodes with the following parameters: wafer size 3×3 mm, interelectrode distance 20 μm, electrode length 2.2 mm, height 0.1 μm, number of fingers 50. Deposition rate was typically 0.5 nm/s, film thickness $\approx$ 200 nm (both measured by quartz crystal microbalance). Then films underwent ion beam implantation (positive C^+ ions) in the pulsed ILU-3 installation with irradiation energy of 30 keV and doses in the range of $10^{12} - 10^{17}$ ions/cm^2.

After completion of the implantation process all films were annealed in vacuum at 430 K during 2 hrs. AFM study was performed with SOLVER P4 (NT MDT, Russia) instrument. Dark electrical and gas testing measurements were carried out in VUP-5 installation.

3. Results and discussion

3.1. AFM measurements. AFM images of the films surface are represented in Figs. 1a–e. As clearly seen, first four irradiation doses cause dramatic changes in the surface topology. Basic parameters are collected in Table 1. Initial film surface has a grain texture with average grain sizes of about 80–100 nm. In general, sizes may vary approx. from 50 to 200 nm, which indicates an inhomogeneity of PcM molecular beam throughout the evaporation process — see Fig.1a. As known, PcM thin film topology can also be affected by at least three deposition factors: deposition rate, substrate material and temperature [5]. Irradiation with $5 \cdot 10^{13}$ and $3 \cdot 10^{14}$ ions/cm^2 doses (Fig. 1b,c) results in smoothing of the surface. Simultaneously, there is a decrease in the surface roughness and

