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Space Charge Limited Current in Films Obtained in Glow Discharge Plasma

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Abstract

The electrical current in thin films obtained by the polymerization of acetonitrile in glow discharge on a heated substrate were investigated in order to determine the mechanism of electrical conduction. The results of the field dependence, sample thickness dependence of the dark conductivity, supported by the results of photocurrent measurements, suggest an exponential energy distribution of traps inside the band gap of the polymer.

1. Introduction

Polymerization in plasma is one of the simple and convenient methods for obtaining thin polymer films from a wide variety of monomers. The excellent physical-chemical properties of these films attract attention of a large number of investigators and have created entirely new technical possibilities in the area of electronics. So the possibility of obtaining films with relatively high electrical conduction and photoconduction in a solar radiation spectral region may determine the future outlook for the application of plasma-polymerized films for solar energy transformation [1, 2]. In [1] it is shown that relatively high conduction is observed in a films obtained from monomers containing polar groups. It was noted that the presence of nitril groups was of great importance in this respect. After this report a number of works dealing with the investigation of photoelectrical properties of polymers obtained by plasma polymerization of monomers containing nitril groups have appeared [3-6].

In the present study, the results of the investigation of some electrical and photoelectrical properties of the films obtained by the glow discharge polymerization of acetonitril on a heated substrate are given.

2. Experimental Technique

The polymerization of acetonitrile has been carried out by the technique described in [7] on the substrate presented by $20 \times 30 \times 0,2 \text{ mm}^3 \text{ Si}$ -wafers which were carefully cleaned in acetone, trichlorethylene and distilled water. Then *Au*, *Al* or *Cu* electrodes were evaporated on the substrate in vacuum.

Electrical studies were carried out on metal-polymer-metal sandwich structures of area $0,3 \text{ cm}^2$ on films annealed under vacuum conditions to eliminate moisture and monomer vapor.

The results given below were obtained for films polymerized in glow discharge at 10 A/m^2 DC with monomer pressure of 133 Pa and substrate temperature of 555 K. For these films the optic absorption coefficient has the values of $10^4 - 10^5 \text{ cm}^{-1}$ in the photon energy region of 1,5-2,5 eV. The results of the thermo e.m.f. measurements indicates the *n*-type conduction in the material investigated.

The film thickness had been measured via microscope to an accuracy of $0,1 \mu\text{m}$. The electrical measurements were carried out on polymer films having thickness $1,2 \mu\text{m}$. A filament lamp and a 500 W mercury lamp were used as light sources. The wavelength selection was performed by a monochromator and a set of glass filters. All measurements were automated. To elucidate the conduction mechanism variation of current density with applied voltage, film thickness, temperature and illumination for different electrode systems was investigated.

3. Experimental Results

1. Dark Current Measurements

Figure 1 shows the dark current-voltage relations for the cell in the system *Cu - Pol - Cu* at various sample temperatures. As is seen in the investigated voltage span these curves consist of two linear sections having a different slopes. At relatively low voltages the slope of $I = f(V)$ shows weak temperature dependence and is approximately 1.

In the second section, at relatively high voltages, the slope decreases gradually from 3,1 at 260 K to 2,0 at $T = 340$ K. Note that the slope of the second section at room temperature and higher is more than 2. It is seen that the voltage during the transition from the first to the second section is increasing with temperature. Studies of the current-voltage characteristics at room temperature for *Cu - Pol - Cu* and *Ag - Pol - Ag* samples with different film thickness have shown that slope of the I-V characteristics in all cases was $2,8 \pm 0,2$ and did not depend on the thickness.

The $I = f(V)$ investigation results at room temperature are given in a wider voltage span in Figure 2.

