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ON THE MECHANISM OF THE PHOTODOMAIN EFFECT IN FERROELECTRICS

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The influence of nonequilibrium electrons on the domain structure and switching of ferroelectrics (photodomain effect) has been investigated in ferroelectric crystals and ceramics. In the present paper this effect is observed and explained as a result of the domain walls screening in frame of Yshibashi – Takagi theory.

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The influence of intrinsic light on the equilibrium domain structure, on the kinetics of its switching and on the properties directly related to the domain structure (such as, for example, the pyroelectric charge, electromechanical hysteresis, etc.) has been called the photodomain effect [1]. The photodomain effect (PD) was first observed in SbSI crystals [2]. The first observations of the PD were performed by indirect methods, such as the influence of illumination on the pyroelectric current and Barkhausen discontinuity [3, 4]. Later the PD effect was observed by the direct observations of the intrinsic illumination on domain structure in SbSI and $BaTiO_3$ crystals [5, 6]. In [7 – 10] the PD effect was observed in PZT and PZLT ferroelectric films and explained by the mechanism of the screening of 90° domain walls (or the walls with boundary which is not parallel to the external fields) by the nonequilibrium carriers. It was shown, that illumination of PZT or PZLT films in the intrinsic optical region leads to the suppression of the switchable polarization in the external field. In the present paper we show, that Yshibashi – Takagi model (YT model) [11] permits to explain the PD effect by the mechanism of the domain walls screening.

In YT model four parameters are required to describe the polarization reversal. The probability of nucleation per unit volume per unit time is given by R, the initial radius of a nucleus by r_c, the domain-wall velocity by ν, and the dimensionality of growth by d.

The fraction of switched volume to total volume is given by $Q(t) = 1 - q(t)$, where $q(t)$ is suppression. The switching current is then found by

$$i(t) = 2P_s \frac{dQ(t)}{dt} = -2P_s \frac{dq(t)}{dt}, \tag{1}$$

where P_s is the spontaneous polarization per unit volume. Thus,

$$P_s(t)/P_s(0) = 1 - q(t). \tag{2}$$

The YT model gives for $q(t)$ the following expressure [11]:

$$\ln q(t) = -\frac{C_d R}{\nu(d+1)}\left[(r_c + \nu \cdot t)^{d+1} - r_c^{d+1}\right], \tag{3}$$

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where $C_d = 2, \pi, 4\pi/3$ for $d = 1, 2, 3$, respectively. The switching current is given by

$$i(t) = 2P_s C_d R(r_c + \nu t)^d \exp\left[-\frac{C_d R}{\nu(d+1)}\left[(r_c + \nu t)^{d+1} - r_c^{d+1}\right]\right]. \tag{4}$$

If the size of a nucleus is negligibly small on the scale of the system, as is usually the case, then equations (3) and (4) have a form:

$$\ln q(t) = -\frac{\theta}{d+1} t^{d+1}, \tag{5}$$

$$i(t) = P_s \theta \cdot t^d \exp\left[-\frac{\theta}{d+1} t^{d+1}\right], \tag{6}$$

where $\theta = C_d R \nu^d$.

This model was successfully applied to the thin ferroelectric films [12, 13].

At the illumination of the ferroelectric crystal (or film) the nonequilibrium electrons influence the kinetics of the ferroelectric switching. In the frame of the YT model the illumination in principle changes R, r_c and ν. The change of r_c is evident because the free surface energy of the domain depends on the concentration of the photoelectrons (due to the screening). The illumination may also increase the nucleation rate R due to the trapping of the photoelectrons. The velocity of the wall ν also depends on the concentration of the photoelectrons. We shall suppose that at $t = \tau_m$, where $\tau_m = \varepsilon/4\pi\sigma$ is Maxwellian time, the switching is finished due to the screening of the walls (see Fig.1). Thus we can obtain from (3) the value $q(t = \tau_m)$, which characterizes the unswitched volume of the crystal or film, see (2). We shall consider the value of $q(t = \tau_m)$ as the degree of the photoinduced hysteresis suppression (or PD effect).

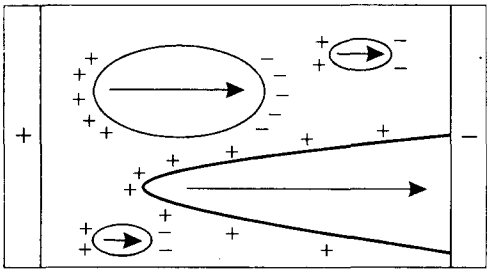

Fig.1. Screening of the domain walls by the non-equilibrium carriers

Substituting $t = \tau_m$ in (3) we obtain:

$$q(t) = \exp\left\{-\frac{C_d R}{\nu(d+1)}\left[(r_c + \nu\tau_m)^{d+1} - r_c^{d+1}\right]\right\}, \tag{7}$$

where $\tau_m = \varepsilon/4\pi\sigma_{ph} = \varepsilon/4\pi\sigma_{ph}^0 \cdot I$ (I is light intensity in the case of the linear dependence $\sigma_{ph} = \sigma_{ph}(I)$, $\sigma_{ph} \gg \sigma_d$, σ_{ph} is photoconductivity, σ_d is dark conductivity).

