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Mechanisms of Conductivity in Metal-Polymer-Si Thin Film Structures

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Thin film structures of the metal-polymer-Si type have been fabricated. The current-voltage characteristics of these structures versus temperature have been measured and analyzed. The results obtained are treated within such models of charge transport as the Schottky thermionic emission, Pool-Frenkel and hopping mechanisms. The preliminary conclusions about the basic mechanisms of charge transport have been made. The charge carriers transport is explained by the Schottky thermionic emission in the case of the metal-polymer interface and the hopping mechanism in a polymer.

Keywords: charge transport; current-voltage characteristic; poly(diphenylene-phthalide)

INTRODUCTION

For last thirty years, new polymer materials with electrical conductivity coming nearer to the conductivity of metals were discovered. Polyacetylene started the investigation in the area of conducting polymers [1]. The discovery was a beginning for the fabrication of various electronic devices on the basis of polymer films, such as sensors, polymer batteries, electroluminescent and Schottky diodes, organic transistors, etc. The

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manufacture of various multilayer film structures based on silicon and polymers [2] and the investigation of the electrical properties of polymers and the mechanisms of charge transfer in them remain as the actual problems.

The authors [3–5] have observed the transitions from the dielectric state to a high-conductivity state (HCS) induced by such abnormally low external influences as an uniaxial mechanical pressure and an electric field or temperature, in thin polydiphenylenephthalide films. The feature of this phenomenon is that the temperature dependence of the HCS conductivity is of the metal type, and the conductivity can be extremely high ($>10^5$ $(\Omega\cdot cm)^{-1}$). The transition takes place in the wide-gap organic dielectric with a band gap of ~ 4.3 eV, and the mechanism of the band structure transformation is unknown till now.

The questions concerning the definition of conditions of the conductive state origin in thin films of a wide-gap polymer dielectric, the relaxation of an excess charge, and mechanisms of its transport represent a large interest from the fundamental and practical points of view. These questions remain the least explored at present. The aim of the present work is to study the conductivity mechanisms in thin polymer films which are included into silicon-based heterostructures.

EXPERIMENTAL

The used samples were of the silicon–polymer–metal "sandwich" type structure, and the polymer/Si junction was investigated. Poly(diphenylenephthalide) (PDP) was used as a polymer. PDP has good film-forming properties on the metallic and silicon substrates. It was shown that PDP can form 0.02–10-μm-thick continuous homogeneous films under certain technological conditions. In addition, the PDP conductivity has no temperature singularities up to the softening point (360°C in air). In the dielectric state, PDP has the following parameters: the energy band gap is 4.3 eV, and the first ionization potential is 6.2 eV; i.e. this is a typical wide-gap organic dielectric. Thin homogeneous polymer films were prepared by the spin coating of a polymer solution on the p-Si wafer surface with the naturally formed layer of silicon oxide. The thickness of this layer is about 2 nm, and its influence on the experimental results is not revealed. After spinning, the samples were immediately thermally dried for 3–4 h before the deposition of the electrode. The top electrode was made by vacuum evaporation of Cu to ensure a good conductance. The metallic electrode was deposited through a mask onto the polymer film surface by vacuum evaporation. The thickness of the films was set by the solution concentration and checked by the interference method with an MII-4

interferometer. It ranged from 0.6 to 1.2 μm. The dc measurements were performed using a controlled current source ANT-1533. The current-voltage (*I-V*) characteristics were recorded with a digital oscilloscope GDS-820C linked to a computer through a standard interface. In the forward bias, the Cu electrode was wired as the cathode.

The measurements of the temperature-dependent *I-V* characteristics were carried out on a setup that consisted of a liquid-nitrogen cooled cryostat, temperature controller, temperature sensor as a

