THE INFLUENCE OF STRUCTURE CHANGE ON ELECTRICAL PROPERTIES OF CONDUCTING LB FILMS PRODUCED FROM HEXADECYL-TCNQ AND HEPTADECYLDIMETHYL-TTF MIXTURE

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Abstract - Conducting Langmuir-Blodgett films of hexadecyl-TCNQ and heptadecyldimethyl-TTF mixture in the ratios from 1:1 to 1:2.5 are studied. Temperature dependence of film conductivity possesses some specific features.Strong increase of conductivity and decrease of activation energy take place after annealing at 307-315 K.On the other hand,the film loses conductance after heating above 315 K. To explain this behaviour the investigations of conducting multilayers by means of electron diffraction,electron microscopy, and X-ray small-angle scattering were carried out. Some relations between changes of electrical properties and structural transformations are ascertained.

INTRODUCTION

Highly conducting Langmuir-Blodgett films with stable and reproducible properties are interesting in view of development of 'nanoelectronics' because their properties seem to give us the possibility for creation of functional elements with the dimensions of the order of one nanometer. It appears that conductance of these films can be easily destroyed when irradiating them by electrons or UV light. Irradiated areas become insulating, but no visible change of multilayer morphology takes place. Thus, some desirable pattern of conducting material can be created in the layer plane. The action of tunneling microscope must be the same with high probability at appropriate conditions of operation. In this case we can obtain very small conducting elements. On the other hand, Langmuir-Blodgett technique possesses unique property of alternation of different layers in the process of film deposition. Conducting layers can be introduced in some parts of multilayer. So a lamellar system with molecular resolution can be built up in the direction normal to the substrate plane. Small elements containing conducting areas with the dimensions of the order of one nanometer made of Langmuir-Blodgett films must be more stable than those produced from non-organic metals or semiconductors because they have very small surface energy and processes of recrystallization are suppressed. Due to these specific features of Langmuir-Blodgett films,a way to 'nanoelectronics' seems to be possible.

For the first time conductivity in the films of N-docosylpyridinium and tetracyanoquinodimethane (TCNQ) charge-transfer salt doped by iodine was discovered [1]. Later on

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conductivity was found in other types of charge-transfer complexes and salts [2-9]. In the previous work [10] we showed that high quality conducting films can be deposited without any doping when using mixtures of neutral acceptor molecules hexadecyltetracyanoquinodimethane (hexadecyl-TCNQ) and donor molecules heptadecyldimethyltetrathiafulvalene (heptadecyl--DMTTF).

Investigations of electrical properties of conducting films [11,12] showed that conductivity is usually realized through activation mechanism. Some works are concerned with structure study [13-17]. A promising possibility of structural investigations is to find relations between electrical properties and structure.

In this work,when studying temperature dependence of conductivity of films produced from hexadecyl-TCNQ and heptadecyl-DMTTF mixture,we discovered unusual behaviour of conductivity under heating the samples. To explain these results we carried out investigations of the films by means of electron microscopy, electron diffraction,and X-ray small-angle scattering. Some dependences between irreversible changes of electrical conductivity and structure are ascertained.

EXPERIMENTAL DETAILS

Two-component films of hexadecyl-TCNQ and heptadecyl--DMTTF mixture in the ratios from 1:1 to 1:2.5 were obtained. Mixture of hexane and chloroform with the composition of 2:1 was used as a solvent. Formation of the films containing 9,15, and 29 monolayers on thin collodion substrates was fulfilled for electron diffraction and electron microscopy studies. The films containing 39 monolayers deposited on sapphire substrates were used for X-ray measurements. Other details of these experiments are given in [10].

Temperature dependence of conductivity was measured by four-probe technique in high vacuum in a range from 110 to 320 K. The samples (Fig. 1) were prepared as follows.The films consisting of 9,15 and 29 monolayers were deposited on sapphire substrates with dimensions of 10x20 mm. Chromium electrodes were evaporated on the substrate before depositing the multilayer. The required pattern was formed in the multilayer due to irradiation of the latter by electrons with energy of 3 keV through a special mask. The unmasked areas become insulating.

The samples were heated with the step of 1-2 degrees and studied by appropriate technique.

