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ANOMALIES OF THE ELASTIC MODULUS OF THIN FILMS OF BARIUM TITANATE

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Abstract. For the single-crystal thin films of barium titanate based on Landau potential for eighth degree dependence of the elastic moduli from the misfit strain at room temperature constructed. Elastic moduli at the phase boundaries indicate abnormal behavior. In the region of the *r*-phase, some modules have the extreme values.

1. Introduction

Ferroelectric state in nanoscale films is associated with high mechanical stresses at the film-substrate arising from the mismatch of the lattice parameters of the film and the substrate, the difference in their thermal expansion coefficients, as well as the occurrence of spontaneous deformation at the phase transition, if the film is deposited at temperatures above the phase transition temperature. The presence of thermal stress can lead to a shift in the temperature of the ferroelectric phase transition in the film, and to change the structure of the low-symmetry phases, which must be considered when designing an acoustoelectronic devices. In most cases, the optimization of operating parameters is carried out in the framework of linear equations of the piezoelectric effect [1, 2] is a linear relationship between the variables of the state and external parameters. Fixing the external parameters determines the state, near which we can rewrite the equation of the piezoelectric. In this case, the material constants, due to the linearity of the equations do not change. For non-linear materials, what are ferroelectrics, large deformations occurring in thin films, lead to changes in the values of physical constants, which leads to the need to involve non-linear thermodynamic models that are used in the simulation of electromechanical properties of ferroelectric thin films [3]. In this paper, based on the Landau potential of the phenomenological theory of phase transitions performed linearization and determine the constants of linear equations for the piezoelectric thin ferroelectric films, depending on external conditions. On the example of single-crystal thin films of barium titanate, the behavior of the elastic constants as a function of misfit strain a studied. Study of material equations constructed on the basis of the Landau potential eighth degree at the room temperature. Analysis showed that the elastic constants exhibit an anomalous behavior at the phase boundaries and have the extreme inside *r*-phase.

2. Calculation of the material constants of the ferroelectric thin films

Description of the nonlinear properties of the ferroelectrics based on the thermodynamic potential of the phenomenological theory of phase transitions.

$$\Phi = G(p_1, p_2, p_3) - Q_{11}\left(t_1 p_1^2 + t_2 p_2^2 + t_3 p_3^2\right) - Q_{44}\left(t_4 p_2 p_3 + t_5 p_1 p_3 + t_6 p_1 p_2\right) -$$

$$-Q_{12}\left(t_1(p_2^2+p_3^2)+t_2(p_1^2+p_3^2)+t_3(p_1^2+p_2^2)\right)$$
$$-\frac{1}{2}s_{11}\left(t_1^2+t_2^2+t_3^2\right)-\frac{1}{2}s_{44}\left(t_4^2+t_5^2+t_6^2\right)-s_{12}\left(t_1t_2+t_1t_3+t_2t_3\right). \quad (1)$$

Here $G(p_1, p_2, p_3)$ is the Landau potential, p_i - the components of the polarization vector, u_k and t_k - strain and stress tensors, respectively, in Voigt notation.

For many materials, particularly for barium titanate, the function $G(p_1, p_2, p_3)$ is a potential for the eighth degree of polarization components, invariant with respect to the cubic symmetry group of the parent-phase [4]. Solution of the equations state

$$\begin{cases} E_i = \dfrac{\partial \Phi}{\partial p_i}, \\ u_k = -\dfrac{\partial \Phi}{\partial t_k} \end{cases} \quad (2)$$

allows you to find all the possible equilibrium (ground) state. For the bulk material in the absence of external forces, the problem reduces to the solution of the first equation (2). The second equation in this case is the definition of spontaneous strains. The material constants of the piezoelectric equations by linearizing the equations of state (2) for fixed external conditions are searched.

