

STUDY OF ELECTRICAL TRANSPORT PROPERTIES IN THERMALLY ACTIVATED ELECTRETS IN PVP AND PMMA BLENDS

Devesh Ahirwar¹, P K Khare², Alkesh Pal³

^{1,2,3} Department of Postgraduate Studies in Physics and Electronics,

Rani Durgavati University, Jabalpur, M.P.

ABSTRACT

Mechanism of conduction in blend of PVP and PMMA in different ratios i.e. 100:0, 95:05, 90:10, 85:05 has been studied under the application of different temperature and fields. The conduction is presented in the form of current–voltage characteristics. The results were analysed on the basis of different existing theories i.e. Poole–Frenkel, Fowler–Nordheim, Schottky effects. It is observed that, Schottky–Richardson mechanism is mainly responsible for observed conduction in present study.

Keywords: Polymethyl Methacrylate (PMMA), Polyvinyl Chloride (PVP), Blends, Poole–Frenkel, Electrical conduction

I. INTRODUCTION

The study of electrical conductivity is an important aid in the investigation of conduction mechanism in the solids. The electrical conduction in polymeric dielectrics is mainly due to transportation of free charge carriers present in the bulk of the polymer and from a number of different conduction processes taking place simultaneously depending upon the experimental conditions. The structure of these materials is sensitive to their electrical, mechanical and thermal history so that the mode of conduction differs from polymer to polymer and the sensitivity of measurement is different for different materials. When a polymer is subjected to different conditions, they often undergo structural transitions making carrier generation and transport phenomenon more complicated.

II. EXPERIMENTAL DETAILS

Circular specimens of pure PMMA, PVP and PMMA : PVP blend, having wt% ratio of 100:00, 95:05, 90:10, 85:15 and 80:20 about 50 μm in thickness obtained from solution grown method in which a clean glass plate which was floating on a mercury pool. Firstly the desired weight percentage ratio of PMMA and PVP was dissolved in DMF. Then this mixture was dissolved thoroughly using magnetic stirrer till a homogeneous solution is obtained. Obtained solution was then spread on glass plate floating on mercury pool stated above.

This mercury pool was then kept in thermostat oven so that solvent can evaporate and a thin film is obtained. Thereafter this film was slowly removed from glass plate. These obtained films were used in the present investigation.

The electrical conduction currents were measured at fields of 50, 70, 90 and 110 kV/cm and temperatures 60 to 90°C in steps with the help of electrometer. Temperature of the sample was recorded with the help of a thermometer fitted in the thermostat.

The procedure adopted for the measurement was as follows. The specimen was sandwiched between the two metallic electrodes of the sample holder kept inside a thermostat. The temperature in the thermostat was maintained at the desired value for 30 min without applying field. It was considered that the thermal equilibrium was achieved during this duration. The desired field was now applied for 30 min. after which the specimen was cooled in equal steps under the application of field and at each temperature steady state value of the current was recorded. The procedure was repeated for different fields and temperatures. The above process is known to eliminate displacement current and hence only the conduction current was recorded.

III. RESULT AND DISCUSSION

Electronic conduction may be due to motion of free carries, electrons in the conduction band and holes in the valence band or alternatively due to the motion of quasi localized carriers which are otherwise described as hopping of bound carriers between localized sites in the dielectric [1]. The former process requires activation energy in order to excite a carrier into the relevant band this energy can normally be supplied thermally or by other free carriers which have acquired a high energy in an electric field, leading to an avalanche process. The activation energy may be affected by electric field as in the case of Poole - Frenkel effect [2]. The hopping process requires less energy than the activation into the free band and this energy may, in the limit of very high density of localized centers, tend to zero as in the case of impurity band conduction in semiconductors [3]. This process is favored in the case of heavily disordered solids, such as amorphous and glassy dielectric films.[4].

Some dielectrics show a region of linear current voltage characteristics i.e. ohmic conduction at low fields [5] especially at elevated temperatures, although more of them in this region cannot be seen at the limit of detection. It is difficult to establish conclusively whether ohmic conduction is due to ionic or electronic processes but ionic conduction would appear more likely.