RESULTS AND DISCUSSION

Temperature dependence of conductivity possesses some specific features (Fig.1). Conductivity is realized through activation mechanism. Activation energy is equal to 0.17 eV in the first cooling process. No changes take place after multiple variations of temperature between 300 and 110 K. Electron diffraction pattern (Fig.2a) shows that the initial film consists of smallest crystallites with in-plane dimensions of 10-20 nm and with poor order of mutual superposition of bilayers. Moreover, the film doesn't have good lamellar order in normal direction. The last fact is confirmed by the pattern of small-angle X-ray scattering (Fig.3) showing no Bragg reflec-

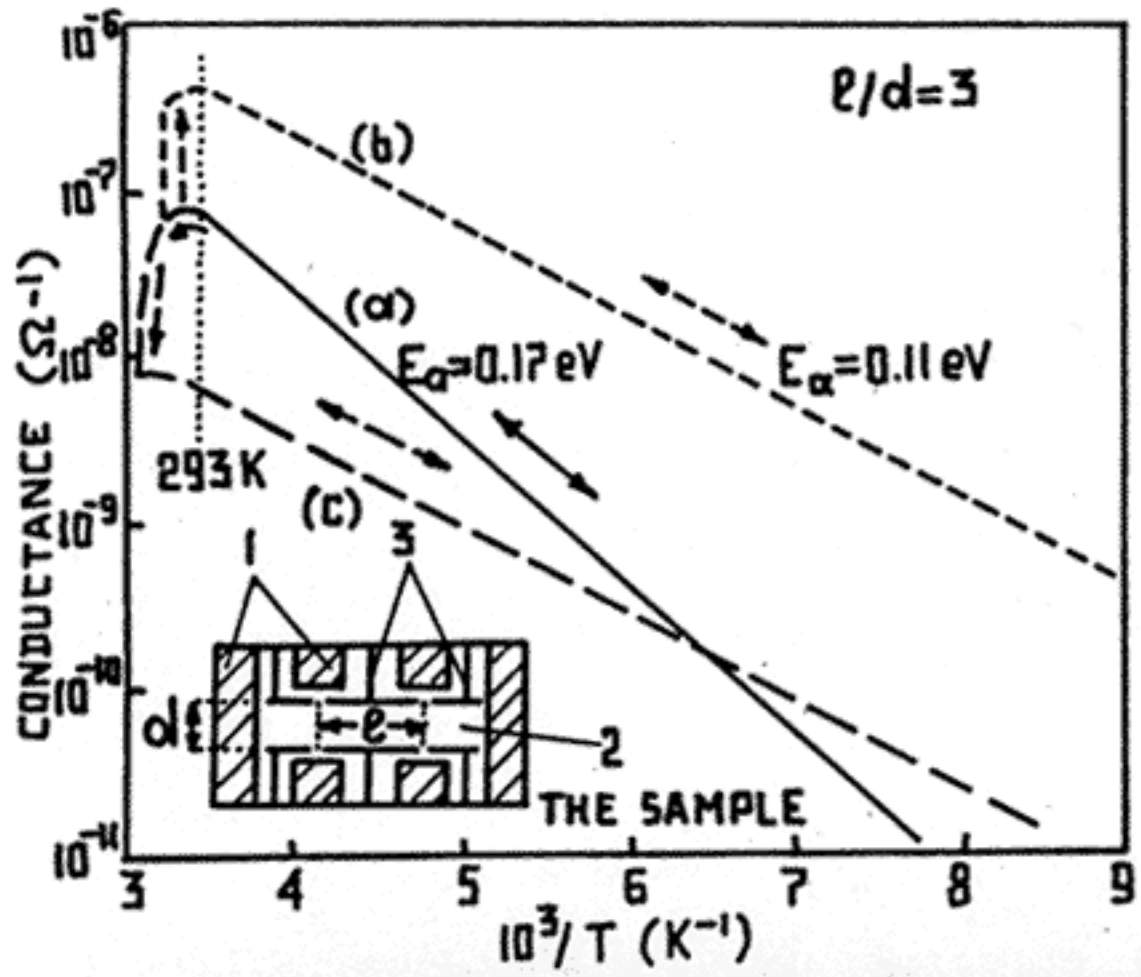

Fig. 1. Variations of temperature dependence of conductivity for 9 monolayers prepared from hexadecyl-TCNQ and heptadecyl-DMTTF mixture in the ratio 1:1 (a- initial film, b- annealing at 310 K, c- heating up to 320 K). The sample contains chromium electrodes (1) and conducting film (2) with non-conducting areas (3).