For a thin film is achieved in two stages. First, the problem is solved with a mechanical clamping conditions [5] (the film on the (001) substrate cut cubic): $u_1=u_m$, $u_2=u_m$, $t_3=0$, $t_4=0$, $t_5=0$. Then we study the possible ground states - constructed a phase diagram "misfit strain (u_m) - temperature (T)". Phase (u_m-T) diagram films of barium titanate depends on the values of the elastic [6] and electroelastic [7] coefficients.

Linearization of the equations state for the potential (1) defines the following set of equations of the piezoelectric effect:

$$\begin{cases} E_i = -g_{i,k}t_k + \beta_{i,j}^T p_j \\ u_m = s_{m,k}^D t_k + g_{i,m} p_i \end{cases} \quad (3)$$

Here we do not distinguish between the variables D and p due to the fact that the value of the dielectric constant of ferroelectrics is almost equal to the susceptibility. The solution of equations (3) with respect to other selected variables determine the material constants taken to the relevant variables. For films strain along with the electric field strength is the determining parameter, so we will be seen as the initial equations of the piezoelectric effect the following equation:

$$\begin{cases} p_i = e_{i,k}u_k + \varepsilon_{i,j}^S E_j \\ t_m = c_{m,k}^E u_k - e_{i,m} E_i \end{cases} \quad (4)$$

Coefficients in (4) are determined by the solution of the equations (3) with respect to (p, t).

3. Elastic modules of thin films of barium titanate

For example, consider a single crystal of barium titanate. The value of its spontaneous polarization at room temperature p_0 = 0.26 C/m^2. Using the experimental values of g-constants of [8], for electroelastic coefficients of the Landau potential obtain Q_{11}=0.1106, Q_{12}=-0.0442, Q_{44}=0.0585 in units of m^4/C^2. For further calculations [8] take the value of high-temperature compliances s_{11}=8.33, s_{12}=-2.68, s_{44}=9.24 in units of 10^{-12} m^2/N, the potential of the eighth degree of $G(p_1, p_2, p_3)$ take [4].

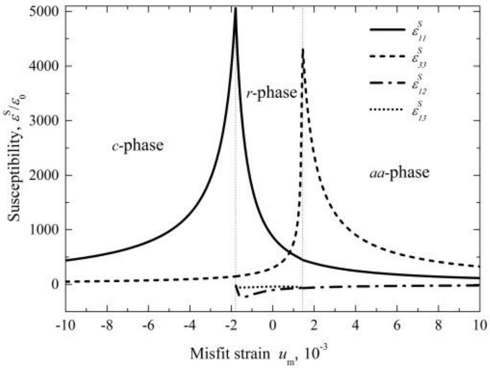

Fig. 1. Misfit strain dependence of different components of susceptibility in the barium titanate thin film at T = 300 K. The dotted vertical lines indicate phase boundaries at u_m=-1.8×10^{-3} and u_m=1.45×10^{-3}.

For the barium titanate film at room temperature and accepted values of the parameters of the potential (1), there are three basic of states - three low-symmetry phase: *c* - phase with symmetry P4mm and the direction of the spontaneous polarization is normal to the plane of the film $p_x=0, p_y=0, p_z\neq 0$; *aa* - phase symmetry Amm2 with polarization, located along the diagonal in the film plane $p_x=p_y\neq 0$, $p_z=0$; and *r* - phase symmetry Cm with the polarization direction intermediate between these two states $p_x=p_y\neq 0$, $p_z\neq 0$. On the axis of misfit strain all phases border each other along the lines of second-order transitions. The material constants calculation based on the system (7) for the film of barium titanate is performed near the ground state, which depends on the magnitude u_m - misfit strain. As can be seen from the phase diagram [9], the phase at room temperature exist in the following areas: *c* - phase at u_m<-1.8×10^{-3}, *r* - phase at -1.8×10^{-3} <u_m<1.45×10^{-3}, and *aa* - phase at u_m>1.45×10^{-3}.