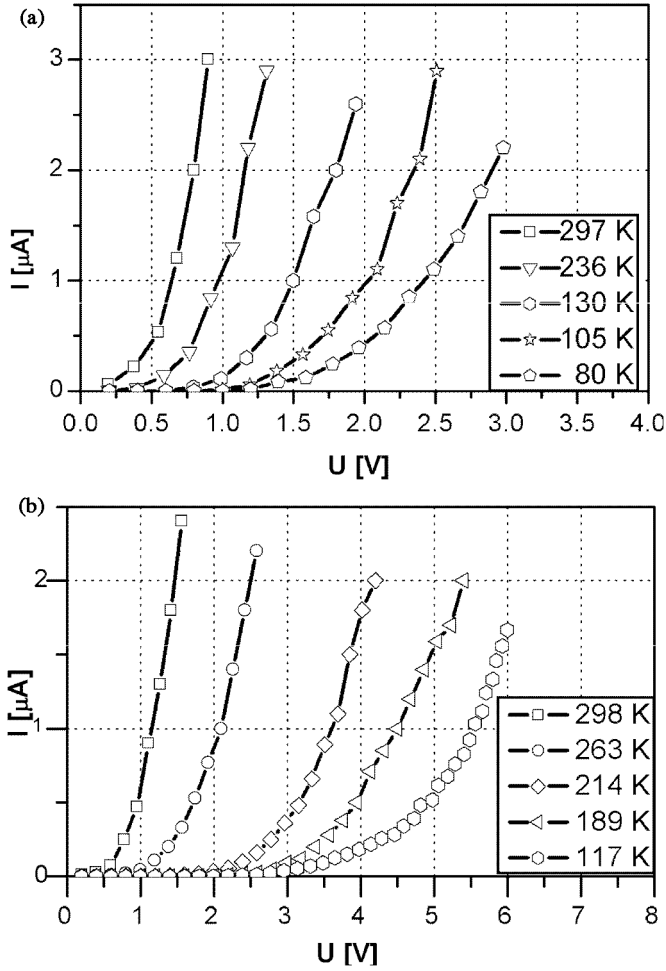

FIGURE 1 (a) Forward and (b) reverse current-voltage characteristics of the samples (the insets show the temperature values).

thermoelectric couple, and an electrical circuit to record the *I-V* characteristics. The temperature was varied between 90 and 300 K.

RESULTS AND DISCUSSION

The forward *I-V* characteristics are presented in Figure 1a. The forward current is defined with positive bias applied to the p-Si substrate relative to the Cu top electrode. Figure 1b illustrates the typical *I-V* characteristics in the case of reverse current. In both cases, we have the nonlinear *I-V* characteristics. The reverse current is smaller by more than one order of magnitude in comparison with the forward current.

The conductance of the polymer film (ln (I/U) vs. inverse temperature $(1000/T)$ is explored and shown in Figure 2. The dependences of the current on the inverse temperature carry the exponential character with different energies of activation on various sites (see Table 1). The analysis of the curves allows us to assume, what kind of the charge transport mechanism predominates in various temperature ranges.

Apparently, the current connected to Schottky thermionic emission acts as the basic component at high temperatures (above 200 K). To confirm this assumption, the dependences in the coordinates ln $(I/T^2) - 1000/T$ were constructed (see Fig. 3). Really, the Schottky emission is described by the equation [6].

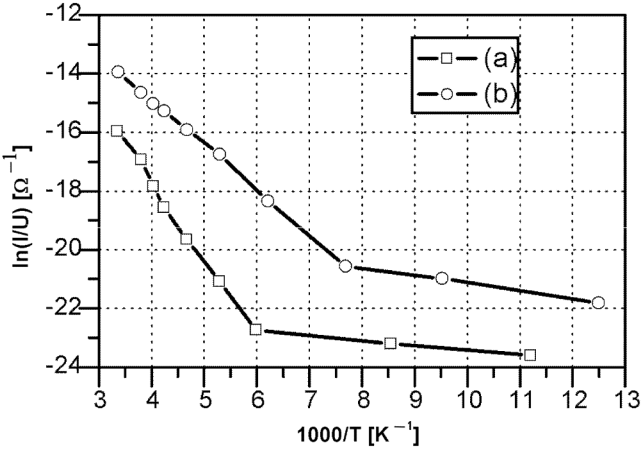

FIGURE 2 Conductance of a polymer film (ln (I/U)) vs. inverse temperature $(1000/T)$: the top curve for forward currents and the bottom curve for reverse currents.