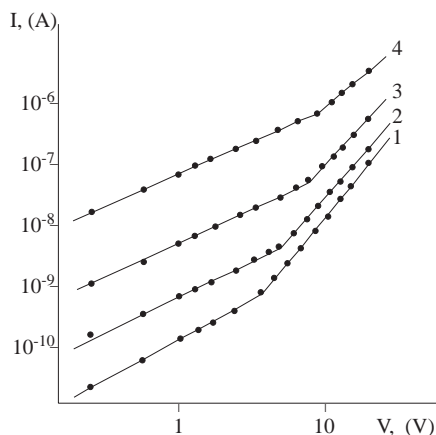


Figure 1. Dark current-voltage relations for the system Cu-Pol-Cu at temperatures of 220 K (1); 260 K (2); 300 K (3); 340 K (4)

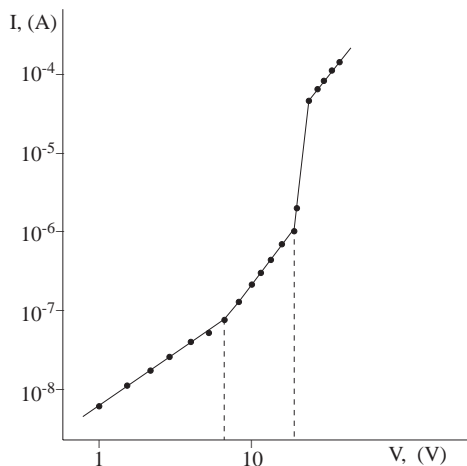


Figure 2. Dark current-voltage relations for the system Cu-Pol-Cu at room temperature in a wider voltage span

It should be noted that new linear sections with different slopes are appearing in $I = f(V)$ due to the increase of the applied voltage. At some voltage value the dark current is first sharply and then monotonously increasing with a slope $\cong 2$.

Investigation of $I = f(V)$ for samples with *Al* electrodes have also shown identical results but this data should be treated with care because of possible formation of oxide layer at the polymer-metal interface, which can dramatically change the properties of plasma-polymer-metal interface. Evidence of this is given by the decrease of conduction with time with the use of *Al* electrodes.

Due to oxidation, the investigation of polymerized in acetonitril plasma films was mainly carried out on samples with *Au*-electrodes. Figure 3 shows dark current-voltage relationships at different temperatures. In contrast to the previous case, the slope of the second section at 278 K=2 and at higher temperature is less than 2. In particular, these differences are shown by temperature dark current dependencies for the systems with *Cu* and *Au* electrodes at 200-400 K (Figure 4).

It is seen that two linear sections are observed in the samples with *Au* electrodes, the transition from the first to the second section being very sharp. Each section is characterized by the activation energy value: conduction has higher activation energy in the higher temperature region. Temperature dependence of the current in the sample with golden electrodes shown in Figure 4 is typical of all samples, obtained for various temperatures. In samples with *Cu* electrodes only one linear section in the investigated temperature region is observed.

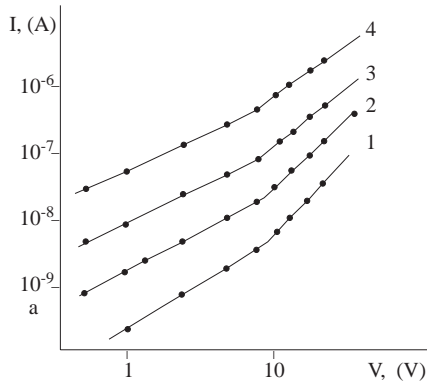


Figure 3. Dark current-voltage relations for the system Au-Pol-Au at temperatures of 130 K (1); 255 K (2); 278 K (3); 335 K (4)

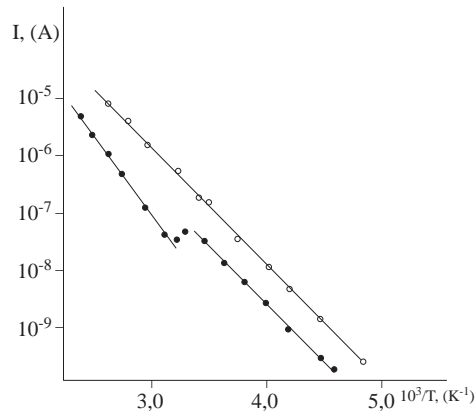


Figure 4. Temperature dependencies of dark current for the system with Cu (o) and Au (•) electrodes ($V = 2$ V)

