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DIMENSIONAL EFFECTS AND SURFACE ENERGY OF FERROELECTRIC CRYSTALS

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To describe the surface tension, a model of the surface layer of atomically smooth ferroelectrics was considered, neglecting the surface roughness. It is believed that a necessary condition for the manifestation of nanostructured properties of a condensed medium is the size dependence of its properties. The surface layer of an atomically smooth crystal consists of two layers, d(I) and d(II). The layer with thickness h = d is called layer (I), and the layer at h≈10d is called layer (II) of an atomically smooth crystal. At h≈10d, the size dependence of the physical properties of the material begins to appear. When h = d, a phase transition occurs in the surface layer. It is accompanied by abrupt changes in physical properties, for example, the direct Hall-Petch effect is reversed. It can be concluded that both previous and current results of studies of the surface of condensed media (metals, dielectrics, ferroelectrics, etc.) are due to size effects and the final structures of their existence.

Keywords: surface tension, surface layer, glycine, atomic volume, size dependence.

Introduction

The development of experimental methods of oriented growth of one crystal on the surface of another led to the possibility of obtaining films and superlattices of complex oxides. The structure, size and morphic effects of such heterostructures differ significantly from the structure and properties of bulk single crystals of the same composition [1].

At present, it is also important to create materials, including composite materials, with ferroelectric properties, as well as with multiferroic properties, which can be used, for example, in the manufacture of memory elements or long-term storage media, high-capacity capacitors, microscopic power sources, etc. [2]. Ferroelectric nanocomposite materials as objects whose properties are extremely sensitive to the size effects caused by the increased role of surface effects, which opens up new possibilities for modifying the properties of materials and functional parameters of the devices, special attention is paid [3].

At present, despite a large number of theoretical and experimental studies on the properties of heterogeneous ferroelectric systems, there is no single complete understanding of the laws of modification of the properties of the components of composites [1-3]. It is believed that a necessary condition for the manifestation of nanostructured properties of a condensed medium is the size dependence of its properties [4].

"Normal" size effects are associated with the contribution of surface energy to Gibbs energy. They are called the size effects of the first kind (after Shcherbakov L.M. [5]). Such size effects are characteristic of any systems and are determined by the scattering of quasiparticles (electrons, phonons, etc.) at the boundaries of the system. The phase size effects (size effects of the second kind) are determined by the whole collective of atoms in the system (collective processes). Such size effects are observed only in nanoclusters and nanostructures [6].

In addition to these classical size effects, there are quantum-size effects [7] associated with the quantization of the energy of charge carriers whose motion is limited in one, two, or three directions. The presence of quantum size effects imposes fundamental restrictions on the use of ultra-small nanoelectronic elements [8]. Quantum-size effects are observed when the size of the structure is comparable with the de Broglie wave (~ 0.01 - 0.1 nm).

In this paper, we consider a model of the surface layer of atomically smooth ferroelectrics, neglecting the surface roughness.

1. Surface energy of some ferroelectrics

In [9], the model of the surface layer of atomically smooth metals proposed by us was generalized. Schematically, this model is presented in Fig. 1.

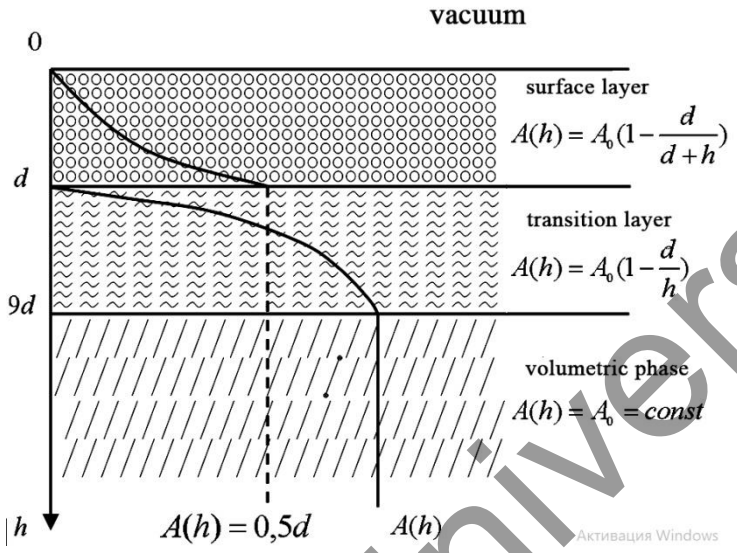

Fig.1. Schematic representation of the surface layer [9].

