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COPPER PHTHALOCYANINE AS "GUEST" IN A THIN LAYER POLYIMIDE MATRIX

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Composite layers PI/CuPc (500 nm thick) were deposited in vacuum by simultaneous evaporation from three evaporation sources. Two types of samples were investigated as deposited and as thermally treated at 200 °C by means of FTIR and optical spectra measurements. It has been shown that the CuPc "guest" particles are embedded in the matrix volume as a α polymorph form and the thermal treatment of the investigated composite layers causes a putative change in the CuPc "guest" particle size due to the PI matrix imidization processes rather than to the CuPc phase transition.

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1. Introduction

The formation of new composite materials is important because the combination of different solid phases makes the synergistic modification of the component material properties possible [1,2]. A lot of recent research has been focused on the preparation of materials which are inhomogeneous on the microscopic scale, the so-called "nanocomposites". An attractive method for nanocomposite formation is the simultaneous vacuum deposition (VD) of the different composite components from the gas phase by multi-source physical vapour deposition. The production of nanocomposite layers by deposition of their components (matrix and "guest"- particles, dispersed in the matrix) from the gas phase is the clue to broadening the prospects for obtaining novel materials in the nanotechnology area [3].

Polyimides (PIs) have the capacity to be a nanocomposite matrix due to their high chemical and thermal stability and suitable optical and dielectric properties [4,5]. The thermally induced chemical reaction (imidization) taking place in the solid phase in the process of formation of a thin-layer polyimide matrix causes certain tensions in the composite volume. Since the method for VDP matrix formation is a vacuum process, it will comply well with other vacuum processes in the fabrication of devices for optical and optoelectronic applications.

Metal phthalocyanines (MPc) represent organic materials of the p- type semiconductores [6,7]. Various techniques have been employed to prepare MPc thin layers. Due to the thermal and chemical stability of the MPc compounds and their small solubility in organic solvents, VD is widely used to fabricate the MPc thin films [8,9].

We have been investigated composite layers (PI/CuPc) deposited in vacuum by simultaneous evaporation from three evaporation sources [10]. Our previous FTIR spectroscopy observations on the composite layers (PI/CuPc) [11] do not give indications of a chemical interaction between the thin layer PI matrix and the "guest" – CuPc, which is expressed in the

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absence of peaks in the IR spectra that would account for the emergence of new bonds (new compounds respectively). The host-guest bond type is established in these composites.

This work is aimed at characterizing the vacuum deposited polyimide / copper phthalocyanine (PI/CuPc) composite layers by comparing data obtained from IR and optical spectra measurements and to show the influence of the PI matrix on the “guest” – CuPc

2. Experimental

2.1. Sample preparation

The thin PI layer matrix was formed by vacuum co-deposition of precursors 4, 4'- oxidianiline (ODA) and pyromellitic dianhydride (PMDA) on linearly moving substrates and ODA: PMDA ratio 1:1. Two types of composite layers were prepared: the "sandwich" type (PI/guest/PI) and composite layers with a “guest” in the matrix volume. To prepare composite samples we used CuPc evaporated from a Knudsen-type vessel source as “guest”. The "guest" concentration in the investigated composite layers was 12%. A part of the samples was thermally treated for 1 h at 200^0C - the optimum conditions, causing minimum changes in the film composition and the surface structure quality [9].

2.2 Methods of Investigation

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra (films on KBr pellets) were recorded on a Perkin Elmer 1600 spectrometer in the 1300-450 cm^{-1} range; resolution 4 cm^{-1}; 1024 scans, interval 0.2. The size of the IR beam was 15 μm in diameter.

The optical spectra were recorded on a Cary 5E spectrophotometer in the 400 - 800 nm range.

3. Results and discussion

The spectral dependencies of the VD PI layer transmission (T) are presented in Fig. 1. The layers display a high T in the range 400 – 800 nm and some bathochromic shift of the absorption after thermal treatment.

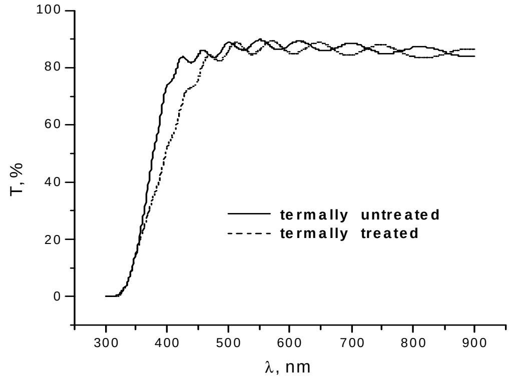

Fig. 1. Optical transmission spectra of VD, 500 nm thick, PI layer.

The optical spectra of the CuPc layers (Fig.2) show a low temperature α polymorph form CuPc - the specific shape of the Q band and a minimum at 600 nm. The thermal treatment in this case does not cause phase transition and the optical spectra remain unchanged. The results from the optical spectra of the "sandwich" type composite layers are the same – no effect of the thermal treatment on the optical properties of the films was registered. Only in the case of the composite layers with a guest embedded in the volume (Fig.3) an influence of the thermal treatment on the optical spectra (Q band) was observed. The transmission spectrum of the composite layer after 1 h of thermal treatment (Fig. 3) is typical of the β polymorph form (minimum at 700 nm). It is known that the α form CuPc is usually transformed into a β form over 300 °C, which is higher than the thermal treatment temperature (200 °C).

Also the FTIR spectra results presented in Figs. 4 and 5 display:

- the VD, thermally untreated CuPc (Fig. 4a) and thermally treated CuPc (Fig. 4b) are in the “x” polymorph form – dimer structure (characteristic peaks of α polymorph form in the area 500-700 nm are not registered). It can be concluded that the thermal treatment at 200 °C does not cause a polymorph transformation.