In interpreting the properties of dielectric films, one frequently employs concepts taken over from the physics of crystalline media. In this way one refers to trapping levels and donor and acceptor levels at discrete energy values. One speaks of energy barriers due to ionized impurities and, in the case of Poole-Frenkel effect one employs the model of hydrogenic impurities in which the bound electron is characterized by a definite effective mass and a ground state orbit of a diameter corresponding to several inter-atomic spacing. These concepts may be valid to a greater or lesser extent in the case of poly crystalline and micro crystalline film, although

allowance may have to be made for the presence of interfacial barriers. It would be very difficult to justify their use in application to amorphous and glassy films. It is appropriate to recall here the salient feature of the theory of amorphous conductors as it applies to dielectric film. The general consensus of opinion is that the basic feature of the band structure, such as the width of forbidden gap, are determined primarily by the short-range order i.e., by the relative disposition of the nearest neighbors in the solid. Since these dispositions are similar in amorphous and crystalline solids, the broad features are preserved on transition from crystalline to amorphous structure. The disappearance of medium and long range order does influence the detailed shape of the band structure: however in that case it cause a considerable blurring of the edges of the conduction and valence bands, and gives rise to a distribution of deep localized levels in the forbidden gap.

In the crystalline solid, there exists a clear distinction between the propagating bands- conduction, valence and forbidden. In the former the carriers propagate freely except for collision on thermal vibrations and other lattice imperfections which determine a mean free path which is greater, usually considerably greater than the lattice spacing. In the forbidden gap, the energy levels that may exist due to imperfections are strictly localized and an electron has to be excited from one of these levels to conduction band before being able to move on. Special cases arise when the localized levels are spaced so closely that their wave functions overlap and give rise to the formation of the so called impurity band, leading to metallic properties with zero activation energy. Alternatively, the spacing may not be as close as is necessary for the formation of an impurity band, but sufficient for photonassisted tunneling between neighboring centers, the so called hopping conduction. Hopping is characterized by an activation energy which is only a fraction of the normal ionization energy of the carrier form the centre into the band and is often accompanied by rather complicated frequency dependence.

The significance of the blurred band edges is that there is no sharp distinction between the propagating and forbidden gap but instead partly localized levels are formed leading to conduction by a process intermediate between impurity band and hopping conduction in which the propagation of carrier is characterized by a small mobility.

Poole- Frenkel mechanism is frequently invoked in the interpretation of electric current in dielectric films at reasonable high electric fields. The physical basis of Poole- Frenkel mechanism is analogous to the Schottky emission. O' Dwyer [6] in a theoretical paper considers an electronic model of dielectric with traps with Schottky emission from an injecting electrode and with Fowler- Nordheim correction for tunneling through the top of the barrier at high fields. In a recent review of Poole- Frenkel mechanism, Simmons [7] points out that experimental data apparently favouring the Schottky mechanism can be made more compatible with Poole- Frenkel mechanisms if it is postulated that shallow neutral traps are present in the dielectric together with deep lying donors. Franks and Simmons [8] consider further the effect of space charge on Poole- Frenkel process.

Struik [9] showed that solid like polymers are not in thermodynamic equilibrium at temperatures below their glass transition. For such materials, free volume enthalpy and entropy are greater than those they would be in

the equilibrium state. The gradual approach to equilibrium affects many properties for example; free- volume of the polymer may be decreased. The decrease in free volume lowers the mobility of chain segments and also charge carriers such as ions and the decrease in mobility may be expected to reduce DC conductivity. At higher electric field, the change in mobility may take place faster than that at lower fields and also recombination of charge carriers may move.

A consequence of the phenomenon of carrier injection is the formation of a space charge cloud [10] of carriers in the vicinity of contacts. Mutual repulsion between the individual carriers limits the total injected charge in the film and resulting current in said to be space limited trapping sites reduce the magnitude of current. The mobile charge carriers are continually interaction with the lattice, Athermo dynamical equilibrium is maintained between the space charge and lattice so that there is a special relationship between the electric field and the drift velocity of the carriers. The trapping sites accentuate this difference even further. Holes or electrons can be injected according to the choice of electrode material [11]. This then brings in the added complication of recombination.