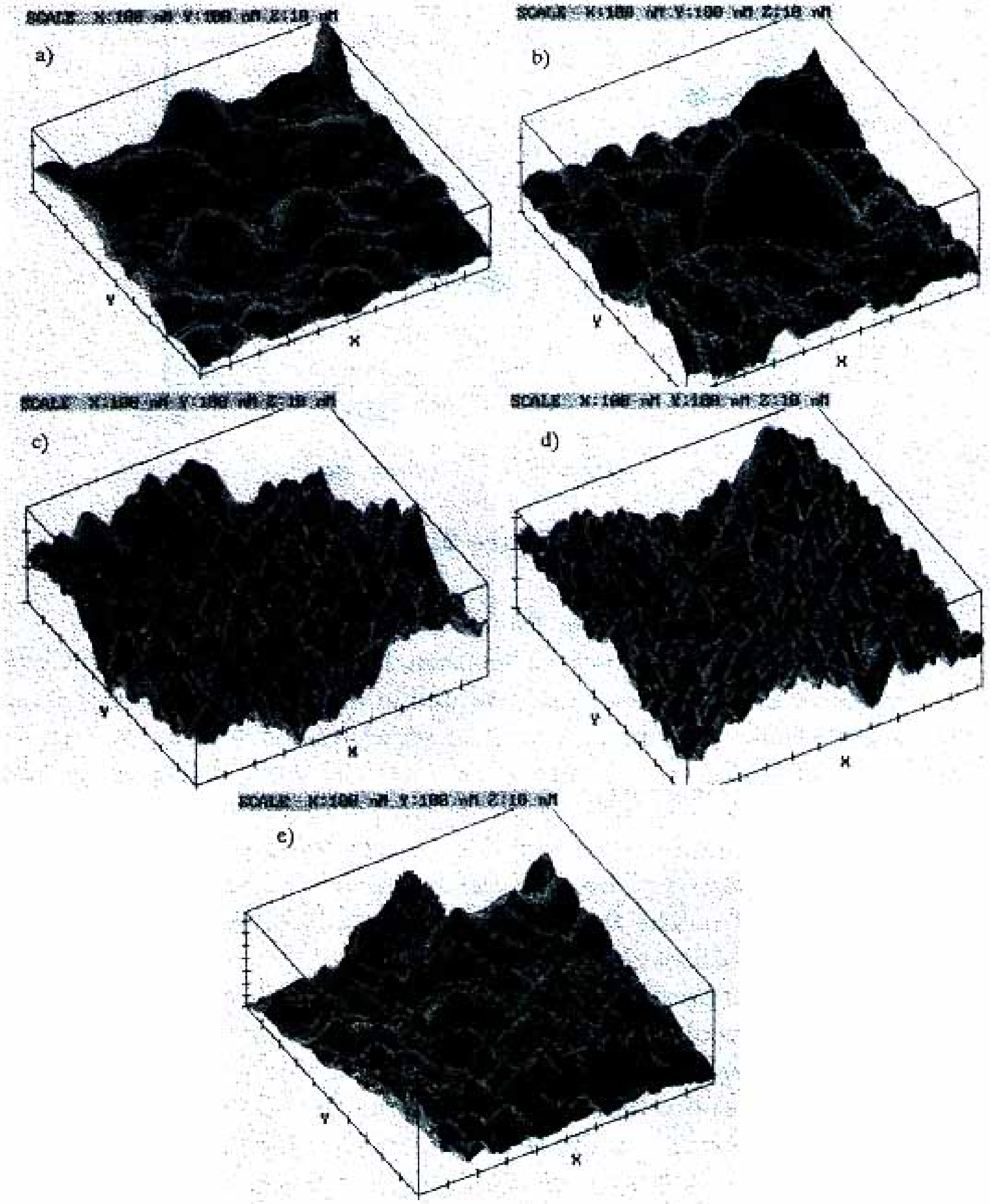

Figure 1.

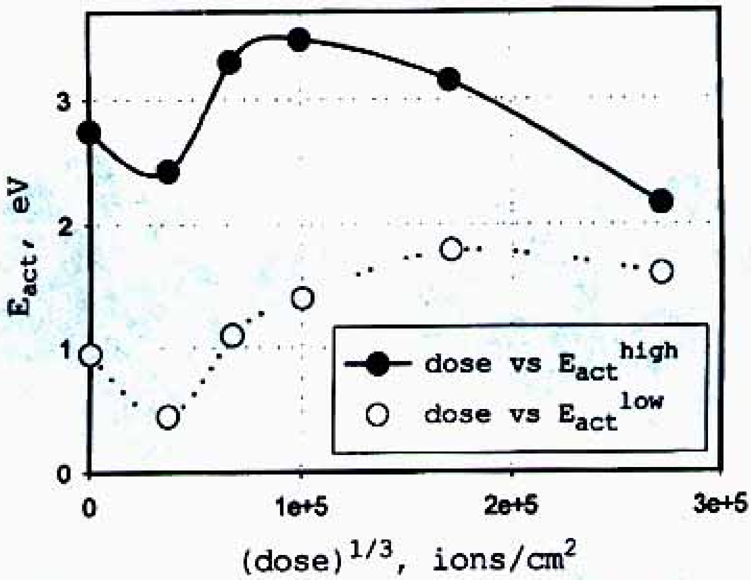

Figure 2.

in dispersion of the peak sizes (see Table 1).

After implantation with doses higher than 10^{15} ions/cm^2 the Cl*PcCu film surface possesses a similar structure presented in Fig.1e. The topology becomes more ordered (Table 1). Previous hill-like structure converts in the two level structure: flat and relatively big formations (150–200 nm in diameter, i.e. much more than for the previous dose — Fig. 1c), each of them contains basically one very small grain less than 30 nm in size. Most likely, the first level corresponds to amorphous and carbonized phase, whereas small grains represent hardly reduced Cl*PcCu microcrystals. The thorough instrumental analysis is then needed to exclude a controversial meaning.

In contrast to our previous experiments with various metal ions [6], where remarkable alterations of the film topology after annealing have been observed, the influence of annealing on C^+-irradiated films is weaker. Similarly to Ref. [6], some faceting of grains accompanied by some decrease of their size can be detected – see, for comparison, Fig.1d (corresponds to initial irradiation dose of $3 \cdot 10^{14}$). Besides, the dispersion of peak geometry is less that leads to better results in electrical measurements. This may be explained by enhancement of re-crystallization processes in PcM film, as it concerns also non-implanted samples. The complete discussion will be published elsewhere.

