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Unstable misfit strain in the sodium niobate thin film

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The possibility of unstable misfit strain at the film/substrate interface is considered by the example of a sodium niobate thin film. The conditions for the existence of an electretlike state of micro-sized blocks on its surface and the use of unstable misfit deformations in obtaining ferroelectric thin-film materials are estimated.

Keywords: ferroelectric, sodium niobate, thin film, misfit strain, temperature dependence.

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Ferroelectric thin-film materials (FTMs) are widely used in high-density electronics, in creating nonvolatile memories and field-effect transistors. Their manufacturing technologies employing specific properties of the film/substrate interface called as „strain engineering" are based on the relationship between polarization and strain. Recent studies and reviews [1–4] are devoted to achievements and problems of these technologies for epitaxial FTMs.

In phenomenological description of the film/substrate interface, the misfit strain (MS) is calculated from the lattice parameters in the interface plane either for the film (a)/substrate (b) pair [5],

$$U = 1 - \frac{a}{b}, \tag{1a}$$

or for the film far from (a) and close to (a_s) the film/substrate interface [6],

$$U_M = \frac{a_s}{a} - 1, \tag{1b}$$

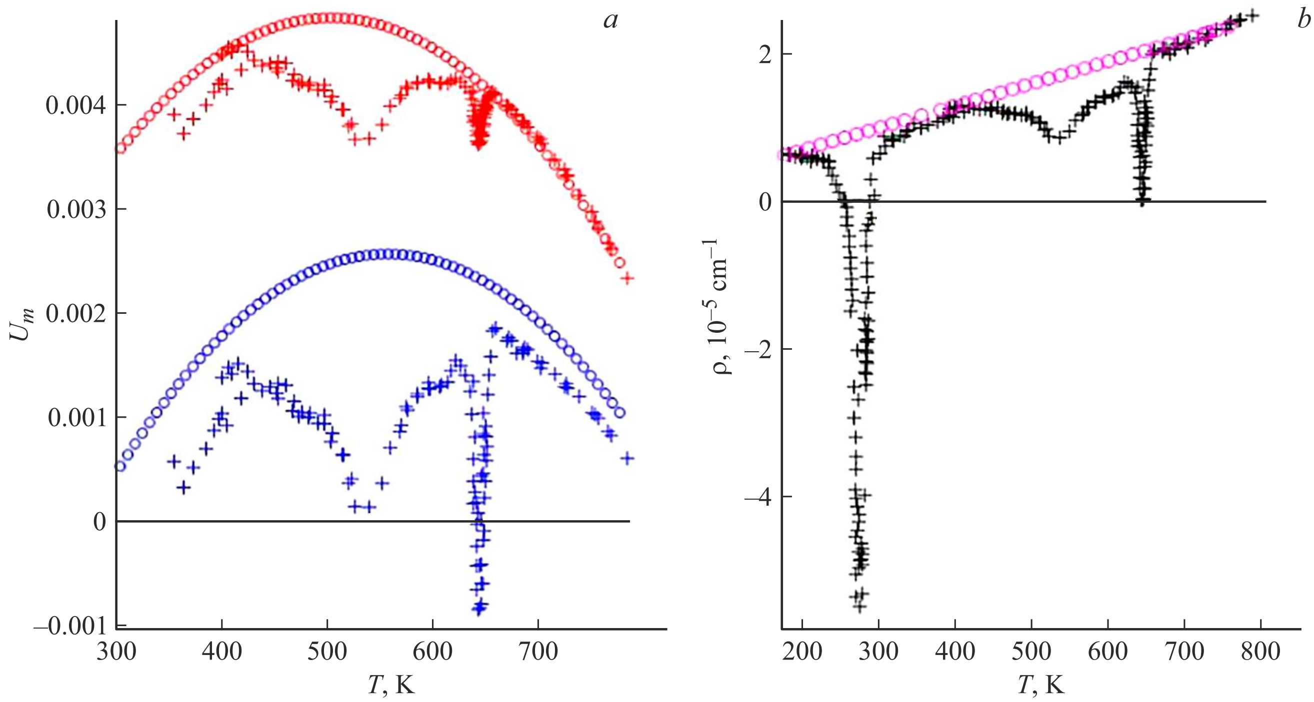
where U_M applied for the description of the misfit dislocations parameters at the interface. Relations (1a) and (1b) do not contain temperature dependences, therefore, in this case the film/substrate MS have a constant value that determines the characteristics of the considering material. However, a different situation is possible.