When the voltage the applied at electrodes it will try to sweep the free carriers through the sample towards the electrodes. During this process some of the carriers may have to cross very close to some of the unfilled traps and more trapping may take place because of this motion. Thus increasing field could accelerate the rate of trapping and this cause a fall in the number of free carriers available for conduction. Thus an increase in applied voltage may lead to cause some decrease in the conductivity of samples. Sub linear dependence of current on applied field, seems to indicate that there is a decrease either in the number of charge carriers and/or their mobility with increasing field and temperature. In the present investigation polyblends can be expected to have a high density of traps. Under equilibrium conditions, some of these traps may get filled while others may remain empty. The number of trapping sites may increase as the temperature of the sample is increased because PMMA and PVP may have different thermal expansion coefficient. Increase of PVP content in the blends may increase number of trapping sites.

Figures 4.1-4.6 represents the isothermal I-V characteristics for pure PMMA, PVP and their polyblend samples respectively. The increment in the current is approximately the same for whole range of temperatures. The nature of the thermogram is non linear but similar for all temperatures. The curves show two distinct regions with different slopes.

It is observed from the current- voltage characteristic curves that two regions of conduction, i.e., ohmic conduction with slope (m value) of curve ≈ 1 at lower field (50 kV/ cm) and a non- ohmic conduction with slope ≈ 1.9 at higher field are observed. The ohmic behaviour can be understood on the basis of the reasonable assumption that at lower fields, there is negligible injection of carriers from the contacts and the initial current is governed by the intrinsic free carrier in the material. The current will be ohmic until injected free carriers density becomes comparable with the thermally created carrier density. The charge carriers have thermal

velocity (V_t) due to thermal agitation. When an electric field is applied across the sample, it produces a drift velocity (V_d) of the charge carriers. Therefore, the resultant velocity is given by $V = V_t + V_d$. At low fields, V_d is less than V_t . Thus, current is proportional to applied field. With the growth of the field, V_d approached V_t and resultant velocity becomes dependent on the field. In this case, we have the relation $J = \sigma_0 E(1 + \beta E^2)$ which shows a deviation

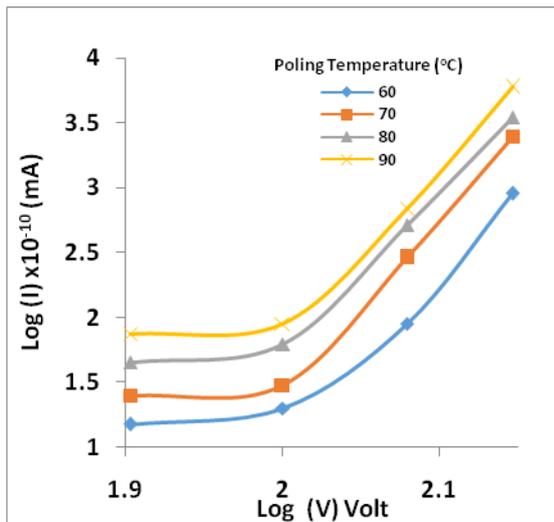


Figure 4.1 : Log I vs Log V plots for PMMA at various temperatures (i.e. 60, 70, 80 and 90 °C).

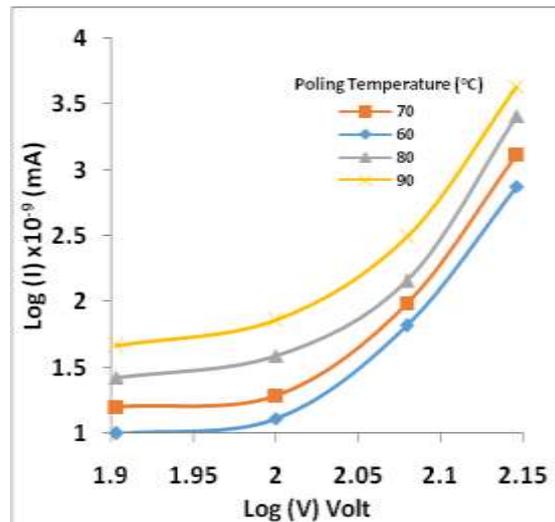


Figure 4.2 : Log I vs Log V plots for PVP at various temperatures (i.e. 60, 70, 80 and 90 °C).

