LASER BEAM SYNTHESIS OF COPPER PHTHALOCYANINE BASED FILMS WITH LOW DIMENSIONAL STRUCTURING

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Thin films of copper phthalocyanine (CuPc) and CuPc – polystyrene (PS) composites were prepared by laser evaporation in vacuum. The crystalline structure and morphology of films were investigated by TEM, AFM and optical absorption methods in relation with dc dark electrical conduction, photoconduction and adsorption-resistive response to NO_2.

Introduction

CuPc compounds are of great interest in optoelectonics [1] and chemical sensors [2]. The dispersion of CuPc in polymer medium increases the surface-volume ratio of active phthalocyanine particles and can improve CuPc response to light and gas adsorption. The aim of this work is to perform comparative study of crystalline structure, morphology, dc dark electrical conduction, photoconduction and adsorption-resistive response to NO_2 of both CuPc and CuPc–PS composite thin films depending on different CuPc content, film thickness and various heat treatment conditions.

I. Experiments

The both CuPc and CuPc–PS composite films with thickness of 10 and 100 nm were prepared by LGN-703 CO_2 laser evaporation in vacuum of 10^{-3} Pa. The facility for laser beam synthesis is shown on the Fig. 1. Targets were pressed tablets of CuPc or CuPc and PS mixture. The evaporated products were co-deposited on the NaCl, glass, mica and alumina substrates at room temperature.

The crystalline structure and morphology of CuPc and CuPc–PS films were investigated by SPECORD-M40 spectrophotometer, EM-125K transmission electron microscope, and Nanoscope IIIa atomic force microscope.

The dc dark electrical conduction of CuPc films and composite films with different concentrations of adsorbed oxygen was measured at temperatures of 290–420 K by high speed cooling method [3] using V7-49 electrometer. The dc light conduction was measured under light exposure by He-Ne laser (wavelength 632 nm) or incandescent lamp with water filter. The adsorption-resistive response to 2 ppm NO_2 in air was measured under dynamic mode at temperatures of 330–470 K. To investigate the influence of annealing on film structure, morphology and properties, the samples were annealed in air and vacuum at temperatures up to 520 K.

II. Structure and morphology

It is well known [1,2], that CuPc compound has two crystalline modifications – metastable α-phase and stable β-phase. The visible spectra of both α- and β-phases have a double peak absorption band with peak wavelength of 615 and 694 nm for α-phase and of 645 and 712 nm for β-phase. Visible spectra show that all laser deposited CuPc and CuPc-PS composite films of both thickness (10 and 100 nm) were crystallized in α-phase. The annealing in air and vacuum at temperatures up to 520 K does not change the CuPc crystalline structure.

AFM shows that the CuPc films of both thicknesses have the low dimensional structuring

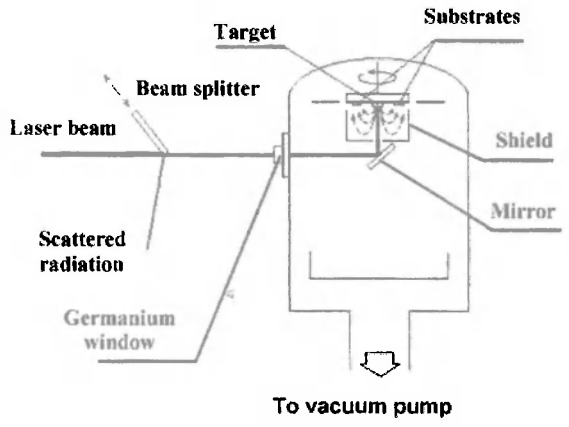

Figure 1. The facility for laser beam synthesis of copper phthalocyanine based films.

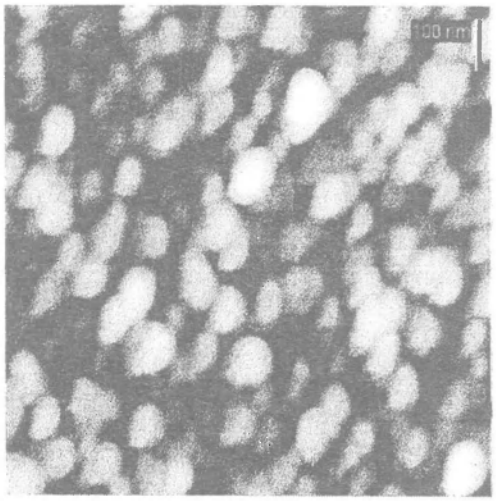

Figure 2. AFM image of CuPc film 10 nm in thickness. Scan size 1 μm × 1 μm. As deposited.