Recently, a single-phase mono-crystalline [001]-oriented heterostructure $NaNbO_3/SrRuO_3/MgO$ 500 nm thick has been studied using high-frequency magnetron sputtering [7]. The morphology and dissipation of the injected charge in this film [7] were studied in [8] by scanning probe microscopy. Beginning from the thickness of ~ 200 nm, the surface-forming blocks become co-directional, and their dimensions are stable. For a film 500 nm thick, they are $\sim (0.8-1.1) \times (0.1-0.3)\,\mu$m with the height of $\sim 20-30$ to 50 nm. The ratio between their major and minor axes in the relief and electric potential images remains almost constant ($\sim (4-5)/1$) in the process of dissipation [8]. In this case, the ratio of the axes of the elliptical spots of the injected potential changes with time, slightly deviating from the „crystallographic" estimate of 2.88 [8]. This means that the surface blocks and the injected charge regions differ significantly in their charge storage capacity, although they are made of the same material. Authors of [7] assumed that ferroelectric properties of a thin film are caused by misfit strain U_m. The $U_m(T)$ may be calculated using the relation dependence from [5]:

$$U_m(T) = 1 - \frac{a(T)}{b(T)} = 1 - \frac{a(T_g)[1 + \rho_a(T - T_g)]}{b(T_g)[1 + \rho_b(T - T_g)]}, \tag{2}$$

where T_g is the film growth temperature, ρ_a and ρ_b are the thermal expansion coefficients. Parameter values are taken: ρ_b for $SrRuO_3$ from [9], experimental dependence $\rho_a(T)$ for $NaNbO_3$ ceramics from [10] (since there are no data on ρ_a for the film, we had to use data from [10]). Expression (2) does not account for nonisotropy of thermophysical and mechanical properties of the film and substrate materials. In [5] it was applied under the conditions: $U_m \ll 1$, ρ_a and ρ_b do not depend on temperature, i.e. only the linear contribution was taken into account, which resulted in expression (1a). The U_m calculations for sodium niobate are presented in the figure, a.

MS depends on temperature in a very complex way (see figure, a), especially for $T \sim 650$ K and in the ranges of $\sim (530-570)$ and $\sim (400-500)$ K where even a small temperature variation strongly changes the current value of U_m (see figure, a). When approximating the experimental dependence $\rho_a(T)$ with a linear function (see figure, b), the possibility of instability remains. The dependence $U_m(T)$ of such kind does not correspond in any way to approximations (1). For the sodium niobate film obtained in [7], relatively small changes in temperature in the range of $T \in 200-650$ K during its preparation, caused by instability or non-uniformity of the plasma forming the film or the substrate temperature, can significantly change the U_m^i of the deposited i-th layer, and U_m^{i-1} for the previous layer or U_m^{i+1} for the subsequent one can not coincide with it. This situation may be characterized as *unstable misfit strain.*



Dependence $U_m(T)$ for the NaNbO$_3$ film. a — $U_m(T)$ calculations via relation (2) in comparison with dependence $\rho_a(T)$ taken from [10] (crosses) or its linear approximation (circles). The substrate temperatures prior to high-frequency discharge switch-on [7] are 673 K (bottom panel) and 783 K (top panel). b — dependence $\rho_a(T)$ [10] (crosses) and its linear approximation (circles).

The analysis of the origin of the sodium niobate peculiar properties for bulk samples [10] and films [11] is based on the consideration of the complex sequence of its phase transitions. Let us apply the same approach to specific features of $U_m(T)$. In the range of $\sim(270-650)$ K there is observed ferroelectric phase Q ($Pmc21$) and two centrosymmetric phases P ($Pbcm$) and R ($Pmmn$) [10] (phase transition temperatures obtained in different studies may be slightly different). The existence of phase Q is possible for small-sized ($< 1-0.5\,\mu$m) particles or in the presence of defects or inhomogeneities that can promote its stabilization [10]. The existence of phase Q in films also depends on the cell multiplication and misfit strain at the film/substrate interface[11]. For nanosized blocks on the film surface, the influence of thermal expansion anisotropy with a local change in symmetry from tetragonal to orthorhombic is possible. At ~ 633 K, the $R \rightarrow P$ transition takes place; at 588 K (560 K) the $Q \rightarrow P$-like phase transition occurce [10]. The $P \rightarrow Q$ transition near 429 K is possible due to inhomogeneities in some regions of the film surface. In the region of $\sim(440-550)$ K, a diffuse temperature-induced phase transition is possible between two different Q phase orientations relative to the interface [11].

