CORRELATION OF MORPHOLOGY AND ELECTRICAL CONDUCTION IN NANOSTRUCTURED PERYLENE PIGMENT FILMS

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Surface morphology and electrical conduction in laser beam deposited perylene based thin films were investigated. It is found that the peak-to-peak value of the surface relief significantly increases with an increase of the substrate temperature at the deposition. Measuring of electrical properties by cyclic thermal desorption method shows that the hopping conductivity mechanism is realized in the films. The conductivity is intrinsic or impurity depending on the concentration of the adsorbed oxygen.

1 Introduction

The perylene derivatives are n-type organic semiconductors. They are of great interest as components for organic electronics. In particular, films of perylenetetracarboxylic diimide derivative (PTCDI) are used as n-layers in heterojunctions of organic solar cells [1]. The industrial application of these materials is now limited by insufficient knowledge about conductivity mechanisms and their correlation with structural features of the films.

In this paper, we compare experimental data on morphology of the vacuum deposited PTCDI films and their electrical conduction. As known [2], the conduction of PTCDI films is strongly influenced by adsorption of the atmospheric oxygen. Therefore, the measured absorbed oxygen concentration dependencies of conductivity, activation energy and tunnel factor are represented and then compared with the theoretical calculations based on the two-level model of the hopping conductivity [3].

2 Methods

The PTCDI films with thickness of 100 nm were prepared by laser evaporation in vacuum of 10^{-2} Pa. The LGN-703 infrared CO_2-laser with output power of 40 W was used for evaporation of powdered PTCDI target. The products of evaporation were deposited onto the glass-ceramic and mica substrates at 20°C (cold) and 150°C (hot). The glass-ceramic substrates contain a preliminary formed interdigital system of nickel electrodes.

Morphology of the films was investigated using AFM FemtoScan-Online (Advanced Technology Center, Moscow State University). The optical spectra in visible range were measured using spectrophotometer SPECORD-M40 (Carl Zeiss Jena). The dc conductivity of the films on glass-ceramic substrates and its temperature dependence were measured by a V7E-42 electrometer (BELVAR, Minsk) by cyclic thermal desorption method [4].

The conductivity σ of PTCDI films depends on the temperature T as described by equation

$$\sigma = \sigma_0 \exp(-E_a / kT),$$

where σ_0 is the tunnel factor, E_a is the activation energy of conduction, and k is the Boltzmann constant. Using this expression and the aforesaid set of experimental temperature dependencies, it is possible to determine the conductivity σ and the parameters σ_0 and E_a corresponding to various concentration of adsorbed oxygen.

The two-level model of hopping conductivity allows calculating from the set of experimental data the fundamental microscopical parameters of hopping conductivity – the electron localization radius and the concentration of localization centers corresponding to the intrinsic and impurity states [3].

3 Morphology and structure of PTCDI films

Fig. 1 shows the contact mode AFM images of the surface of PTCDI films deposited onto the cold and hot mica substrates. The films on glass-ceramic substrates demonstrate the same morphology. The PTCDI films with thickness of

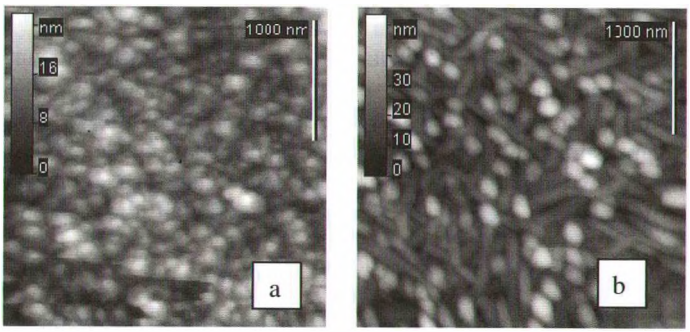

Figure 1. The AFM images of the surface of PTCDI films deposited on the substrates at 20°C (a) and 150°C (b).

100 nm have a polycrystalline structure with typical grains of 60–100 nm. The films deposited onto the hot substrates seem to have the greater peak-to-peak value of surface relief and the greater surface area of grain boundaries in comparison with its volume. Spectroscopic measurements show that the films deposited onto the both hot and cool substrates have coinciding absorption peaks at 478 nm and 570 nm. This fact demonstrates that both types of films have the same crystalline structure.

4 Electrical conduction properties

The measured dependencies of the conductivity, activation energy and tunnel factor on the concentration of adsorbed oxygen show that the hopping mechanism is realized in nanostructured PTCDI films. The main features of the electrical properties can be explained by means of Fig. 2, where x is the ratio of the adsorbed oxygen concentration to the full concentration of localization centers in the material. Lines A-A and B-B show the theoretical values for intrinsic and impurity

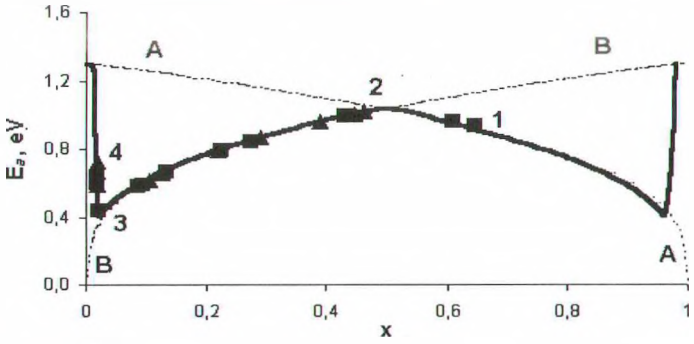

Figure 2. The dependence of conductivity activation energy on the relative concentration of adsorbed oxygen molecules.

conduction, respectively. More thick solid line corresponds to the calculated data for a two-component (PTCDI + oxygen) system. The experimental data for the films deposited onto the cold and hot substrates are marked by triangles and squares, respectively. The electron localization radius of intrinsic states is equal to 0.87 Å, and one of impurity states is equal to 0.90 Å at full concentration of localization centers of $3.3 \cdot 10^{21}$ cm^{-3}. At a high initial concentration of adsorbed oxygen (point 1), the conductivity is determined by the electron transport through the intrinsic states. As oxygen is desorbed, the amount of impurity states decreases while that of the intrinsic states accordingly increases. This leads to an increase in the activation energy (interval 1-2). At a critical oxygen concentration corresponding to point 2 the Fermi level is trapped at the impurity states and the electron transport through these states becomes dominating in the conductivity of

PTCDI films. Under this conditions, desorption of oxygen causes a decrease of activation energy (interval 2-3). Further decrease of adsorbed oxygen concentration causes the change in the conductivity type back from impurity to intrinsic one (interval 3-4).

5 Conclusion

Conductivity measurements of PTCDI thin films show that the films deposited onto cold and hot substrates have the same microscopic parameters of hopping transport whereas macroscopic values are different. The film on hot substrate has higher concentration of absorbed oxygen. No difference was found in the crystalline structure of the films. But the films significantly differ in surface morphology. The films on hot substrate are more porous and have significantly higher total area of grain boundaries. Therefore, the influence of oxygen on electronic properties of the PTCDI films is determined mainly by film morphology.

Acknowledgements

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