Comparison of all these relationships shows that dark current activation energy in samples with *Cu* electrodes corresponds to that in samples with *Au* electrodes for the low temperature region. Hence it is possible to assume that this activation energy value is defined by the bulk film properties and does not depend on the material of electrodes.

Figure 5 shows the dark current dependencies on the film thickness at a fixed voltage and at two temperature values (230 and 300 K) for samples with *Au*-electrodes. It was stated that the dark current dependencies on the film at different temperatures have different slopes: at $T = 230$ K, $n = 4, 6$ and at $T = 300$, $n = 1, 7$. It gives evidence that, in fact, different processes are responsible for the conduction mechanism in different temperature regions.

4. Photocurrent Measurements

It is known that photocurrent measurement is a good additional methodology to understand the conduction and carrier trapping mechanism, since the free carrier density can be changed without changing the sample temperature. Figure 6 shows the $I = f(V)$ relationship under monochromatic light illumination at different intensities, including dark current, at room temperature. Both characteristics have two linear sections with different slopes. In the first section the slope of both characteristics is nearly identical and $\cong 1$. In the second section the slope of light characteristic is less than that of dark. With an increasing light intensity there is less variation among $I = f(V)$ -slopes.

We have also investigated the dependence of photocurrent (the total current under illumination without the dark current) on incident monochromatic light intensity. Figure 7 shows the sample having similar dependence under illumination with light of wave length $\lambda = 546\text{nm}$ at different voltages and $T = 300$ K.

It is seen that this dependence consists of two linear sections. At low light intensities the slope value is $0,8 \div 1,0$ and at rather high light intensity values the slope is $0,55 \div 0,65$. With increasing applied field intensity the slope of the first section is increasing to 1 and that of the second is decreasing to 0,55.

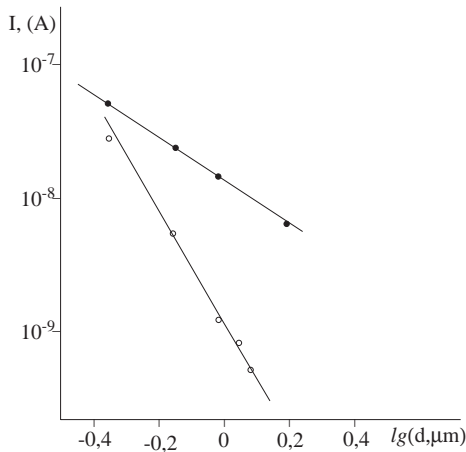


Figure 5. Thickness dependence of a dark current in a Au-Pol-Au at a fixed voltage at two different temperatures 230 K (o) and 300 K (•) ($V = 12 \text{ V}$)

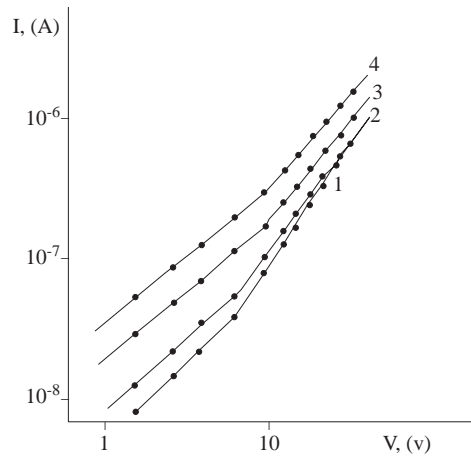


Figure 6. Dark current (curve 1) and photocurrent (curves 2-4, with increasing intensity, respectively) - voltage relations for the system Au-Pol-Au at room temperature

