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DC-conductivity of thin films of 1,4-cis-polybutadiene doped with SiC

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ABSTRACT

In this paper the results of DC-conductivity investigation of 1,4-cis-polybutadiene thin films doped with 5% weight of silicon carbonate (SiC) of nanocrystalline form with the size of grains being about 20 nm are presented. The aim of the study was to receive a knowledge about the electrical properties and DC-conductivity mechanisms depending on film thickness, temperature and electric field magnitude. The investigated films thickness ranged from 1 to 12 μm. The investigations were carried out for both undoped and doped with nanocrystalline SiC polymers. The current flow through the material bulk changed from 10^{-12} to 10^{-4} A with applied electric fields of 0 to 3×10^7 V/m and temperature of the film varying from 15 to 325 K. It was observed that the magnitude of the current flow through the investigated material bulk is governed by a phase state of the polymer and the presence of SiC in the bulk. The charge transport through the material bulk is controlled by the Poole-Frenkel phenomenon as well as by hopping. The determined activation energies were between kT and 0.36 eV.

1. Introduction

Physical properties of organic polymers that are insulators and semiconductors are determined by their surface and internal structure. In the case of polymer materials doped with nanocrystalline semiconducting SiC we deal with a low-ordered or non-ordered materials (amorphous areas and crystallites). In these two cases we mean both short-range and long-range ordering. Electrical properties, and consequently, applications of the material will be decided by the shape of IV characteristics. A huge influence on these properties has the distribution of traps in energy scale as well as the traps concentration in the material bulk. In polymers, instead of a well-defined energy forbidden gap we observe an area filled with trapping states characterized by different energy. The energy diagrams of strongly compensated crystalline semiconductors and polymer materials are very similar. Polymers and tiny crystallite are very convenient objects to investigate conductivity with hopping in a wide range of temperature and electric fields.

2. Experimental

The subject for the investigation was pure 1,4-cis-polybautdiene containing 96% of cis and 45 of trans form. The polymer was a matrix in which nanocrystalline SiC was placed. We have investigated an influence of SiC on DC-electrical properties of the polymer film SiC doped [1–3]. 1,4-Cis-polybutadiene BR-150 Ubepol was the product of very high purity obtained from Tokyo Kasei Kogyo Co. Ltd. The detailed data concerned that material are presented in [4,5]. SiC characterized by a large monodispersion was obtained in the way presented in Fig. 1. SiC nanocrystals were obtained with the use of a certain equipment (Fig. 1) by using a pyrolitic method. The basic material, which was synthesized in the laser beam, was a mixture of gaseous SiH_4 and C_2H_2. As an effect of laser infrared light interaction dissociation of the gases mixture took place, which was followed by the creation of nanocrystalline SiC. The size of nanocrystallites depended on the synthesis conditions (temperature, pressure, the rate of the gases flow, the mixture composition). The chemical reaction of SiC synthesis is described as follow:

$$2SiH_4 + C_2H_2 \rightarrow 2SiC + 5H_2$$

During the process of synthesis it is possible to study chemical structure of the product, its electro-optical properties as well as its optical nonlinearity [6]. SiC may be obtained in two forms, which id decided by reacting gases composition:

1. When C to Si ratio is much less than 1 the obtained material is very sensitive to oxidation.
2. When C to Si ratio is higher than 1 carbon layers cover Si particles and the obtained material is stable in air, but its internal structure is rebuilding.

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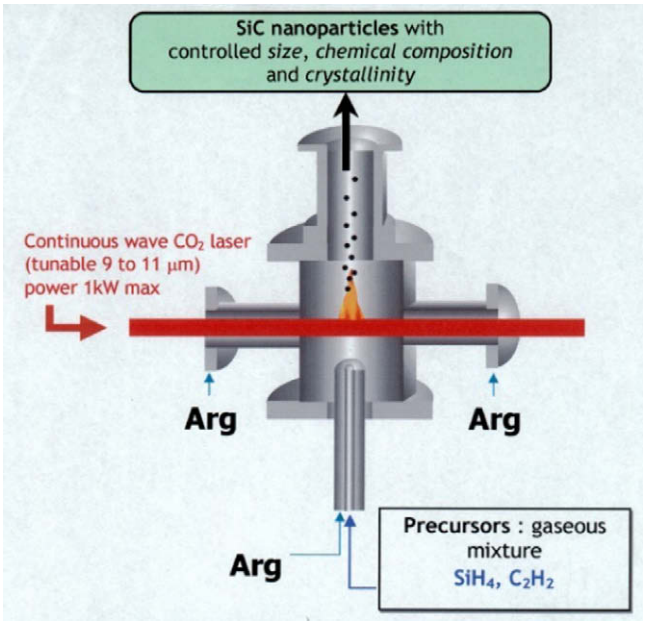

Fig. 1. The method of obtaining nanocrystalline SiC.

