Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Edward N. Korol & Margaret A. Manoylo (1994): The Conductivity of Ion-Implanted and Deposited Polymer Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 248:1, 137-141

To link to this article: http://dx.doi.org/10.1080/10587259408027174

Mol. Cryst. Liq. Cryst. 1994, Vol. 248, pp. 137–141
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Printed in the United States of America

THE CONDUCTIVITY OF ION-IMPLANTED AND DEPOSITED POLYMER FILMS

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Abstract The analysis of temperature dependence of the electroconductivity of ion-implanted as well as deposited metallized polymer films allowed to make some conclusions about the conduction mechanisms in these disordered materials.

INTRODUCTION

Thin polymer films begin to play an essential role as materials for active circuit elements in microelectronics and computers. They have a number of evident advantages over metallic or usual semiconductor materials. Usually polymers with a system of conjugated bonds (conjugated polymers), such as polyacetylene, polythiophene etc., are used as such new materials. In order to increase their conductivity they have to be doped with other atoms or molecules (Na, K, J_2, AsF_5 etc.). This procedure leads to an increase of the concentration of the carriers which move along the conjugated chains.

It should be noted, however, that preparing of thin films of conjugated polymers requires some technologic complications, whereas non-conjugated polymer films (such as polyethylene, polyethyleneoxide, polyamide etc.) are more widespread. And though they are not conductors but good dielectrics (because of the absence of conjugated chains) we have shown earlier that there are at least two methods of enhancement of the conductivity, σ, of such polymers right up to the σ of semiconductors.

These methods are as follows:

1) an ion implantation of various ions into free polymer film which leads to the

creation of a thin (about 1000 Å) layer in the film with $\sigma \sim 10^{-4}$ - 10^{-1} S/cm;
2) a simultaneous thermovacuum deposition of polymer and metal which leads to formation of a thin deposited composite film with σ, varying within a broad interval (10^{-5} - 10^{4} S/cm) dependent on metal content.

The absence of conjugated chains in such materials causes conduction mechanisms different from that for conjugated polymers. The investigation of features of the conduction mechanisms in ion-implanted and deposited metallized polymer films is the subject of this paper.

EXPERIMENTAL

Ion implantation was made into polymer films of polyethylene (PE), polyethyleneterephtalate (PETP), polypropylene (PPr) and polyamide (PI) with thickness of 10-50 μm using the implanting unit "Lada-20". Ions of Ar^+, CO^+,CO_2^+, BF^+, BF_2^+, and BF_3^+ with energy of 60 keV, current density of 0,75 A/cm^2 and fluency of $F = 10^{16}$ - 10^{17} ions/cm^2 were chosen for implantation. The thickness of the conducting layer was estimated to be 500-550 Å for various polymers. The conductivity, σ, was measured using the "surface type cell" method [1] at various temperatures of films.

Thin composite films were fabricated by the method of simultaneous thermovacuum deposition of PE and a metal (silver, copper or aluminium) as a filler in the exhaust unit VUP-5. Dielectric (glass) plates were used as the base. Silver strips were deposited on them to create ohmic contacts with polymer film. The thickness of deposited films was measured by ellipsometric method and was equal to 10^{-5} cm.

The sign of carriers charge was determined by the sign of thermopower: all of the deposited films had n-type of carriers. Conductivity of the films was varying in the interval $\sigma = 10^{-5}$-10^{4} S/cm depending on the metal content.

RESULTS AND DISCUSSION

We shall see further that conduction mechanisms in conducting layers of ion-implanted polymers and in deposited films are rather different. That is why the results obtained are considered separately for these two objects.

Ion-implanted polymers

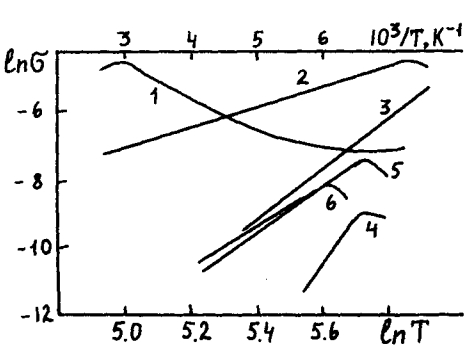
In order to clear up the conduction mechanism we measured the carriers mobility, temperature and dose dependencies of conductivity, σ . The magnitude of the mobility was estimated by the Hall current method and was found to be less than 10^{-1} $cm^2/V.s$. This magnitude is typical for disordered materials. It permits us to consider ion-implanted as well as deposited polymer films as disordered semiconductors which usually have the $\sigma(T)$-dependence of the following type: $\ln\sigma \sim T^{-\alpha}$, where $\alpha=1$, 1/2 or 1/4 for different mechanisms of the conductivity.