3.2. Electrical measurements. Electrical conduction in sublimed PcM films corresponds to a mixed bulk/surface mechanism, the latter dominating accord-

Parameter,	Irradiation dose, ions/cm^2			
nm	0	$5 \cdot 10^{13}$	$3 \cdot 10^{14}$	10^{15}
$R_{max}^{1)}$	69.6	38.5	26.6	23.5
$R_a^{2)}$	8.0	4.5	3.3	3.2
$R_q^{3)}$	10.3	6.4	4.2	3.9
Fig.1	a	b	c	d

Table 1. $^{1)}$max-min difference $R_{max} = Z_{max} - Z_{min}$;
$^{2)}$roughness $= (1/N_x N_y) \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} |Z|$;
$^{3)}$root $-$ mean $-$ square $= \sqrt{(1/N_x N_y) \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} (Z)^2}$.

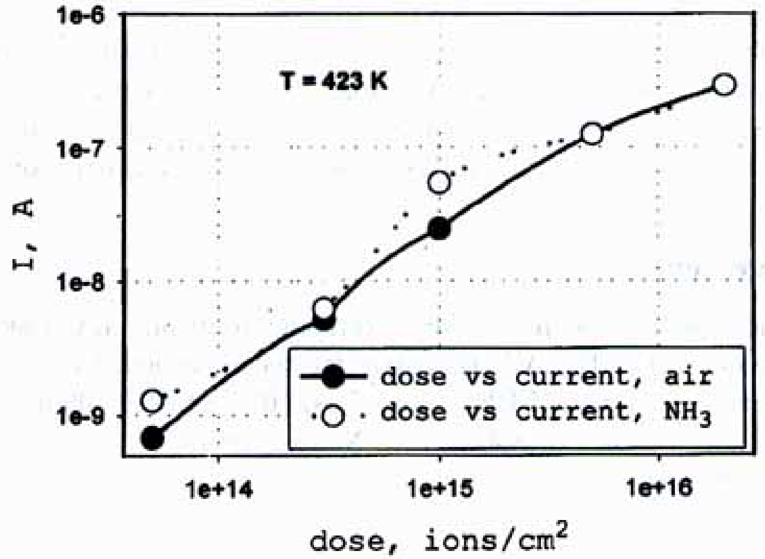

Figure 3.

ing to Ref. [5]. The total conductivity (σ) vs. absolute temperature dependences as plotted in lgσ-$1/T$ coordinates are straight lines consisting of two parts. The intersection point lies around 375–380 K and corresponds obviously to the transition from extrinsic conductivity to the intrinsic one, accompanied by the loss of impurities, e.g. water [1]. The dependence of the calculated thermal conduction activation energy E_{act} for both high and low temperature sections is shown in Fig.2.

Structural changes of the film surface observed in AFM images lead to a decrease of the difference in tangents of the slope angles between these two sections. Based on results of Ref. [7] we admit that $\Delta E = E_{act}^{high} - E_{act}^{low}$ tends to zero with the growth of irradiation dose or energy because of the increasing role of growing carbon concentration (islands). By extrapolation of the curves shown in Fig.2 one can get $E_{act} \approx 0.4 - 0.6$ eV at the intersection point.

It was established that gas sensing properties of implanted Cl*PcCu films do not change essentially with implantation dose. Electrical response of the Cl*PcCu film at 433 K to the presence of 100 ppm ammonia in air in comparison with the non-impacted film is shown in Fig.3. Such a trend is typical of all the temperatures used. The best straight lines were plotted in $\lg\sigma = \mathrm{const}x(\mathrm{dose})^{1/3}$ coordinates, indicating quadratic law dependence of conductivity on the concentration of admixtures.

4. Conclusion

In conclusion, we may ascertain that the most promising, from practical viewpoint, results should be estimated for low energy metal ions irradiation (compare with Ref. [3]), where implanted admixtures will determine such useful film parameters as time stability, initial conductivity and gas response.

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