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РОЗДІЛ 2

ХІМІЧНІ, ФІЗИЧНІ ТА МАТЕМАТИЧНІ МЕТОДИ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ТА АПАРАТІВ

INTERRELATION BETWEEN SPACE CHARGE AND POLARIZATION IN A POLYMER FERROELECTRIC

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Polymer ferroelectrics such as polyvinylidene fluoride (PVDF) are not ideal dielectrics. They are two-phase materials with crystalline and amorphous components that have some electrical conductivity due to presence of impurities. After electrification of the polymer ferroelectric, the distribution of polarization and space charges is generally uneven in the thickness direction of the films that in some cases leads to deterioration in the performance of sensors made of such films. Therefore, the question of the relationship between polarization and space charge is relevant both for physics and practical application of the materials.

The distribution of polarization in electrified PVDF films have been studied [1], while the distribution of the space charge was not paid enough attention. The purpose of this paper is to establish the relationship between polarization and captured charges and to determine their localization.

The source of ferroelectricity in the ferroelectric polymers is the crystalline regions of the polymer, while electric charges can be injected from electrodes, or be result of impurities dissociation. Thickness of the films x_o is much smaller than their other linear dimensions, so a one-dimensional case can be considered. According to the Poisson equation

$$\frac{\partial D}{\partial x} = \rho(x,t) \tag{1}$$

where D is the displacement, x the coordinate in the direction perpendicular to the surface, ρ the density of the excess charge. Since the main component of the polarization is the ferroelectric component $P(x)$, it can be written that

$$D = \varepsilon_o E + P(x), \tag{2}$$

From (1) and (2) we obtain

$$\varepsilon_o \frac{\partial E}{\partial x} = \rho(x,t) - \frac{\partial P}{\partial x} \tag{3}$$

The Maxwell relaxation time $\tau = \frac{\varepsilon_o \varepsilon}{g}$ in PVDF is of the order of 100 s, where ε_o is the electric constant, ε the effective permittivity, g the conductivity. Any gradient of the field during the time τ will cause redistribution of charges in such a way that at any point $E=0$ at $t > \tau$, and, consequently, $dE/dx=0$. Therefore,

$$\rho(x,t) = \frac{\partial P}{\partial x} \quad \text{at } t > \tau \tag{4}$$

In conclusion, it follows from (4) that the real uncompensated charges are trapped in the places where polarization gradients are located, i.e. at the boundaries of the polarized regions. To improve the polarization uniformity one should apply rather high voltage to the virgin samples in order to form the boundaries near the surface of the film.

Scientific Advisor – Prof. S.N. Fedosov, DSc (Physics & Mathematics)

Literature

1 S.N. Fedosov, A.E. Sergeeva, *et al* Polarization profiles in corona poled P(VDF-TFE) copolymer studied by piezoelectrically induced pressure step method // J. Phys. D: Appl. Phys. **29** (1996), – P. 3122-3128.

TWO COMPONENTS OF POLARIZATION IN FERROELECTRIC POLYMERS

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Ferroelectric polymers differ considerably from conventional polar electrets, because they possess spontaneous switchable polarization in β phase crystallites [1]. But still almost half of the volume is occupied by the polar amorphous phase. It means that ferroelectric properties of FPs may interfere with their electret properties. The purpose of this paper is an attempt to separate the ferroelectric component of polarization from the electret component.

It is known that polarization in electrets is usually thermally frozen and unstable thermodynamically, while ferroelectric polarization is stable, provided the depolarizing field is neutralized anyhow [2]. We have shown that injected and trapped charges play an important role in the buildup of polarization in FPs. It was proved that ferroelectric polarization and trapped charge form a self-consistent system with its stability governed by that of the space charge [3]. In this paper, the important role of the space charge is confirmed. Moreover, we obtained evidence that the space charge stabilizes not only the ferroelectric component of polarization, but also the electret one.

We studied thermally stimulated depolarization (TSD) currents in short circuit (SC) and open circuit (OC) modes in differently poled polyvinylidene fluoride (PVDF) and copolymers of PVDF with trifluoroethylene P(VDF-TrFE) and tetrafluoroethylene P(VDF-TFE). A new phenomenon was observed, namely a double inversion of the TSD current in the OC mode and appearance of two well structured peaks in the SC mode in poled samples stored more than one year, indicating that two different kinds of polarization exist in ferroelectric polymers, both accompanied by deeply trapped charges. The difference between the two currents is quite essential, because two pairs of peaks were seen instead of one. Independence of the phenomenon on the material and poling conditions indicated that it was rather fundamental. The more stable component of polarization had presumably a ferroelectric nature, while the less stable one was attributed to polarization in amorphous phase.

It follows from our results that very slow redistribution of charges and polarization takes place in ferroelectric polymers after completion of poling until the electret and ferroelectric components of polarization are finally separated, both accompanied by the trapped charges. For the first time, existence of these four relaxation processes in ferroelectric polymers has been clearly shown.

In order to obtain high and stable polarization in ferroelectric polymers, it is necessary to remove the unstable electret component of polarization. For example, in case of P(VDF-TFE) films poled at 85 °C through a glass, it is sufficient to heat poled sample to 60 °C. The procedure may not be the same for other ferroelectric polymers.

Scientific Advisor – Prof. S. N. Fedosov, DSc (Physics & Mathematics)

РОЗДІЛ 2 – ХІМІЧНІ, ФІЗИЧНІ ТА МАТЕМАТИЧНІ МЕТОДИ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ТА АПАРАТІВ

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