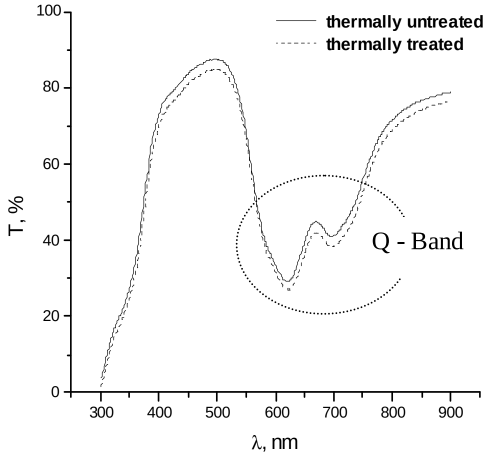

Fig. 2. Optical transmission spectra (Q-Band) of VD, 200 nm thick CuPc layers, evaporation rate 5 A/sec.

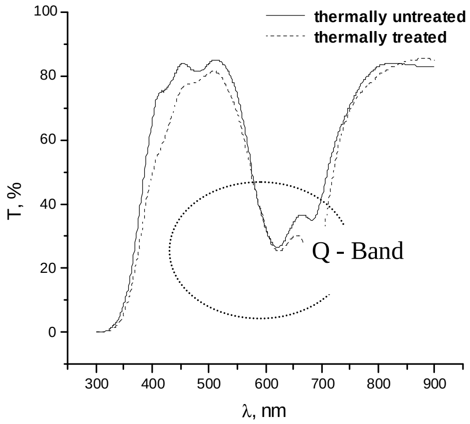

Fig. 3. Optical transmission spectra (Q-Band) of, VD, 500 nm thick, composite layers – PI/CuPc- the “guest” is embedded in the volume.

- in the bulk material CuPc is mainly in the low temperature α polymorph form (Fig.4c). The correlation of signals in the 1070-1170 cm^{-1} region and the peaks in the 500-700 cm^{-1} range are typical of the α form [12]. Obviously after the VD CuPc is transformed from an α form to the “x” polymorph form (a dimer structure), (Fig.4a).

- in the two types of thermally treated composite layers (Fig. 5b and 5c) the guest is in the low temperature α polymorph form, by contrast to VD thermally treated CuPc (Fig.5a), which are in the “x” polymorph form (dimer structure). This is probably due to the thermally caused imidization processes, taking place in the PI matrix in the composite layer formation, a phenomenon observed by other authors as well [13].

A conclusion can be draun suggesting that the changes observed upon thermal treatment are not caused by the transition from the α polymorph form to the β form. It is possible for this to be the result from the change in the particle size of the "guest" under the impact of the morphology changes by the thermal treatment of the PI matrix. The influence of the matrix is much greater when the guest is embedded in the matrix volume and its particles are in an intimate contact with the polyimide. For reasons of additional clarification in the interpretation of the presented experimental results, Electron - microscopiy examinations of the morphology changes are also carried out, which will be the object of our next paper.

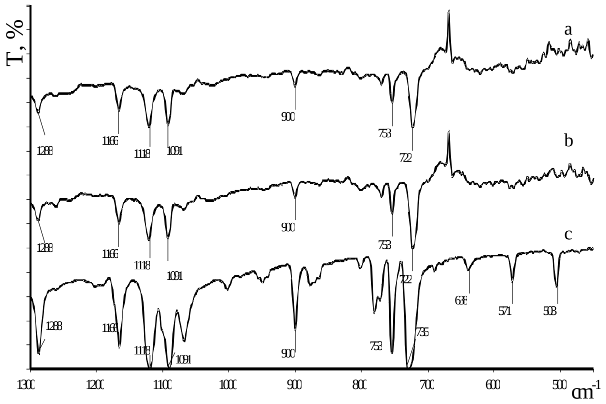

Fig. 4. FTIR spectra of CuPc: (a) – VD 200 nm thick layer, thermally untreated, (b) – VD 200 nm thick layer, thermally treated 1h 200^0C, (c) – bulk material.

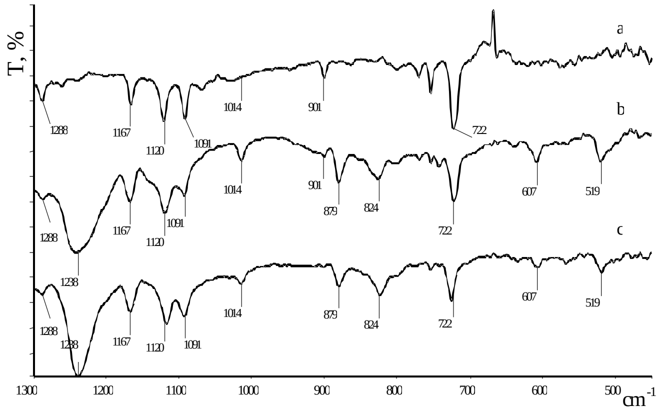

Fig. 5. FTIR spectra of VD, thermally treated (1h 200^0C) layers: (a) - CuPc layers, (b) – composite layers – PI/CuPc- the "sandwich" type, (c) - composite layers – PI/CuPc - the "guest" is embedded in the volume.

4. Conclusion

Polyimides are very attractive materials for composite matrix construction, because the morphological change through the thermally induced chemical reaction (imidization) in their production causes a stress upon the "guest" particles and can crush them into smaller pieces. In that case there is a possibility of influencing the particle size of the "guest" which other polymer matrices (a polyurea matrix, for example [14]) would not yield.

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