The values of the component of dielectric susceptibility $\varepsilon^S_{i,j}$ depending on the magnitude of misfit strain film of barium titanate at a temperature of T = 300K shown in Fig. 1. The phase transition *c-r* accompanied by an increase $\varepsilon^S_{11}=\varepsilon^S_{22}$ that corresponds to the appearance of planar polarization components. The anomaly ε^S_{33} in the phase transition *r* - *aa* associated with the disappearance of the normal component of polarization. At the phase boundaries extreme components of the permittivity are finite: $\varepsilon^S_{11}=5059$ at *c-r* phase boundary with u_m=-1.8×10^{-3} and $\varepsilon^S_{33}=4303$ at u_m=1.45×10^{-3} at the phase boundary *r-aa*.

The set of material constants in equation (7) for different phases varies and is determined by the symmetry of the ground state. For convenience in the calculation of material constants will use a single, original, coordinate system with axes located along the high-symmetry directions of the cubic phase. In *c* - phase the set of material constants of the equations (7) are ε^S_{11}, ε^S_{33}, e_{31}, e_{33}, e_{15}, c^E_{11}, c^E_{33}, c^E_{12}, c^E_{13}, c^E_{44}, c^E_{66}, the same as that of the bulk sample of the barium titanate. In *aa* - phase symmetry material are defines constants ε^S_{11}, ε^S_{12}, ε^S_{33}, e_{11}, e_{12}, e_{13}, e_{16}, e_{34} and c^E_{km}, with the index values km = 11, 12, 13, 16, 33, 36, 44, 45, 55.In the *r* - phase have the ε^S_{ij} material constant values with indexes ij = 11, 12, 13, 33; e_{im} - with indexes im = 11, 12, 13, 14, 15, 16, 31, 33, 34, 46. For the elastic constants c^E_{km} values km equal with simultaneous permutation of the indices 1-2, 4-5. These indexes correspond to nonzero constant (7) which have different magnitudes.

The behavior of the elastic moduli c^E_{km} as a function of misfit strain shown in Fig. 2. Here, the main features associated with phase transitions. As the misfit strain at the boundary *r* and *c* phases elastic modulus c^E_{44} decreases to zero. Further, in the *r*-phase, it increases reaching a maximum at 98 GPa with misfit strain u_m=0.74×10^{-3}, and then decreases. At the boundary between the phases *r* - *aa*, its value is equal to 56.2 GPa. With further increase of misfit strain u_m, in *aa* - phase, the elastic modulus c_{44}^E increases monotonically. Within the domain of existence of *r*-phase, most of the elastic moduli behaves abnormally: near the borders there is a sharp change in the absolute value, then the module reaches the extreme value.

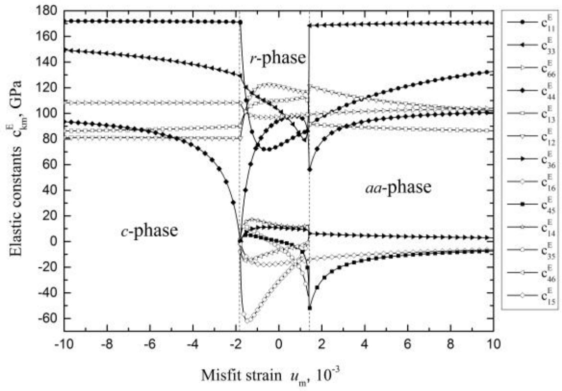

Fig. 2. Misfit strain dependence of different components of elastic modulus of the barium titanate film at the temperature T = 300K. The dotted vertical lines indicate phase boundaries at u_m=-1.8×10^{-3} and u_m=1.45×10^{-3}.

Conclusion

These results show a significant change in the elastic properties of thin films as compared with the bulk material. Change is particularly high near the phase boundaries, where the misfit strain of the film is close to the critical value. For barium titanate there is a region of small misfit strain, the region *r*-phase, where the most significant changes occur. Calculations show that by controlling the value of the misfit strain can control the properties of the films. This can be achieved by the selection of the substrate material and sputtering technology.

Acknowledgements

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