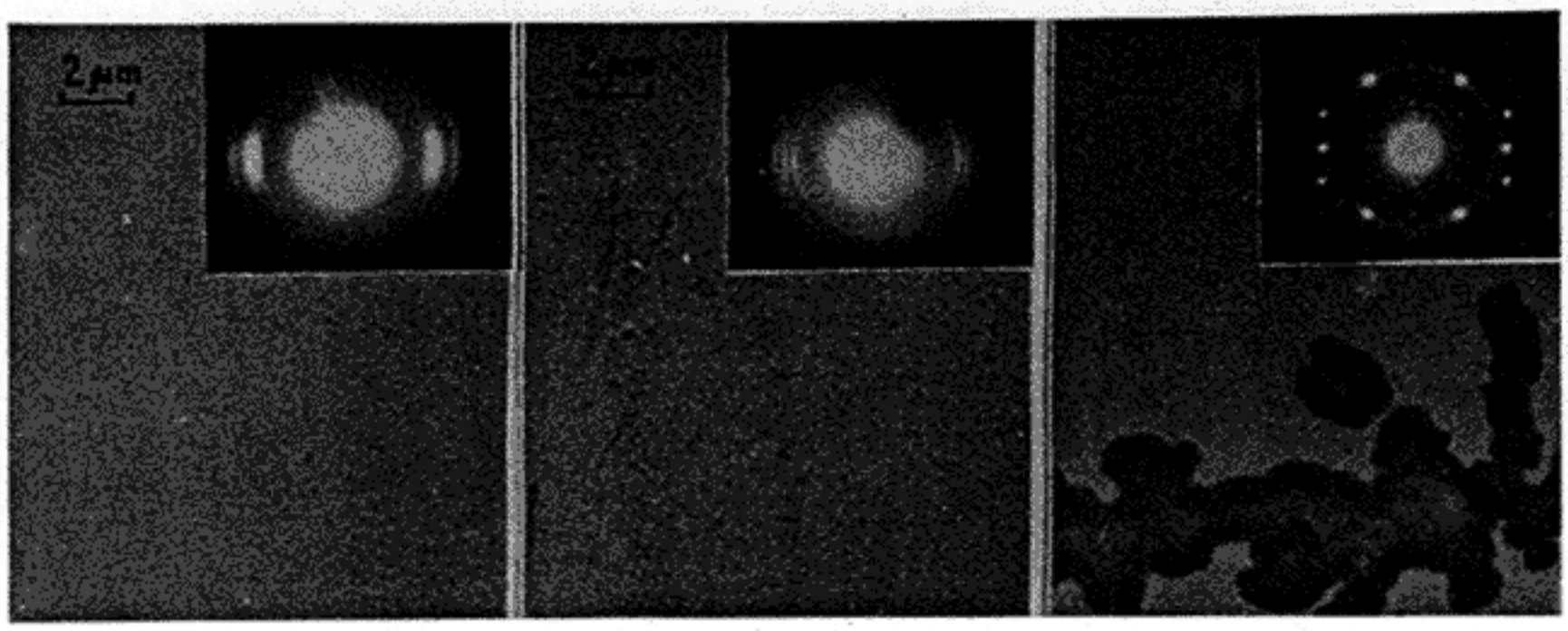

Fig. 2. Electron micrographs and electron diffraction patterns of the films containing 15 monolayers. Mixture of hexadecyl--TCNQ and heptadecyl-DMTTF in the ratio of 1:1 (a- initial film, b- annealing during 15 min at 310 K, c- heating up to 320 K).