We can see from (3) and (7) that at $t = 0$ $q(0) = 1$ and $P_s(t) = P_s(0)$. At $t = \tau_m$ $q(\tau_m) < 1$ and correspondingly $P_s(\tau_m) < P_s(0)$. Thus we obtain the PD effect. It is seen from (7), that the PD effect increases with the light intensity. The equation (7) does not describe the kinetics of this effect because we did not take into account the dependence of R, r_c and ν on the light intensity. If we neglect this dependence, the equation (7) will describe the dependence of the photoinduced hysteresis suppression on the time of

illumination. Of course, the all this approach is valid, providing that Maxwellian time is comparable with switching time.

If the size of a nucleus is negligibly small in comparison with grown and screened domains ($r_c \ll \nu\tau_m$), the photoinduced hysteresis suppression is given by (8):

$$q(\tau_m) = \exp\left[-\frac{C_d R \nu^d}{d+1}\tau_m^{d+1}\right]. \tag{8}$$

It is seen from (8), that $q(\tau_m) \sim \exp\left[-\text{constant} \cdot \tau_m^{d+1}\right]$ and effect increases with light intensity. From the dependence $q(\tau_m) = q(I)$ we can determine in principle the dimensionality of the domain growth d.

The effect of the photoinduced hysteresis suppression is determined by $q(\tau_m)$. The dependence of q on the light intensity I is given by (8), if we substitute in (8) the value τ_m:

$$\tau_m = \varepsilon/4\pi\sigma_{ph}(I).$$

If the photoconductivity σ_{ph} linearly depends on the light intensity I

$$\sigma_{ph} = \sigma_{ph}^0 \cdot I$$

the dependence $q = q(I)$ is given by (9):

$$q = \exp\left[-\frac{C_d R \nu^d}{d+1}\left(\frac{\varepsilon}{4\pi\sigma_{ph}^0}\right)^{d+1} I^{-(d+1)}\right]. \tag{9}$$

It is seen from (9) that the effect of the photoinduced hysteresis suppression q increases with light intensity I.

The experimental data [9, 10] show, that illumination of PZT and PZLT ferroelectric ceramics in the intrinsic optical region leads to the increase of q. This effect of the hysteresis suppression may be explained qualitatively by the developed model. For the numerical comparison we need the experimental investigation of q as a function of the light intensity.

We investigated PZT thin films with thickness $l \cong 3\mu$, which were prepared using the sol-gel deposition techniques [14,15]. This technology performs the single-phase perovskite structure. As a semitransparent electrode we used Pt (150 Å) sputtered-deposited on the film. As a second electrode we used Pt, sputtered-deposited on the oxidized silicon wafer. The illumination of the film was performed through the semitransparent electrode. The illumination of the films was performed by Xe-lamp and monochromator ZMR in the spectral region 300–800 nm. The low-frequency Sawyer – Tower system was used for the measurements of the dielectric hysteresis loops ($f = 70$ Hz).

The effect of the photoinduced hysteresis suppression is shown on Fig.2. The initial hysteresis loop is shown by curve *1*, the photoinduced hysteresis loop is shown by curve *2*, the effect of the photoinduced hysteresis suppression q is determined by (2). In accordance with [9, 10] we used the following measurements sequence. We applied the external voltage $V = 1$, 3 or 9 V to the electrodes for 100 sec with simultaneous illumination of the film by the band-gap light $\lambda \cong 368$ nm. The external electric field was less than coercive one [9, 10]. After switching off external field and illumination the photoinduced hysteresis loop was measured. Then the hysteresis loop was restored by the band-gap illumination

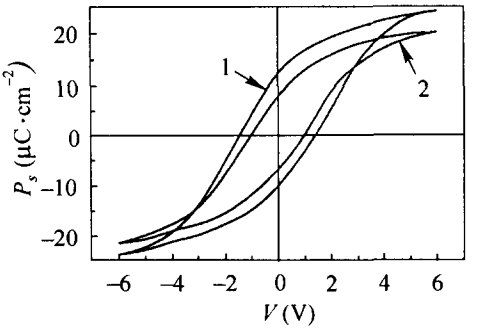

Fig.2. The effect of the photoinduced hysteresis suppression in PZT: *1* – the initial hysteresis loop; *2* – the suppressed hysteresis loop; $\lambda \cong 368$ mm, $I = 4.5\,\mathrm{mW{\cdot}cm^{-2}}$, $V = 3$ V

in the external low-frequency voltage $\cong 80$ V. The measurements of q was performed for different band-gap light intensities I.

