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Abstract

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ON THE CONDUCTIVITY OF FILMS OF A POLYMERIC COMPLEX OF TETRACYANOETHYLENE WITH METALS

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In works (^{1,2}) it was shown that films of the polymeric complex of tetracyanoethylene with various metals exhibit a semiconductor dependence of resistance on temperature. The effective dielectric constant and the resistivity of films of the polymeric complex of tetracyanoethylene (TCNE) depend on the frequency of the alternating current at which the measurements are made and on the magnitude of the dc voltage simultaneously applied to the film. The mechanism determining this behavior of the polymer films apparently reduces to the following. When an alternating field is applied to the film, not all electrons participate in through conduction, but only those among them that possess energy sufficient to overcome the barriers between macromolecules. Electrons with lower energy participate only in local displacements under the action of the field. In this process polarization occurs in that part of the medium in which these displacements are confined. Charge transfer between individual macromolecules has the character of jumps, analogous to the mechanism first proposed by Verwey for ferrites (^{3}). This is true irrespective of whether the barriers constitute a separate phase in a substance with a heterogeneous structure, or whether they are of a purely virtual character.

In the present work we attempted to compare a model of a heterogeneous structure (^{4,5}) with the experimental results obtained for the films. The model assumes that the film consists of at least two "kinds" of polymer. The better-conducting layers or grains of the main substance have a resistivity ρ_1 with an activation energy of conductivity ΔE_1. The material of the thin interlayers separating the well-conducting layers has a resistivity ρ_2 with an activation energy ΔE_1. The thickness of the barriers is much smaller than the thickness of the layers of the main substance, and $\Delta E_2 > \Delta E_1$, as is always observed experimentally when $\rho_2 \gg \rho_1$. The dielectric constant ε of both layers is assumed to be the same.

In this case $C_2 \gg C_1$, $R_2 \gg R_1$ and, consequently, $\tau_2 \gg \tau_1$, where C_1 and C_2 are the capacitances of the main substance and of the interlayers, R_1 and R_2 are the resistances of the main substance and of the barrier material, and $\tau = RC$. The capacitance and resistance of such a system depend on frequency. As the frequency is increased, the barrier layers become short-circuited, and the dielectric properties of the main substance are manifested. At low frequencies, increased values of the dielectric constant should be observed owing to the appearance of charge at the boundaries between grains.

In accordance with the model, films of the polymeric complex with metals exhibit a high effective dielectric constant. Thus, for example, for films on iron its value is 50–70, while on aluminum it reaches 1000 at a frequency of 5 kHz. When the frequency of the alternating current is increased, charge at the interface does not have time to form, and the effective dielectric constant tends toward its true value. The conductivity increases owing to an increase in losses.

As the model requires, the resistance and the effective dielectric constant of the films decrease with increasing frequency of the alternating current.

Figure 1, 1 presents the dependence of the resistance of a polymer film on iron on the logarithm of the frequency. When a constant voltage of 1 V, 0.5 V (curves 2 and 3) is applied, the character of the frequency dependence is preserved. It is also seen from the figure that the resistance depends very strongly on the applied constant voltage at low frequencies, when the barrier parameters are measured.

(Figure: Fig. 1 and Fig. 2)

Fig. 1. Dependence of the resistance of a film on iron on the logarithm of the frequency at voltages of 0 V (1), 0.5 V (2), and 1 V (3) (resistance in arbitrary units)

Fig. 2. Dependence of the specific resistance of a film on aluminum on the applied voltage at temperatures from 60° (upper curve) to 200° (lower curve)

This effect, proceeding from the model, should be observed if the resistance of the barriers is considerably greater than the resistance of the grains of the main substance, and the thickness of the barriers is small in comparison with the thickness of the main substance. In this case almost all of the constant voltage applied to the film falls across the barriers. Because of the large field strength in the barriers, the resistance of the interlayers decreases owing to the Poole effect, which is what is observed at low frequencies. As the frequency is increased, when the resistance of the barriers is shorted by their large capacitance, the resistance of the grains of the main polymer appears; because of the small field strength in the grain, it is almost independent of the constant voltage applied to the film.

