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Scaling of the coercive field in ferroelectrics at the nanoscale

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The scaling of the coercive field in ferroelectric films at the nanoscale is investigated experimentally. The scaling in the films of copolymer vinylidene fluoride and $BaTiO_3$ with thickness equal by the order of value to the critical domain nucleus size 1–10 nm reveals deviation from the well known Kay and Dunn low. At this thickness region coercive field does not depend on thickness and coincides with Landau–Ginzburg–Devonshire value.

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The Kay and Dunn scaling of coercive field

$$E_c \sim l^{-2/3} \quad (1)$$

is observed for the broad values of thickness l of the ferroelectric films [1]. The relation (1) is caused by the domain dynamics [1, 2], which till 1998 was considered as a common mechanism of ferroelectric switching. The mechanism of this switching was successfully explained by theory of Kolmogorov–Avrami–Ishibashi (KAI theory) [3–5].

The application of Langmuir–Blodget film growth method for the first time permitted to obtain ferroelectric copolymer films with thickness in the region $l^* = 1-10$ nm [6, 7] equal by the order of value to the critical size of domain nucleus [1, 8, 9]. For example Miller and Weinreich obtained $l^* \approx 5$ nm [9]. Ferroelectric films with $l \approx l^*$, investigated in [7], have shown switching. Later in subsequent papers [10–13] have been shown, that copolymer films with thickness l^* equal by the order of value to the critical size of domain nucleus reveal homogeneous switching. The homogeneous LGD switching (switching without domains) was never observed before 1998 neither in crystal nor in the films. The results, obtained in [7, 10–13], led many authors [1] to the conclusion, that this polymer ferroelectric switching is possibly an exception. But recently the same results were obtained for laser-epitaxial $BaTiO_3$ films with thickness $l^* = 3-10$ nm [14]. These measurements were performed (as for polymeric films) in condenser by means of PFM.

In the present paper we summarize the data about scaling of coercive field both for the ferroelectric copolymer and $BaTiO_3$ films at the nanoscale $l \approx l^*$.

Fig. 1 shows the scaling $E_c = E_c(l)$ for the ferroelectric vinylidene fluoride copolymer P[VDF–TrFE]

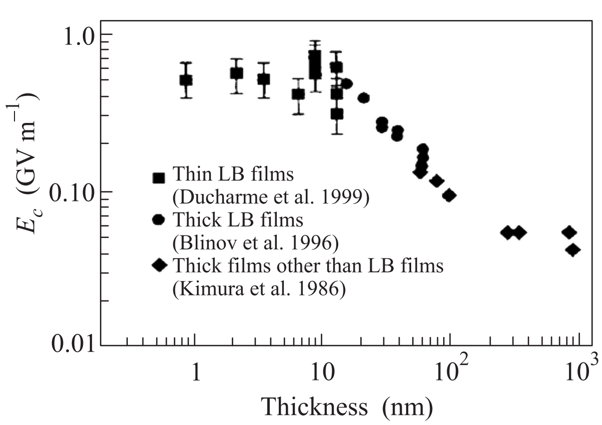

Fig. 1. Scaling of E_c in copolymer films

films obtained by Langmuir–Blodgett (LB) method [15]. The LB films thinner than 10 nm show $E_c = E_c^{(th)}$ which does not depend on film thickness l. Thicker LB films (circle symbols) and thick films, obtained by spun method (diamond symbols) show scaling possibly Dunn and Kay (1). Correspondingly films in the interval 1–10 nm reveal LGD homogeneous switching kinetics [10]:

$$\tau^{-1} = \tau_0^{-1} \left(\frac{E}{E_c^{th}} - 1 \right)^{1/2}, \quad (2)$$

where τ is switching time, τ_0^{-1} is constant, E is switching field, and E_c^{th} is LGD coercive field. The homogeneous switching kinetics characterized by the threshold E_c^{th}: the switching of ferroelectric film takes place only at $E > E_c^{th}$. At $E < E_c^{th}$ there is no switching. On the contrary at $l > 10$ nm (Kay and Dunn scaling) the copolymer ferroelectric films reveal switching, governed by domain dynamics (KAI mechanism) [5]:

$$\tau^{-1} = \tau_0^{-1} \exp\left(\frac{E_0}{E} \right), \quad (3)$$

where E_0 is constant. The results shown on Fig. 1 were obtained in condenser Al–P[VDF–TrFE]–Al by the usual Sawyer–Tower method.

The authors [2] supposed that deviation of these results from (1) are caused by the gap between Al electrodes and copolymer film. But dependence of condenser capacity on the number of LB monolayers (or on the film thickness) did not reveal any gap (Fig. 2 [16]).