Fig.3 shows the experimental dependence of q on the light intensity I for different values of V. The saturation of the curves on Fig.3 at $q \ll 1$ and deviation of experimental curves from the theoretical dependence $|\ln q| = aI^{-3}$, obtained for two-dimensional domain growth may be connected with many factors. The main possible cause of this deviation is dependence of the domain-wall velocity ν on the screening: the velocity ν in (9) is the function of light intensity I and $\nu = \nu(I)$ decreases with I. The more common reason for this deviation is the infinite-grain approximation, which was used in (3). Anyway (8) describes the main feature of the phenomenon: increase of the photoinduced hysteresis suppression with light intensity.

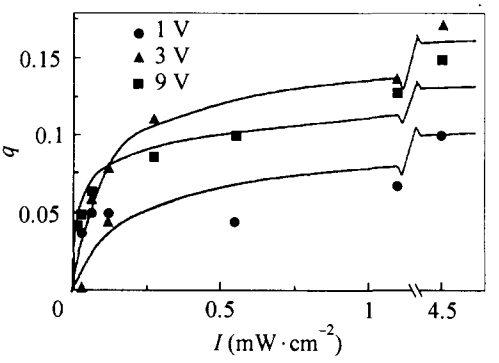

Fig.3. Experimental dependence of q on light intensity I for different voltages

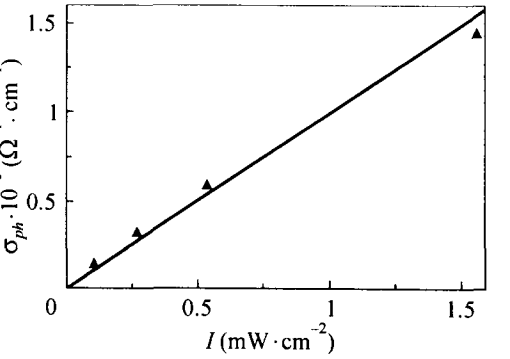

Fig.4. The linear dependence of the photoconductivity σ_{ph} on the light intensity in PZT; $\lambda \cong \cong 368$ mm

The dependence of the domain-wall velocity ν on the electric field follows from the behavior of the experimental curves of Fig.3 at small values of I. It is seen from (5) and (9), that $dq/dI \sim q\nu^d I^{-(d+2)}$ and therefore on the initial part $q = q(I)$ (far from the saturation) the initial value of dq/dI increases with voltage V. The curves of Fig.3 confirms this conclusion.

The proposed mechanism of the photoinduced hysteresis suppression is fulfilled at the condition:

$$\tau_m \leq t_1, \tag{10}$$

where $t_1 = t_1(E)$ is the effective time of the swithing of polarization, E is external electric field and τ_m is Maxwellian relaxation time:

$$\tau_m = \frac{\varepsilon}{4\pi(\sigma_{ph} + \sigma_d)}, \tag{11}$$

where σ_{ph} and σ_d are photo- and dark conductivity. The dependence of the photoconductivity of the investigated PZT films is shown on Fig.4 ($\lambda \cong 368\,\text{nm}$). It shows that in the interval $I \cong 10^{-1} \div 0.5\,\text{mW}\cdot\text{cm}^{-2}$ the photoconductivity $\sigma_{ph} = 10^{-7} \div 10^{-6}\,\Omega^{-1}\cdot\text{cm}^{-1}$ ($\sigma_{ph} \gg \sigma_d$). Therefore for $\varepsilon \cong 10^3 \div 10^4$ the relaxation time $\tau_m = 10^{-1} \div 10^{-3}$ sec.

The time $t_1 = t_1(E)$ depends on the external electric field E. The used values of $E \leq 3{\cdot}10^4\,\text{V}\cdot\text{cm}^{-1}$ are much less than coercive field in PZT films $E_c \geq 10^5\,\text{V}\cdot\text{cm}^{-1}$ [16]. Therefore t_1 is much larger than the real switching time, $t_1 \gg t_{SW}$. We can suppose therefore, that condition (10) is fulfilled. Nevertheless the value of q depends on the external electric field E. At small value of the field $t_1 \gg \tau_m$, but the domain structure change is very small. At high values of the field $t_1 \leq \tau_m$ and the screening is not effective. It explains the nonmonotonic behavior the saturation values of $q = q(V)$ on Fig.3.

Thus the photoinduced hysteresis suppressing in the ferroelectric PZT films may be explained as a result of the screening of the domain walls by the photocarries. The YT infinite-grain model switching kinetics permits to explain the increase of this effect with light intensity. The describtion of the kinetics of this effect must take into account the dependence of the domain-wall velocity and nucleation rate on the concentration of the photocarries. It does not mean, that the screening of the domains walls is the common mechanism of the PD effect in ferroelectrics.

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