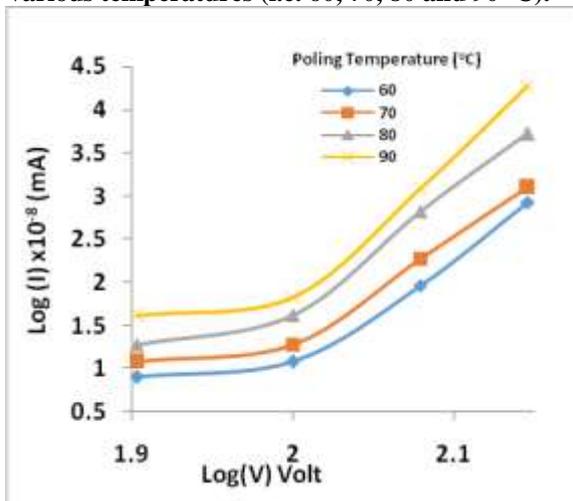


Figure 4.3 : Log I vs Log V plots for 95:05 blend samples at various temperatures (i.e. 60, 70, 80 and 90 °C).

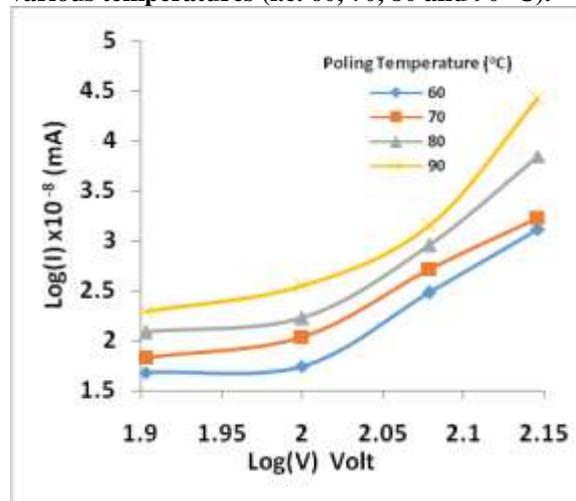


Figure 4.4 : Log I vs Log V plots for 90:10 blend samples at various temperatures (i.e. 60, 70, 80 and 90 °C).

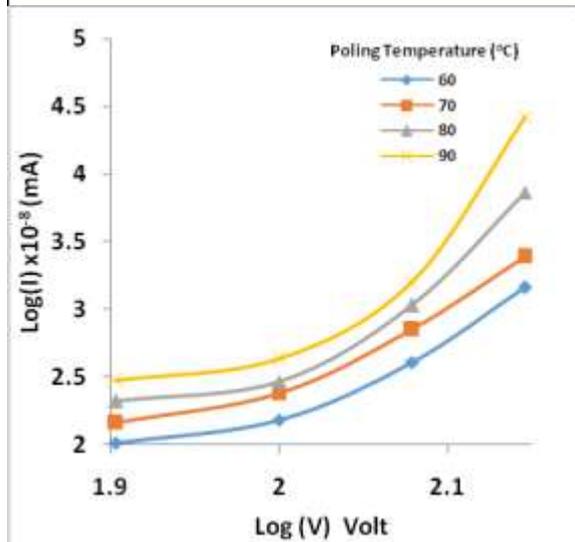


Figure 4.5 : Log I vs Log V plots for 85:15 blend samples at various temperatures (i.e. 60, 70, 80 and 90 °C).

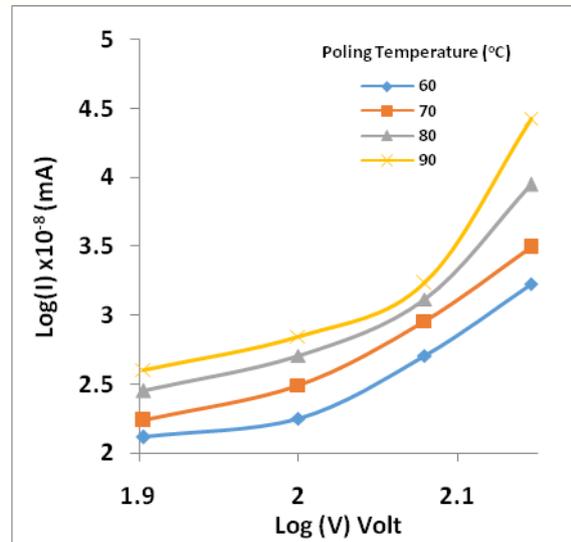


Figure 4.6 : Log I vs Log V plots for 80:20 blend samples at various temperatures (i.e. 60, 70, 80 and 90 °C).

from ohms law. The defects and impurities can govern the conduction mechanism and also act as trapping centers and get populated by injected charge carriers from the electrodes. Charge carriers from these localized levels are thermally excited to their respective transport bands causing thermally activated ohmic conduction. Depending upon the population of these levels and their respective transport bands conduction may change from ohmic to Schottky emission. Other possible mechanisms are (a) charge carrier injection into the film from the electrode contact via field assisted lowering of the metal insulator- potential barrier, i.e., Schottky- Richardson (SR) emission, and (b) release of charge carriers from traps via field assisted lowering of trap depth, i.e., the Pool- Frenkel (PF) effect which is a bulk effect.