5. Discussion

On the base of the voltage exponent value defined from the nonohmic section of $I = f(V)$ it is supposed that the film conduction in the 200-320 K temperature region for the system with Cu-electrodes and that in temperature region of 200-280 K for the system with Au-electrodes corresponds to the mechanism based on the space charge limited current theory. The value of voltage exponent shows that the traps in the band gap of polymer have either exponential or gaussian energy distribution [8, 9]. The assumption that an SCLC-mechanism exists is also confirmed by the character of the dark current dependence on the film thickness. Since the voltage exponent is kept constant up to the region of maximum trap filling it can be concluded that the traps inside the band gap are exponential distributed. The experimental data show the characteristic distribution temperature

$$T_c = 540K \left(\ell = \frac{T_c}{T} = 1,8 \text{ at } T = 300K \right)$$

The character of photocurrent dependence on light intensity may be based on the assumption of the exponential energy distribution of traps inside the band gap of

the plasma polymerized films. In fact, as is shown in [10] in this case, the following dependencies of the photogenerated carrier density on the light intensity in the strong absorption region may be expressed as

$$n = \frac{G(C^{\circ}/C^{\pm})^{T/T_c} \exp[(E_C - E_{F_0})/KT_C]}{4C^{\circ}H_BKT(1 - 2C^{\circ}/C^{\pm})^{T/T_c}} \quad (1)$$

at low light intensities and

$$n = \left(\frac{G}{4C^{\circ}H_BKT} \right)^{\frac{T_C}{T+T_C}} \left(N_C \frac{C^0}{C^{\pm}} \right)^{\frac{T}{T+T_C}} \quad (2)$$

at relatively high light intensities. Here,

- T is the measurement temperature,
- T_C characteristic distribution temperature,
- G photocurrent generation rate,
- $E_C - E_{F_0}$ equilibrium Fermi level for electrons,
- H_B trap density,
- N_C state density in the conduction band,
- C^0 and C^{\pm} are trapping coefficients.

From the expressions (1) and (2) it follows that the photocurrent dependence on the light intensity at low illumination of the sample must be linear and at the relatively high light intensity the photocurrent is proportional to $G^{(T_C/T_C+T)}$. This is in accordance with our experimental data for polymerized acetonitril plasma films. Moreover, the calculated value of $(T_C/T_C + T) = 0,64$ is in a good agreement with the experimental value of lux-ampere characteristic slope in the high light intensity region at relatively low electrical field values. Consequently the obtained results are not in contrast to the previous thought that the distribution of traps inside the polymer band is of exponential character.

The obtained experimental data allow to define a number of important electrical-physical film parameters. So, from the $I = f(V)$ approximation in the region of the maximum trap filling up to the ohmic section, we can define the transition voltage value according to that of nontrapping material (Figure 2).

Hence the equilibrium carrier density value in the polymer can be defined at room temperature from an expression:

$$V_{tr} = \frac{8 n_0 d^2 e}{9 \epsilon \epsilon_0}. \quad (3)$$

With $V_{tr} = 0,04eV$, $d = 1,2 \cdot 10^{-6}m$, $\epsilon = 5,3$ we find that $n_0 = 9,2 \cdot 10^{18}m^{-3}$. Further assuming that in electrical fields corresponding to the ohmic section of $I = f(V)$ the dark current temperature dependencies are defined by the thermal carrier generation we can estimate the state density in the conduction band by the value of the conduction activation energy

$$N_C = n_0 \exp\left(\frac{E_C - E_{F_0}}{KT}\right)$$

at $E_C - E_F = 0,4eV$, $T = 300K$ and after substitution of n_0 we find $N_C \approx 5 \cdot 10^{25} m^{-3}$. Knowing the state density value we can define the total trap density in the polymer from [8, 9]:

$$H_B = \left(\frac{8}{9} N_C \right)^{\frac{1}{2}} \left(\frac{V_{TFL} \epsilon \epsilon_0}{ed^2} \right)^{\frac{\ell-1}{\ell}} \left(\frac{\ell}{\ell+1} \right) \left(\frac{2\ell+1}{\ell+1} \right)^{\frac{\ell+1}{\ell}}, \quad (4)$$

where V_{TFL} is the trap filled limit voltage and $\ell = T_C/T$.