TABLE 1 Activation Energy at Different Temperatures

T (K)	300–160	300–130	160–90	130–90
E_a (eV) for reverse current	0.24	–	0.01	–
E_a (eV) for forward current		0.13	–	0.02

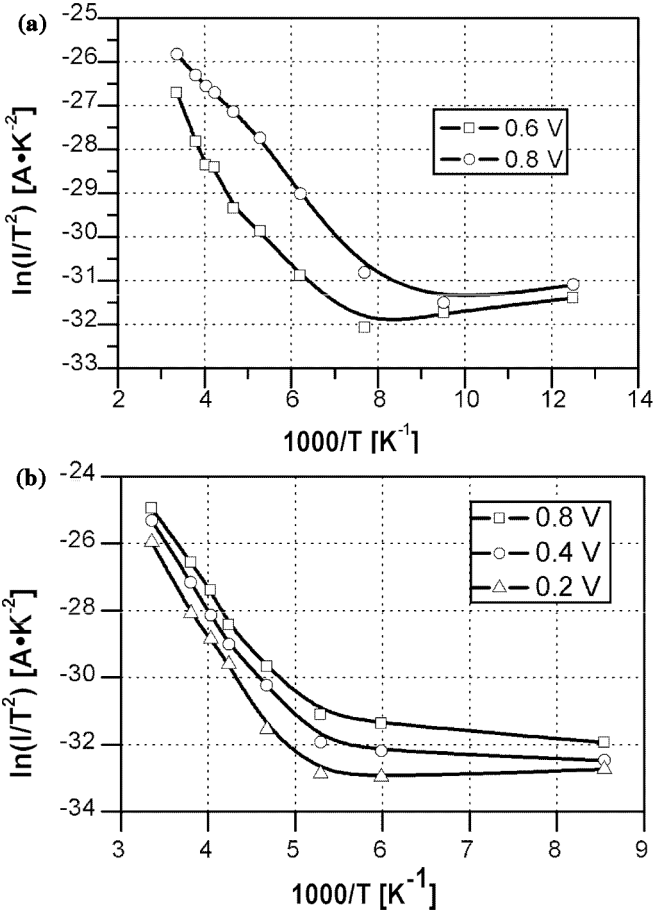

FIGURE 3 Schottky plots: (a) for forward and (b) reverse currents, a good fit is seen above the temperature of 200 K (the inset shows the voltage values).

$$J = A^* T^2 \exp\left[\frac{-q(\varphi_B - \sqrt{qF/4\pi\varepsilon\varepsilon_0})}{kT}\right],$$

where J is the current density, A^* is the Richardson constant, φ_B is a barrier height, F is the applied electrical field, ε is the relative permittivity, and ε_0 is the dielectric constant.

The high-temperature asymptotes result in energy barriers of 0.32 and 0.35 eV, respectively, at the applied voltages of 0.8 and 0.2 V, for reverse currents. For forward currents, the energy barriers are

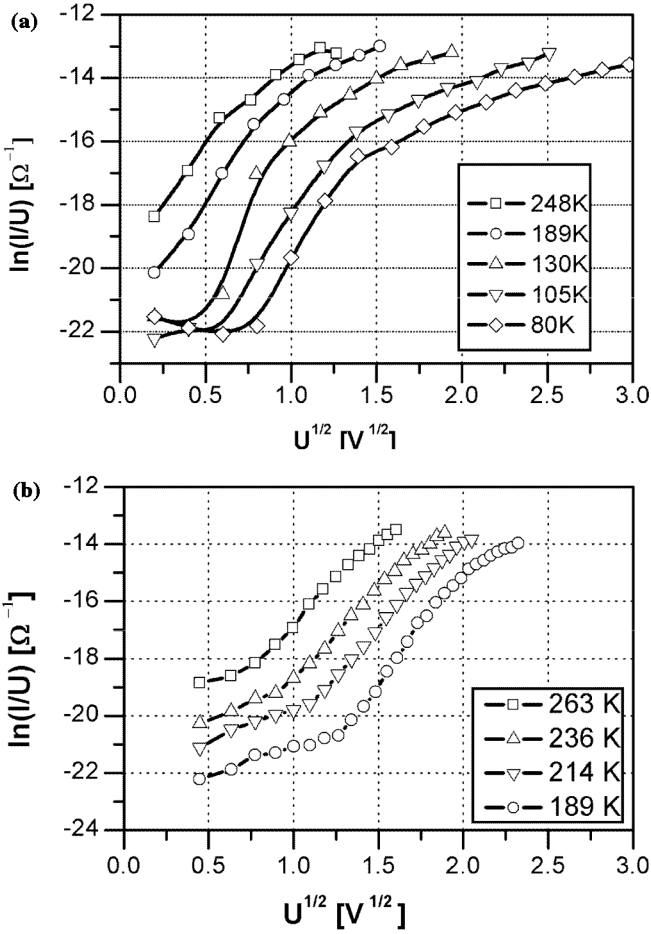

FIGURE 4 Pool-Frenkel plots: (a) for forward and (b) reverse currents, a good fit is seen at medium voltage values (the inset shows the temperature values).

less than those for reverse currents and equal 0.135 and 0.145 eV, respectively, at the applied voltages of 0.8 and 0.2 V. These values are comparable with the activation energies for the temperature interval 300–200 K (see Table 1).