The PF mechanism assumes that once the carriers are thermally activated from their trapping sites with the assistance of the field, they are free to move un-obstructively within the conduction band of the insulator. However, the concept of un-obstructive motion of charge carriers is incompatible due to low mobility of charge carriers involved in the case of polymeric dielectric. According to Jonscher and Ansari [12] the conduction in polymeric dielectrics with low mobility charge carriers should be interpreted as conduction by localized charge carriers performing hopping like motion between the localized states. The presence of a large number of localized traps both above and below the Fermi level has been justified on the ground that the polymeric system contains a large number of structural disorders.

The PF and RS mechanisms (for a plane electrode) result from the lowering of a coulombic potential barrier by an applied electric field. The Schottky effect is associated with the barrier at the surface of a metal and semiconductor. The PF effect is associated with the barriers in the bulk of a material. Donor sites, acceptor sites and traps as well as electrons in the valance band experience the PF effect [13]. For a trap to experience the effect, it must be neutral when filled and positive when empty [14]. A trap that is neutral when empty and charged when filled will not experience the effect because of the absence of the Coulomb.

The current voltage relationship for SR emission is given by [15]

$$I = AST^2 \exp \left[-\frac{\varphi_s}{kT} + \beta_{SR} V^{\frac{1}{2}} \right] \quad \dots (4.20)$$

where β_{SR} is field lowering constant.

Although the restoring force in both effects is due to Coulomb interaction between the escaping electron and a positive charge, they differ in that the positive image charge is fixed for PF barriers but mobile with Schottky emission [16]. This results in a barrier lowering twice as great for the PF effect i.e.

$$\Delta\varphi_{PF} = \left(\frac{\epsilon^3 E}{\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}} = \gamma_{PF} E^{\frac{1}{2}} \quad \dots (4.21)$$

$$\Delta\varphi_S = \left(\frac{\epsilon^3 E}{4\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}} = \gamma_S E^{\frac{1}{2}} \quad \dots (4.22)$$

where, $\gamma_{PF} = \left(\frac{\epsilon^3}{\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}}$ and $\gamma_S = \left(\frac{\epsilon^3}{4\pi \epsilon \epsilon_0} \right)^{\frac{1}{2}}$, $\Delta\varphi_{PF}$ and $\Delta\varphi_S$ are the barrier lowering for PF and RS emissions respectively.

These effects are governed by equations of the form-

Pool-Frenkel-

$$J_{PF} = \mu n_o E \exp \left[-\frac{\varphi_{PF} - \Delta\varphi_{PF}}{kT} \right] \quad \dots (4.23)$$

Schottky-

$$J_{RS} = AT^2 \exp \left[-\frac{\varphi_s - \Delta\varphi_s}{kT} \right] \quad \dots (4.24)$$

where, μ is the carrier mobility in the insulator and n_o is the carrier concentration.

Two distinct regions of ohmic and non ohmic conductivities can be seen and they indicate different slopes at lower and higher temperature regions and therefore, different associated thermal activation energy in two regions. The increase in the conductivity at higher temperature region can be due to the softening of the substance, and because of this the injected charge carriers can drift more easily into the volume to dielectric. This gives rise to a large current (conductivity) at higher temperature. According to O' Dwyer, there exist shallow traps of low energy range (ΔW) and deep traps of higher energy range (W) in the sample. The shallow traps exist the continuum of free levels, while deep traps are between conduction band and valance band. At

sufficiently low temperature electrons are trapped at deep traps but with increase in temperature they get excited and leave the deep traps to enter into shallow traps or conduction band. Conduction under the influence of applied electric field, the low value of activation energy (< 1 eV) is indicative of predominance of electronic conduction in the present case.