By substitution of $N_C = 5 \cdot 10^{25} m^{-3}$, $\ell = 1,8$ and $V_{TFL} = 20V$ in Eq. (4) we obtain $H_B = 9,8 \cdot 10^{23} m^{-3}$.

From the experimental $I = f(V)$ and a value of equilibrium carrier density the carrier mobility in polymer n_0 can be estimated according to

$$\mu = \frac{I_d}{en_0V}, \quad (5)$$

which is $1,4 \cdot 10^{-9} m^2/V.s$. Such a low value of mobility is typical for polymerized plasma films.

One of the basic electrical-physical parameters of materials is also the quasi Fermi level value, which can be obtained from the conduction temperature dependencies at different applied voltages.

For the case of the exponential trap energy distribution, the quasi Fermi level depending on the charge accumulation coefficient and the applied voltage is defined by [8]:

$$E_{FV}(V) = kT_C \ln \left[\frac{(\ell+1)^2}{\ell(2\ell+1)} \cdot \frac{eH_B d^2}{\epsilon \epsilon_0 V} \right]. \quad (6)$$

The measurement results presented in Figure 8 are in good agreement with equation (6). In this case, the H_B value was chosen so that experimental data satisfy expression (6) at the corresponding voltage. This approximation gives $H_B = 2,9 \cdot 10^{24} m^{-3}$ at $V = 12V$ and satisfactorily agrees with the value $9,8 \cdot 10^{23} m^{-3}$ calculated from equation (4).

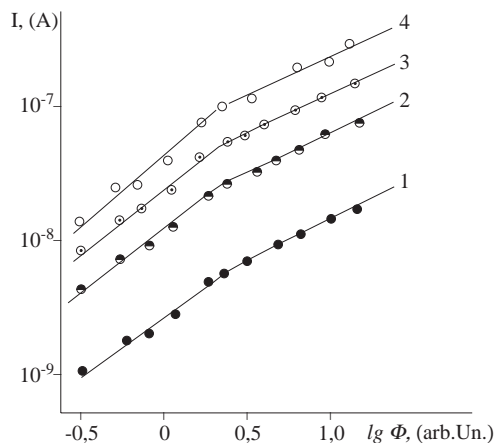


Figure 7. Light intensity dependencies of photocurrents in Au-Pol-Au system at different voltages: 0,1 V (1); 0,5 V (2); 1 V (3); 2 V (4). ($T = 300$ K)

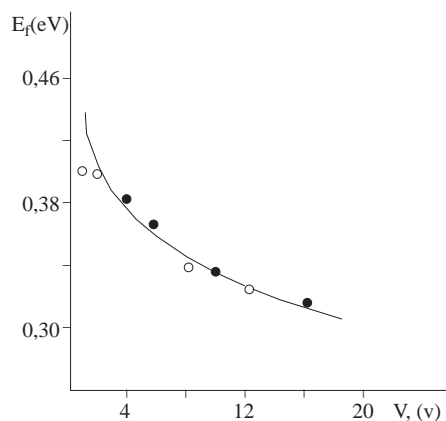


Figure 8. Voltage dependencies of the quasi-Fermi level in SCLC-condition

- injection from the Cu-electrodes
- injection from the Au-electrodes
- theoretical curve.

Thus the study of SCLC allows to define both the characteristics of the traps, the presence of which in films obtained by the glow discharge polymerization of acetonitril, as a rule, is difficult to avoid; and such important electrical-physical parameters of polymer as mobility and density of nonequilibrium charge carriers.

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