Fig.1 (curve 1) represents the dependence of $\ln\sigma$ vs 10 /T for PI implanted with Ar^+ ions ($F=10^{14}$ ions/cm^2). It is seen that attempts to describe this dependence with the law of $\ln\sigma \sim T^{-\alpha}$ are invalid. This situation made us to appeal to another model of conductivity which is realised for some complex disordered solids [2]. The main idea of this model is that the carriers move through the levels located in energy region of the exponential "tails" of the state density near the edges of allowed energetic bands.

This model gives a reverse Arrenius law $\sigma = \sigma_0 \exp(T/T_0)$ which was confirmed experimentally for great number of materials, such as solid solutions of type $Ge_{1-x}Si_x$, polycrystalline films of diamond and PbS, glass-like materials like As_2Te_3 etc.

For another type of solids (metal-oxide films of V-P-O, V-Te-O, WO_3) the contribution of multiphonon processes plays an essential role and dependence $\sigma(T)$ is rather different: $\sigma = \sigma_0 T^n$ ($n>1$).

It is know that in organic semiconductors electron-phonon interaction is essential and leads to appearance of polarons and bipolarons as current carriers [3].It gave us a reason to hope that the last dependence would be realised in ion-implanted polymer films as well.



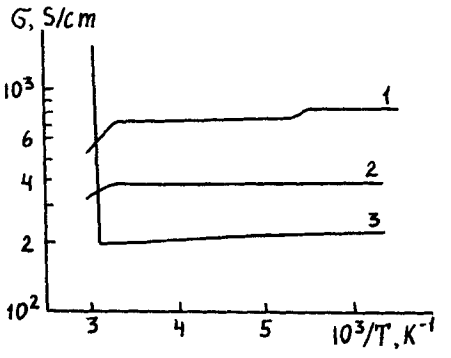


FIGURE 1 (left) σ(T)-dependence for ion-implanted polymers. 1 - PI, Ar^+, F=10^{17} ions/cm^2, lnσ= f(1/T); 2 - idem, but lnσ= f(lnT), n=3; 3 - PPr, Ar^+, F=10^{17} ions/cm^2, n=7; 4 - PE, CO_2^+, F=10^{15} ions/cm^2, n=13; 5 - PE, CO_2^+, F=$8\cdot10^{15}$ ions/cm^2, n=6,9; 6 - PE, CO_2^+, F=10^{16} ions/cm^2, n=6,4

FIGURE 2 (right) σ(T)-dependence for deposited polymer films. 1 - PE+Al; 2 - PE+Cu; 3 - PE+Ag.

Curves 2-6 give the σ(T) dependence for some pairs of polymer-dopant. One can see that the law $\sigma = \sigma_0 T^n$ is valid for various polymers in the interval T=100-300 K, and n depends on the sort of polymer and decreases when fluency, F, increases (curves 4-6). At temperatures T>330 K one can see decreasing of σ which may be explained by melting of polymer and destruction of conducting cluster formed by implanted ions in polymer matrix.

Deposited metallized films

σ (T) dependence for these films is represented in Fig.2. In the interval T=160-330 K high conducting samples with $\sigma=(4\text{-}7)\cdot10^2$ S/cm demonstrate metallic-like dependence. Apparently, in these films the conductivity is realized by tunneling of electrons between metallic particles situated on the surfase of polymer

globules. When T increases in the range T>330 K the conductivity of PE+Al (curve 1) and PE+Cu (curve 2) films decreases. But PE+Ag films show rather different behaviour at T>330 K (curve 3). More detailed investigation showed that $\sigma(T)$ dependence at T >330 K may be described quite well by the law $\ln\sigma \sim T^{-1}$. This difference in the behaviour of the films under investigation can be probably explained by oxidation ability of Cu and Al particles in polymer matrix meanwhile Ag is known to be steady to oxidation.

CONCLUSION

In spite of apparent similarity in disordered structure of ion-implanted and deposited polymer films their conduction mechanisms are seemed to be different. Widespread opinion that the hopping mechanism is determinative for ion-implanted films is to all appearance invalid, most likely we observe the carrier transfer along percolation cluster accompanied by multiphonon energy relaxation [2], this mechanism is described by the law $\sigma = \sigma_0 T^n (n > 1)$.

In metallized deposited polymer films we observe probably the electron tunnelling between metallic particles (islands); at high T (more than 330 K) the conduction mechanism is more complicated.

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