The electron jumps between the localized states near the Fermi level (E_F) will be of importance in the low-temperature region. In this case, the dependence of the electrical conductivity on temperature looks like: $\sigma \sim \exp(-E_a/kT)$, where E_a is the activation energy of a jump. In our films, $E_a = 0.01$–0.02 eV. According to Mott [7], the temperature dependence in this case should have the form: $\sigma \sim \exp(-B/T^{1/4})$, but it was difficult to test this relation in the restricted low-temperature range investigated here.

Besides its temperature dependence, the hopping transport is also characterized by the electrical field dependence conductivity. To find out the features of charge transport, the dependences of the films conductance $\ln(I/U)$ vs. $U^{1/2}$, i.e., in the Pool-Frenkel coordinates, are also constructed (see Fig. 4). The calculation gives value $\beta_{PF} = 4.17 \cdot 10^{-4}$ eV $(\text{cm/V})^{1/2}$ within the framework of the Pool-Frenkel model. The values β obtained from our plots have the following values: $6.0 \cdot 10^{-4}$ eV$(\text{cm/V})^{1/2}$ for reverse currents and 3.5–$9{,}5 \cdot 10^{-4}$ eV$(\text{cm/V})^{1/2}$ for forward currents at various temperatures. As is visible, the experimentally found values β differ from β_{PF}. For the explanation of these distinctions, we have involved the hopping model with a Gaussian distribution of localized levels [8–9], according to which $\ln \mu \sim F^{1/2}$.

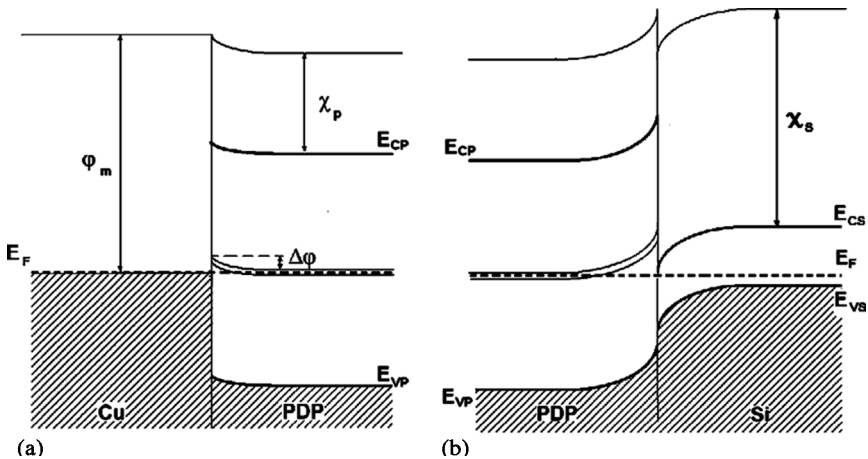

FIGURE 5 Energy-level diagram of the metal-polymer interface.

It is possible to explain the results of this work from that fact, that a wide-gap polymer was used as a transport layer of the investigated structures. The application of a wide-gap polymer does not allow us to explain the calculated values of activation energies by the charge transfer above a barrier. In this case, the barrier height should be equal to 1–2 eV. Apparently, the barriers are formed on the metal-polymer boundary (see Fig. 5a) in such a manner that their height $\Delta\varphi$ is not determined by a relation between the work function of a metal φ_m and the energy of an electron affinity of a polymer χ. The value of $\Delta\varphi$ is the difference between the energy of the contacting electrode Fermi level and the energy of trapping levels which are formed near the middle of the forbidden gap of a polymer. The occurrence of these levels is stipulated by that the excess charge in a polymer can create deep trapping states by the mechanism described in [10]. The narrow band of trapping states can be formed near the Fermi level as a result of the process indicated above that confirms the data published in [11].

Thus, the experiments performed in the given work allow us to make preliminary conclusions about the basic mechanisms of charge transport in various electric field and temperature intervals. In our samples, the charge carriers transport is explained by the Schottky thermionic emission in the case of a metal-polymer interface and the hopping mechanism in a polymer.

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