In Fig. 2a picture of nanoparticles taken with TEM (tunneling microscope) method is presented. Fig. 2a and b shows SiC nanoparticles obtained in 1200 and 1400 °C, respectively. It is seen that the increase of temperature causes an inhomogeneous growth of crystallites.

The measurements of electrical conductivity were performed for the sandwich samples with Au and Al electrodes. Au electrode is a hole injector when in contact with organic material, and Al electrode makes a blocking contact at the boundary with the organic material. Thin films of the polymer doped with SiC, (with the thickness of 1–10 μm) were obtained by centrifugal spinning from a solution. This method was applied to obtain 25 samples on one substrate in the same physical conditions. The DC investigation was accompanied with the measurement of the value of electric charge flowing through the sample bulk dependent on electric field magnitude and temperature. The temperature during measurements varied from 15 to 325 K. The quantity of SiC in relation to the mass of pure 1,4-cis-polybutadiene was 5%. It is the most often applied value of doping in polymer matrices in the study of electroluminescent distribution.

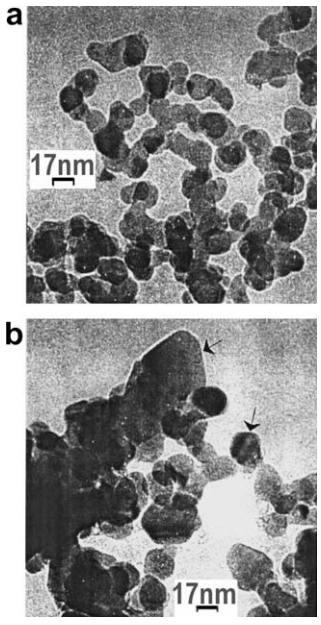

Fig. 2. Nanocrystalline structures of SiC observed in TEM. (a) homogeneous SiC (T = 1200 °C) and (b) inhomogeneous SiC – clearly seen variation in grains size ($T \sim$ 1400 °C).

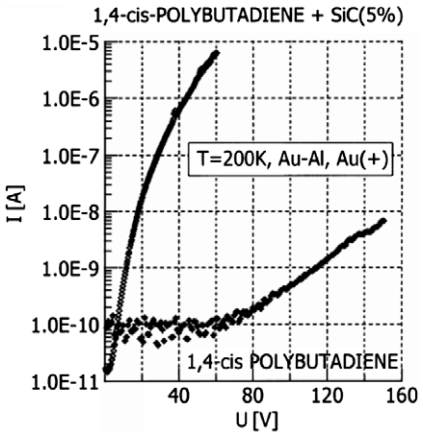

Fig. 3. The $I = f(U)$ dependences in semi logarithmic coordinates for the samples of 4.5 μm thickness in 100 K taken for pure 1,4-cis-polybutadiene and 1,4-cis-polybutadiene doped SiC.

3. Results and discussion

An analysis of the obtained results of DC-conductivity let us claim that various mechanisms take part in charge transport through the investigated material bulk depending on the electric field magnitude, measurement temperature and electrode polarization. It was observed that addition of 5% of SiC to 1,4-cis-polybutadiene causes considerable increase of conductivity – nearly of five orders of magnitude, which is seen in Fig. 3.

Mechanism different from ohmic is indicated by the shape of IV characteristics that are plotted in logarithmic coordinates as presented in Fig. 4. It is well seen from the figure that reverse polari-

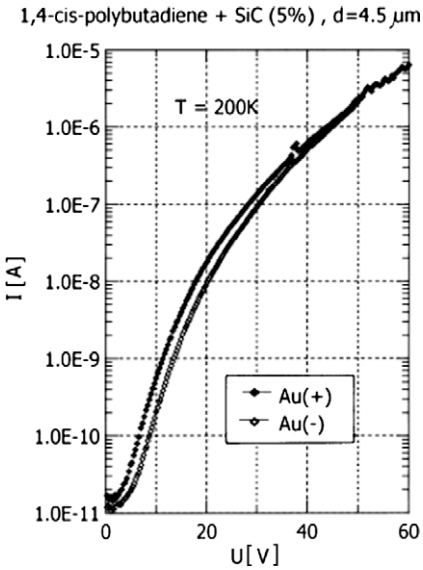

Fig. 4. The log $I = f(U)$ dependence for 1,4-cis-polybutadiene 5% SiC doped in 200 K for different polarization of electrodes. The film thickness d = 4.5 μm.