In the case of NaNbO$_3$, the MS characteristics are determined by the properties of the film material itself, but can also be determined by the substrate material. The difference in thermal expansion coefficients between the film and the substrate is called thermal mismatch in [2]. Being cooled from the growth temperature to ambient one, it may be significant in the interface plane [2]. In the NaNbO$_3$ film, an additional feature is the instability of $U_m(T)$, the values of which may change rather sharply. Due to different DN of adjacent layers, regions of significant inhomogeneities with a deformation gradient can form during film synthesis. For them, lattice distortion accompanied by a shift of B-cations can cause polarization even in a centrosymmetric material, i.e., a flexoelectric effect. This was discussed in [12], and in [13] the possibility of the emergence of bound ferroionic states combining properties close to those of ferroelectrics and electrets was shown. Previously, the possibility of the emergence of an electret-like state in thin layers of ferroelectrics was considered in [5].

Let us estimate the criteria for the existence of the electret-like state of the NaNbO$_3$ film surface blocks by using the $U_m(T)$ calculations and criteria from [5] where the estimation was performed for PbZr$_{0.5}$Ti$_{0.5}$O$_3$ (PZT50/50) (assessment via the model from [6] would need data on misfit strain at the interface). In [5], the following parameters were calculated: MS-induced internal field $E_m \approx 2\pi U_m/[d_{31}h(1+\Lambda_z)]$ and critical film thickness l_z, below which the existence of the electret-like state is possible. Here $h = l/(2l_z)$, l is the film thickness, $l_z = \sqrt{\delta_z/\alpha_z}$, δ_z, α_z are the free energy expansion coefficients, Λ_z is the parameter. Let us take for the NaNbO$_3$ film two (max and min) values for $U_m = 0.0005$ and 0.005 (see panel a in the figure); values $\Lambda_z = 50$ and $h = 10$ remain the same as in [5]; assume δ_z and α_z to be the same as in [14] (hence, $l_z = 2.3\,\text{nm}$) and $d_{31} \approx -6.4\,\text{pC/N}$ according to [15,16]. As a result, $E_m \approx -(10-150)\,\text{kV/cm}$ was obtained, which is quite close to the coercive field experimental value of $11-50\,\text{kV/cm}$ [15]; $l_z = 2.3\,\text{nm}$, which (at $h = 10$) gives $l = 46\,\text{nm}$ (most likely this is the upper estimate) given that the height of the surface block is equal to $\sim (20-50)\,\text{nm}$ (for comparison: $l_z = 0.25\,\text{nm}$ for PZT50/50 [5]). In general, according to the criteria established in [5], the combination of parameters $U_m > 0$, $E_m < 0$ and large l_z „favors" the possibility of the electret-like state existence on the $NaNbO_3$ film surface. Dissipation of its charge may differ from that of artificially injected one. Detailed description will be the subject of a separate study. In addition, the value of $E_m < 0$ explains the left shift of the $d_{33}(U_m)$ hysteresis loop (film unipolarity) revealed in [7].

These estimates indicate that unstable thermal MS can create particular properties of the sodium niobate film surface. However, this is not mentioned in [15]. A possible reason for this may be a difference in the film growth temperatures obtained in [15] (below 650 K, i.e. to the left of the sharp anomaly in $U_m(T)$ (see figure *a*)), and in [7] (673 or 783 K, i.e. to the right of the anomaly).

In conclusion, note that, on the one hand, the necessity of accounting for temperature dependence $U_m(T)$ complicates the control and theoretical description of the MS influence on FTM. On the other hand, by varying the film synthesis techniques and temperature conditions it is possible to obtain unusual material parameters (preferably without adjusting the combinations of the film/substrate pair components). In addition, it has recently been shown that the vacancy gradient is able to change the surface response [12,14]. In combination with unstable thermal MS, this may become one of the ways to improve modern FTM technologies.

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Conflict of interests

The authors declare that they have no conflict of interests.

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