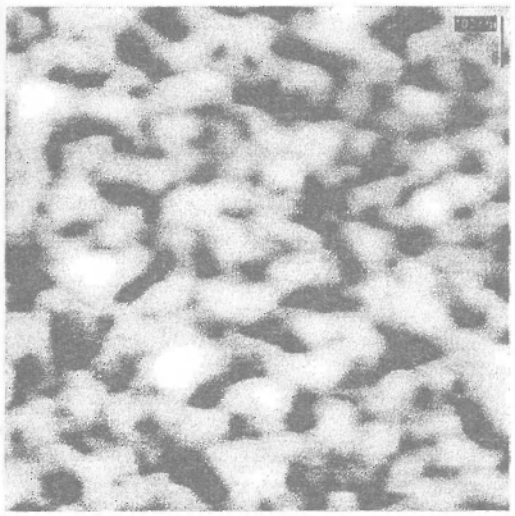

Figure 3. AFM image of the 20% CuPc – PS film 10 nm in thickness. Scan size 1 μm × 1 μm. As deposited.

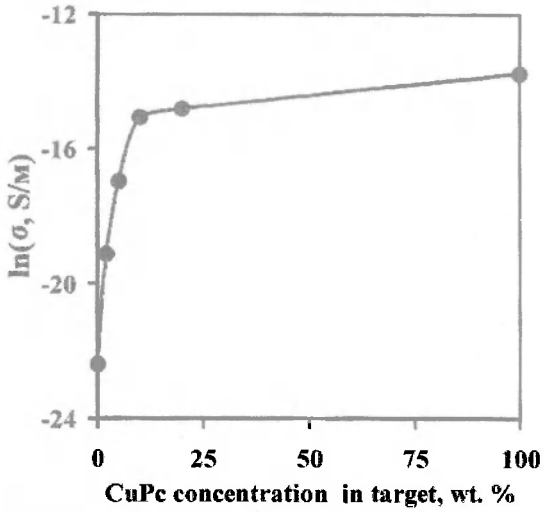

Figure 5. Concentration dependence of conductivity of the CuPc – PS film 100 nm in thickness.

with typical crystallite size about 50 nm (Fig. 2). Both TEM and AFM show that the composite films are CuPc nanoparticles dispersed in polysterene matrix. The size and shape of nanoparticles change after annealing at different temperatures and environment independently from the film thickness. AFM image of as deposited CuPc–PS composite film 10 nm in thickness is shown on Fig. 3. Annealing in air at temperatures below 470 K for 1 hour does not changes significantly surface morphology of the films. Annealing in air at temperatures above 470 K causes the recrystallization of CuPc in the film with formation of needle-like crystallites of 150-200 nm in length and of 40-60 nm in width [3]. Annealing in vacuum at 470 K leads to the formation of grain morphology of the composite film surface with grain size of 50-70 nm. Friction mode of AFM shows that films surface consists only from CuPc crystallites for the both annealing environments and films thickness.

Thus, the laser beam deposited CuPc films have the polycrystalline structure with low dimensional structuring. The CuPc–PS composite films are the amorphous polystyrene medium containing dispersed α-phase CuPc nanoparticles. The annealing changes the size of low dimensional elements in these films.

III. Electrical conduction properties

It is known that electron transport in the CuPc films conditioned by a hopping conduction mechanism [4, 5]. Therefore, the dependence of conduction G on temperature T can be expressed as

$$G = G_0 \exp(-E_a/kT), \qquad (1),$$

with tunnel factor [4]

$$G_0 = G_{03}\exp[-(4\pi/3)^{1/3}\alpha e^2/\varepsilon a E_a], \qquad (2)$$

where E_a is the activation energy, k is the Boltzmann constant, α is the percolation constant, e is the electron charge, ε is the dielectric constant, a is the electron radius of localization.

Fig. 4 shows the relation between tunnel factor G_0 and activation energy E_a for CuPc and CuPc – PS composite. Every experimental point corresponds to value of G_0 and E_a for constant oxygen concentration. The sets of measured G_0 and E_a for different oxygen concentrations give a linear lnG_0–$1/E_a$ plots.

The electron transport in CuPc films is carried out in accordance to (2) at states with electron radius of localization equal to 0.97 nm. Oxygen desorption increases the concentration of localization centers. Therefore, adsorbed oxygen molecules block electron transport centers. Concentration of localization centers in CuPc–PS during the oxygen desorption at first increases, afterwards - decreases. This fact shows that during oxygen desorption the transition from impurity to intrinsic electron transport

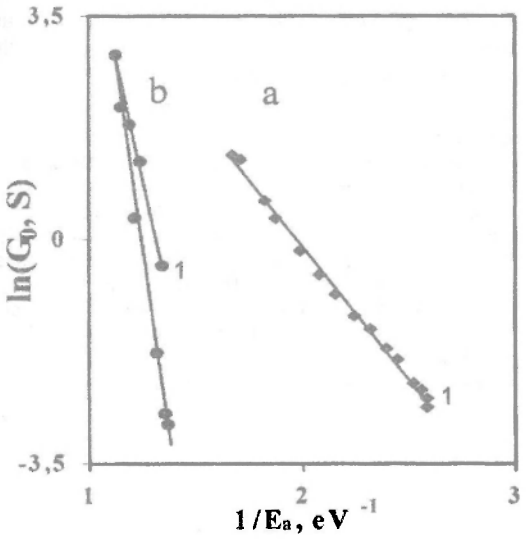

Figure 4. The experimental data for CuPc (a) and 20%CuPc–PS (b) films 100 nm in thickness. Points 1 correspond to maximum oxygen concentration.