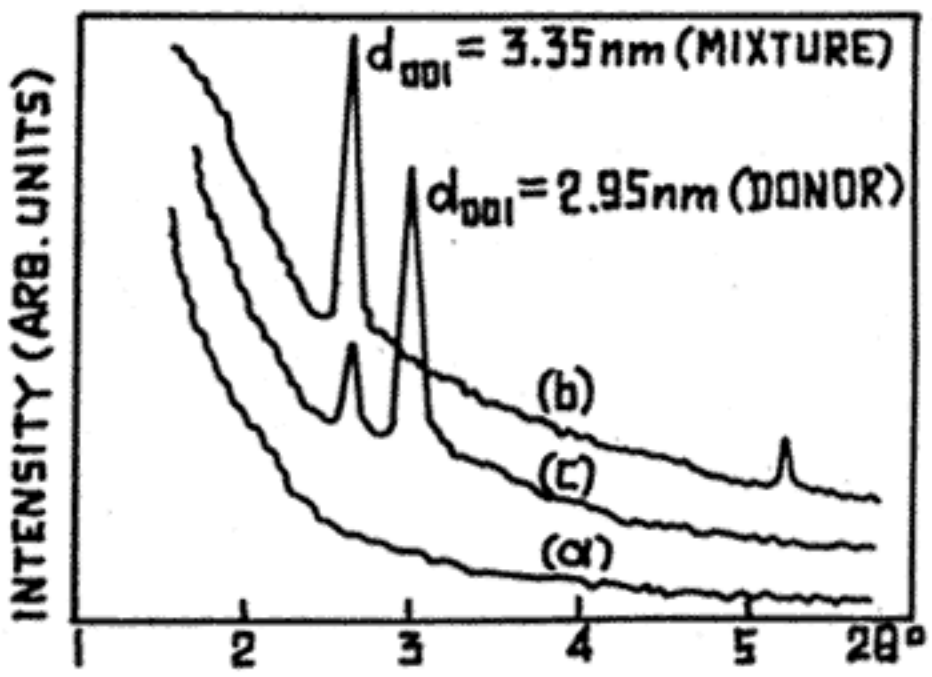

Fig. 3. Patterns of X-ray small-angle scattering from the film consisting of 39 monolayers (a- initial film with the ratio of acceptor and donor molecules equal to 1:1, b- the same film after annealing during 15 min at 310 K, c- the film with the ratio of acceptor and donor molecules equal to 1:2.5 after annealing during 15 min at 310 K).

tions. Spacings corresponding to electron diffraction pattern in Fig.2a are the following:0.769, 0.629, 0.513, 0.439, 0.385, and 0.332 nm. X-ray and electron diffraction patterns as well as electron micrograph (Fig.2a) of the film do not change after multiple variation of temperature between 300 and 110 K.

But when annealing of the sample is performed at temperature 305-307 K, small irreversible decrease of conductance happens. Electron diffraction pattern shows that the film becomes amorphous.Some decrease of conductivity can be explained by this transformation. X-ray diffraction pattern shows no change. The same result takes place when quick heating up to temperature 315-320 K and subsequent cooling are performed. Some reversible decrease of conductivity is observed also in the above mentioned interval, but this behaviour can not be explained by our results.

However, if the temperature is maintained at 307-315 K during approximately 10-20 min, strong irreversible increase of conductance occurs. In some experiments for the films with composition of donor and acceptor molecules equal to 1:1 conductivity increases 10 times. When the composition varies from 1:1 to 2.5:1, the change of conductivity diminishes. Activation energy decreases after such annealing. Slow transformation of electron diffraction pattern is observed in this process.First of all, crystallites arise in amorphous film. Then total recrystallization of the latter happens. Nevertheless, no deterioration of film morphology occurs. This is demonstrated by electron micrograph and diffraction pattern (Fig.2b). But the dimensions of crystallites become equal to 100-200 nm.Besides, a very good lamellar system arises, because strong Bragg reflection corresponding to two-component film appears in X-ray diffraction pattern. Thus, the increase of conductivity is caused by growth of crystallites and by improvement of three-dimensional crystalline order. X-ray diffraction pattern of the film with the composition of donor and acceptor molecules equal to 2.5:1 after annealing shows that donor crystallites precipitate. Only small amount of ordered two-component phase arises. For this reason the change of conductivity of such films after heating at 307-315 K is small.

After heating the sample above 315 K, conductance usually decreases. In the case shown in Fig.1 heating between 307 and 315 K was performed quickly. When the temperature is kept between 315 and 320 K for a long time, the film loses conductance. Electron diffraction and electron microscopy study (Fig.2c) explain this fact. Slow irreversible recrystallization with the formation of large crystallites takes place in this temperature interval, and the film becomes finally discontinuous.

Spacings corresponding to electron diffraction pattern of the film in Fig.2c are equal to 0.762, 0.620, 0.510, 0.434, 0.384, and 0.356 nm. Intensities of reflections differ from those of initial film, but all spacings excluding the last one are practically the same. When registrating also electron diffraction pattern of the crystals in Fig.2c with the tilt of sample to electron beam, we find that the unit cell of the structure is orthorhombic with parameters a=1.030 nm, b=0.766 nm, and c=7.09 nm. Calculations show that both non-coinciding spacings can be found in this structure. Strong changes of intensities including disappearance of reflections can take place due to interference caused by arising of three-dimensio-

nal order. For this reason packing patterns of molecules in bilayers seem to be the same before and after annealing. Thus, we can also propose that an activation of carriers occurs from some traps located at the boundaries of crystallites because only boundaries change in the process of annealing. Appearance of traps of new type and variation of activation energy can happen as a consequence.

CONCLUSIONS

Irreversible changes of conductance of films under heating in temperature interval between 305 and 320 K are caused by structural transformations. Small decrease of conductivity at 305-307 K is explained by transition into amorphous state. Strong increase of conductivity at 307-315 K without deterioration of film morphology is caused by recrystallization of the film and improvement of crystalline order. Decrease of conductance after heating above 315 K occurs due to formation of large crystals, so that finally the film becomes discontinuous. Change of activation energy after annealing seems to be caused by modification of boundaries between the crystallites.

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