It follows from the model that, with increasing temperature, the resistance of the barriers decreases faster than the resistance of the main substance ($\Delta E_2 > \Delta E_1$). In direct current or at low frequencies, when mainly the resistance of the barriers is measured, the specific resistance of the film should depend less and less on the applied constant voltage as the temperature is raised, since an ever smaller part of the applied constant voltage falls across the barriers.

Figure 2 illustrates the dependence of the specific resistance of a film on aluminum on the applied voltage at different temperatures. The upper curve, obtained at a temperature of 60°, reveals a substantially stronger dependence of the resistance on the applied voltage,

than the lower one, taken at 200°. From the adopted model it follows that, when a constant voltage is applied to a film measured at low frequencies, one should observe not only a decrease in the resistance of the barriers, but also a change in the activation energy of conduction, which can be estimated according to the formula:

$$R = R_0 e^{\frac{\Delta E - \frac{eV}{2n}}{KT}}, \tag{1}$$

where R is the resistance of the sample, ΔE is the activation energy of conduction, V is the voltage applied to the film, and n is the number of barriers.

(Figure: Fig. 3. Dependence of the specific resistance of a film on aluminum on reciprocal temperature at a frequency of 400 Hz. 1 –0 V, 2 –1 V)

Fig. 3. Dependence of the specific resistance of a film on aluminum on reciprocal temperature at a frequency of 400 Hz. 1 –0 V, 2 –1 V

(Figure: Fig. 4. Dependence of the specific resistance of a film on aluminum on reciprocal temperature at different frequencies. 1 –20 Hz, 2 –400 Hz, 3–5 kHz, 4–50 kHz, 5 –200 kHz)

Fig. 4. Dependence of the specific resistance of a film on aluminum on reciprocal temperature at different frequencies. 1 –20 Hz, 2 –400 Hz, 3–5 kHz, 4–50 kHz, 5 –200 kHz

Figure 3 shows the dependence of the specific resistance on reciprocal temperature for a polymer film on aluminum at a frequency of 400 Hz. When a constant voltage of 1 V is applied to the film, the activation energy decreases, as is evident from comparison of the slopes of the lower and upper curves.

Using the frequency dependences of the capacitance and resistance of the sample, one can, by the simplest model of a two-layer capacitor, find the average specific resistance and thickness of the layers. Thus, for example, for a polymer film on aluminum with a thickness of 5000 Å it was found that the high-resistance layer has a total thickness of 700 Å and a specific resistance of $2 \cdot 10^9$ $\Omega \cdot$cm, while the low-resistance layer is 4300 Å thick and has a specific resistance of $2 \cdot 10^4$ $\Omega \cdot$cm.

If, at a frequency of 20 Hz, the capacitance and resistance of the barriers are measured, and at 200 kHz the parameters of the base material, then, using the same model, one can calculate the change in the capacitance and resistance of the film with frequency. Table 1 compares the experimental and calculated values for a film of the polymer complex of TCNE with aluminum at 60 and 300°.

Using formula (1) and the dependence of the sample resistance on the applied voltage, one can estimate the number of high-resistance barriers and their thickness. From experimental data for the same film on aluminum one can find that $n \sim 13$. Then the average thickness of one barrier is equal to 54 Å, and the average thickness of a well-conducting layer is about 320 Å.

Proceeding from the accepted model of the film, one should expect that the activation energy of the conductivity must decrease with increasing alternating-current frequency.

Figure 4 presents the dependence of the specific resistance of the film on aluminum on the reciprocal temperature at frequencies from 20 Hz to 200 kHz. From the figure it follows that the activation energy decreases up to a frequency of 5 kHz. At a frequency of 50 kHz there is again an increase in the activation energy, which is possibly connected with an increase, occurring at these frequencies, in dielectric losses having a different temperature dependence.

Table 1

Frequency, Hz	60° C	300° C						
Frequency, Hz	R_{exp}, ohm	R_{calc}, ohm	C_{exp}, mF	C_{calc}, mF	R_{exp}, ohm	R_{calc}, ohm	C_{exp}, mF	C_{calc}, mF
20	7000	7000	0,4	0,4	330	330	0,5	0,62
400	2800	6050	0,36	0,39	330	331	0,5	0,48
5000	290	242	0,235	0,36	200	314	0,43	0,44
50000	46	32,2	0,046	0,043	23	18,9	0,303	0,35
200000	27,8	28,3	0,014	0,015	3,5	7,6	0,217	0,17

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