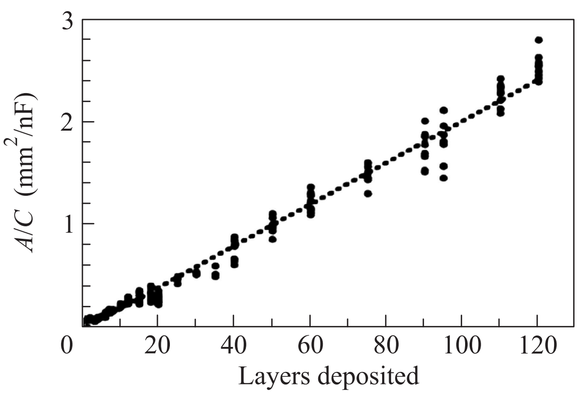

Fig. 2. Dependence of reciprocal capacity on the number of copolymer monolayers

Here we show the same deviation from (1) for the laser-epitaxial $BaTiO_3$ ultrathin films with $l < 10$ nm [17, 18]. The measurements were performed in condenser Pt–$BaTiO_3$–Cr by means of PFM, which tip contacted one of the electrodes. The electrodes on the surface of $BaTiO_3$ were deposited by lithography and had form of circles with radius of a few microns. Fig. 3 shows hysteresis loops obtained for film thicknesses of 3 (Fig. 3a), 8 (Fig. 3b), and 38 nm (Fig. 3c). The film thickness was measured by Rutherford backscattering spectrometry (RBS) with 2 MeV He^{++} ions with 10% accuracy [17, 18]. Fig. 3 shows also the scaling of $E_c = E_c(l)$ in the region 3–40 nm (Fig. 3d). At $l > 10$ nm the scaling follows (1), but at $l < 10$ nm the coercive field weakly depends on l and its value is near $E_c \approx 10^8$ V/m, what coincides with LGD value E_c^{th}. Correspondingly the films with $l = 3$ and 8 nm reveal homogeneous LGD switching kinetics (2) and thicker films – KAI behavior (3) [14].

Of course ultrathin films with $l \approx l^*$ (in the region of critical domain size) must reveal the existence of two competing polarization reversal mechanisms: domain-driven and homogeneous. One of these mechanisms prevails depending on the thickness and external field. This our conclusion was confirmed recently from the first principles approach [19].

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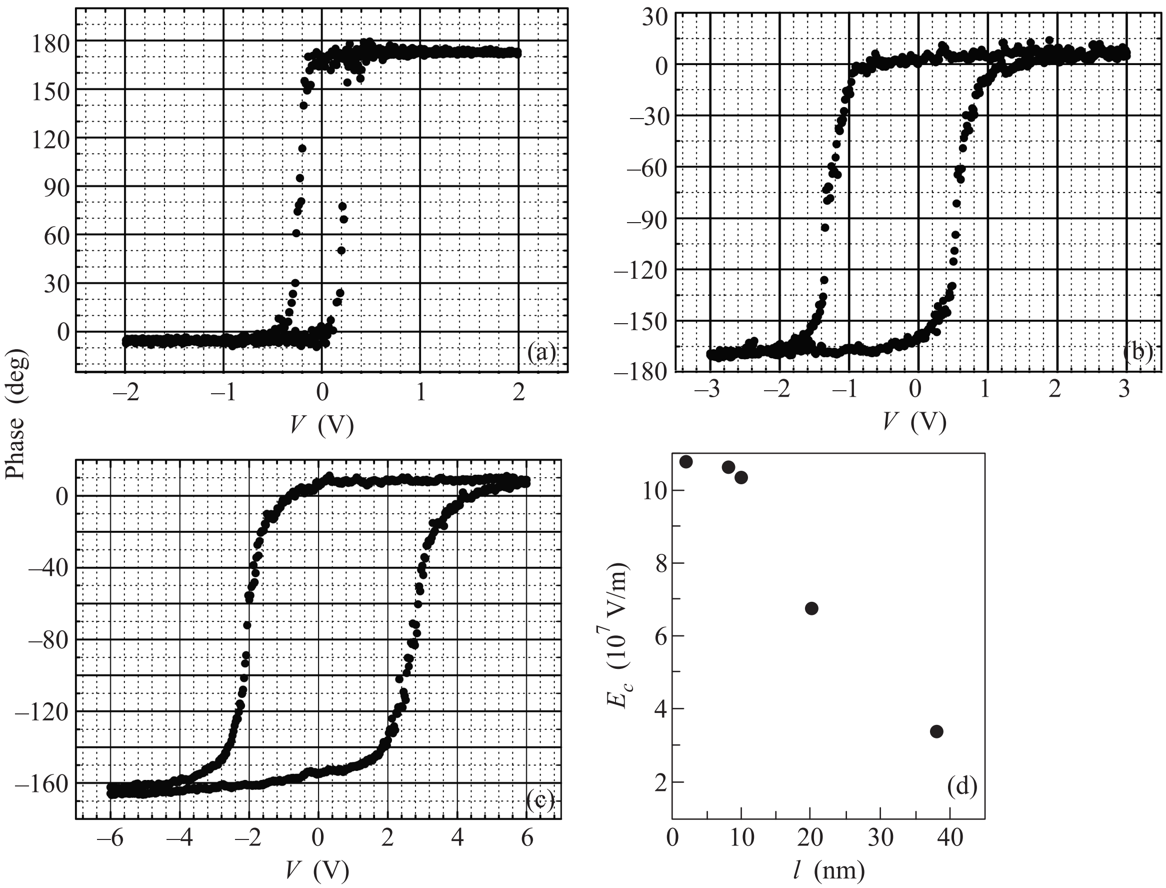

Fig. 3. Hysteresis loops and scaling of the coercive field for the ultrathin $BaTiO_3$ films

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