In the presence of an applied field, the potential barrier is lowered by an amount

$$\Delta\varphi_s = \left(\frac{\epsilon^3 E}{4\pi\epsilon\epsilon_0} \right)^{\frac{1}{2}} \quad \dots (4.26)$$

The polymer blend is a heterogeneous mixture and as such it has a very large number of trapping sites [17]. It seems that at lower charging temperatures, only shallow traps are involved which get emptied at different temperatures. As the temperature raises deeper traps gets involved. The trapping of charge carriers (holes and electrons) in the deep trap levels may lead to induced dipole formation. The conduction below T_g takes place by thermal activation of carrier from one disordered state to another. Beyond T_g , the traps are immobilized because of segmental chain motion or entire chain motion. Hence current and conductivity show a jump. In polyblends, intermolecular interaction will lead to considerable increase in ionization of dipoles and the traps associated with these ionized species. Therefore, the effect of these traps in the charge carrier generation and transport is so effective that PF mechanism is masked and SR mechanism is predominated in the polyblends at higher temperature.

IV. CONCLUSION

After studying electrical condition through pure and polyblend samples under various existing mechanism it is observed that at lower value of fields, ohmic conduction prevails but due to structural disorder charge present at trap level in the bulk of the insulator develops deviations from ohmic conduction. The behaviour of pure PMMA, PVP and polyblends samples can be closely described by both SR and PF mechanism. Fowler-Nordheim mechanism is not operative. It seems that trapping sites created by the dipoles of individual polymer are responsible for PF mechanism. In polyblend, intermolecular interaction will lead to considerable increase in the ionization and the traps associated with these ionized species. Therefore, the effect of traps in the charge carrier generation and transport is so effective that PF mechanism is masked and SR mechanism is predominated in the pure and polyblends at higher temperature.

REFERENCE

- 1 Scher H. and Montroll F. W., Anomalous transit-time dispersion in amorphous solids, Phys. Rev., **B12** (1975) 2455.
- 2 Frenkel J, On Pre-Breakdown Phenomena in Insulators and Electronic Semi-Conductors., Phys. Rev. Lett., **54** (1938) 647.

- 3 Grunewald M. and Thomas P., A hopping model for activated charge transport in amorphous silicon Phys. Stat. Sol. (b), **9** (1979) 125.
- 4 Beyer W., Fischer R. and Overhof H., Transport in lithium-doped amorphous silicon, Phil. Mag, **39** (1979) 205.
- 5 Sakamoto H. and Yahagi K., Relation between Electrostatic Capacity of Polyethylene and Electronic Space Charges Induced by High Field Application, Jpn. J. Appl. Phys., **17** (1978) 1959.
- 6 O'Dwyer, J. C., Current- Voltage Characteristics of Dielectric Films, J. Appl. Phys., **37** (1966) 599.
- 7 Simmons J. G., Poole-Frenkel effect and Schottky effect in metal-insulator-metal systems, Phys. Rev., **166** (1968) 912.
- 8 Frank R. I. and Simmons J.,
- 9 Space- Charge Effects on Emission- Limited Current Flow in Insulators, J. Appl. Phys., **38** (1967) 832.
- 10 Struik L. C. E., Physical Aging in Amorphous Polymers and Other Materials, Elsevier, Amsterdam, 1978.
- 11 Shatzkes M., Injection into insulators in the presence of space charge, J. Appl. Phys., **49** (1978) 4868.
- 12 Takai Y., Osawa T., Chikao K., Mizutani T. and Ieda M., Effects of Electrode Materials on Photocurrents in Polyethylene Terephthalate, Jpn. J. Appl. Phys., **14** (1975) 473.
- 13 Jonscher A. K. and Ansari A. A., Photo-currents in silicon monoxide films, Phil. Mag., **23** (1971) 205.
- 14 Mead C.A., Electron Transport Mechanisms in Thin Insulating Films, Phys. Rev., **128** (1962) 2088.
- 15 Simmons J. G., Poole-Frenkel Effect and Schottky Effect in Metal-Insulator-Metal Systems, Phys. Rev., **155** (1967) 657.
- 16 Chybicki N., Electrical properties of metal-polymer-metal (MPM) and metal-polymer-silicon (MPS) structures with thin polymer films, Phys. Stat. Sol. (a), **39** (1977) 271.
- 17 Hall R. B., The Poole-Frenkel effect, Thin Solid Films, **8** (1971) 263.
- 18 Perlman M.M.(Ed.), Electret storage and transport in dielectric, Electrochem. Soc., Perston, 1973.