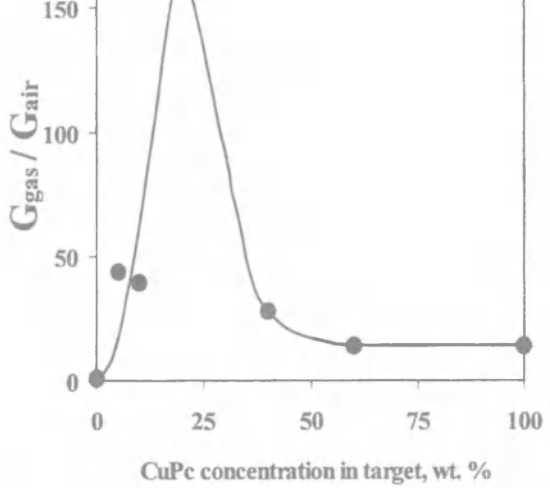

Figure 6. Concentration dependence of relative response to 2 ppm NO_2 of the CuPc – PS films 100 nm in thickness.

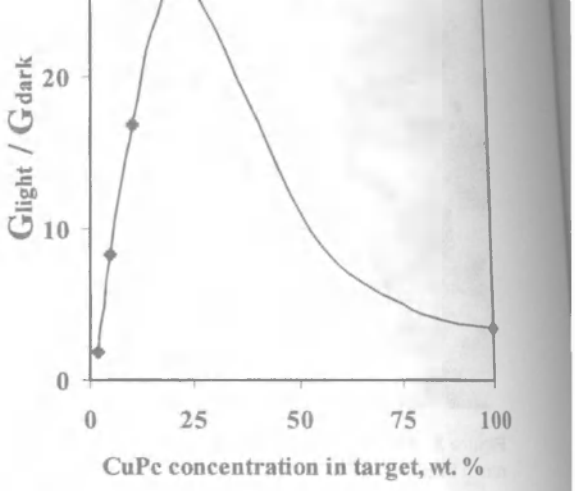

Figure 7. Concentration dependence of relative response to light exposure of CuPc – PS films 100 nm in thickness.

states occurs with decreasing of electron radius of localization from 0.26 nm to 0.17 nm, which are significantly less in comparison to CuPc films due to reducing of intermolecular interaction.

Fig. 5 shows the concentration dependence of conductivity of laser deposited films which has an abrupt decreasing by CuPc concentration which is equal to about 10 – 20%. This value is nearly to theoretical value of percolation threshold which is equal to 17%.

IV. Gas and light sensitivity

The relative response G_{gas}/G_{air} is a ratio of film conductance in presence of NO_2 to conductance in pure air. This response was measured in presence of 2 ppm NO_2 by different operational temperatures after annealing under different temperatures. G_{gas}/G_{air} decreases during annealing process accordingly with crystallization of CuPc and increases by increasing of operational temperature. The maximum response corresponds to annealing temperature of 420 K and operational temperature of 420 K. Fig. 6 shows the dependence of relative response by stated conditions on the concentration of CuPc in evaporated target. The composite film formed on base of 20%CuPc–PS target has a maximum adsorption-resistive response to NO_2 and minimum times of response and recovery.

Fig. 7 shows the relative response to light exposure of incandescent lamp with water filter of laser deposited films with different concentration of CuPc. The maximum of response was obtained by 20% CuPc concentration in CuPc – PS composite film under light exposure by incandescent lamp and by He-Ne laser. The relative light response G_{light}/G_{dark} is a ratio of film conductance under light exposure to dark conductance.

The maximum of both gas and light responses correspond to percolation threshold of CuPc cluster in PS matrix.

Conclusions

Thus, laser evaporation allows to prepare thin films of CuPc with low dimensional structuring. The laser co-evaporation of CuPc and PS allows to prepare thin films containing CuPc nanoparticles in PS matrix. The low dimensional structuring of CuPc and CuPc – PS films causes the electron localization in films. The hopping conduction in the films is realized through intrinsic or adsorbed oxygen electron states. The CuPc–PS films can be used as photodetectors and chemical gas sensors with enhanced sensitivity and speed of response.

References

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