The surface layer of an atomically smooth metal consists of two layers, d(I) and d(II). The layer with thickness h=d is called layer (I), and the layer at h≈10d is called layer (II) of an atomically smooth crystal (Fig. 1). At h≈10d, the size dependence of the physical properties of the material begins to appear. When h=d, a phase transition occurs in the surface layer. It is accompanied by abrupt changes in physical properties, for example, the direct Hall-Petch effect is reversed [10]. The values of the d(I) layer for some metals are given in table 1.

Table 1. The thickness of the surface layer d(I) of some pure metals [9]

Me	d, nm	Me	d, nm	Me	d, nm	Me	d, nm	Me	d, nm	Me	d,nm
Li	0.7	Sr	5.8	Sn	1.4	Cd	1.3	Fe	2.2	Gd	5.3
Na	1.5	Ba	6.2	Pb	1.8	Hg	0.6	Co	2.0	Tb	5.3
K	2.6	Al	1.5	Se	1.3	Cr	2.7	Ni	1.9	Dy	5.3
Rb	2.9	Ga	0.6	Te	2.5	Mo	4.6	Ce	3.8	Ho	5.5
Cs	3.6	In	1.1	Cu	1.6	W	5.8	Pr	4.2	Er	5.5
Be	1.3	Tl	1.9	Ag	2.2	Mn	2.0	Nd	4.5	Tm	5.2
Mg	2.2	Si	3.4	Au	2.3	Tc	3.6	Sm	4.4	Yb	4.6
Ca	4.9	Ge	2.8	Zn	1.1	Re	4.6	Eu	5.8	Lu	5.7

Experimentally, the thickness d (I) can be determined by the method of sliding x-rays. Thus, for gold and silicon, d(I) = 2.4 and 3.4 nm were obtained [11], respectively, which almost coincides with the table. 1.

To determine the thickness of the surface layer of various compounds, we used the dimensional dependence of some physical property A(r):

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$$A(r) = A_0 \cdot \left(1 - \frac{d}{r}\right), \qquad r >> d$$
$$A(r) = A_0 \cdot \left(1 - \frac{d}{d+r}\right), \quad r \le d. \qquad (1)$$

The parameter d is associated with the surface tension σ by the formula:

$$d = \frac{2\sigma\upsilon}{RT}. \qquad (2)$$

Here, σ is the surface tension of the bulk sample; υ is the volume of one mole; R is the gas constant; T is temperature. In the work [9], and also [12], it was shown that the relation is fulfilled with great accuracy:

$$\sigma = 0.7 \cdot 10^{-3} \cdot T_m, \qquad (3)$$

where T_m is the melting point of the solid (K). The ratio is performed for all metals and for other crystalline compounds. If we substitute it in (2), then at $T = T_m$ we get:

$$d(I) = 0.17 \cdot 10^{-3} \upsilon. \qquad (4)$$

Equation (4) shows that the thickness of the surface layer d (I) is determined by one fundamental parameter - the molar (atomic) volume of the element ($\upsilon = M/\rho$, M is the molar mass (g/mol), ρ is the density (g/cm^3)), which periodically changes in accordance with the table D.I. Mendeleev.

Table 2. Surface tension and thickness of the surface layer of ferroelectrics

Ferroelectric	T_m, K	σ, J/m^2	d(I), nm	d(II), nm
$Ba(NbO_3)_2$	1728 (T_C = 393)	1.329	13.1	131
ТГС	423 (T_C = 320)	0.296	32.5	325
$PbTiO_3$	1836 (T_C = 766)	1.285	7.1	71
$SrTiO_3$	2363 (T_C = 10)	1.654	6.1	61
$FeTiO_3$	1723 (T_C < 120)	1.206	5.2	52
$LiNbO_3$	1516 (T_C ~ 1483)	1.061	5.4	54
$KNbO_3$	1373 (T_C = 708)	0.961	6.6	66
$BiFeO_3$	1220 (T_N = 646)	0.654	7.8	78
$PbCu_3(VO_4)_2Cl_2$[1]	743	0.520	24.7	247

In our experiments, we used the size dependence of the dielectric constant [13], magnetic susceptibility [14], and luminescence intensity [15]. In the coordinates $A(r)/A_0 \sim 1/r$, a straight line is obtained in accordance with (1), the tangent of which gives d.

From table 2 it can be seen that the thickness of the surface layer d (I) of ferroelectrics varies from 5 nm for $FeTiO_3$ to 7.8 nm for $BiFeO_3$. Table 2 shows that the surface layer d(II) of some $Ba(NbO_3)_2$ and TGS ferroelectrics exceeds 100 nm, which is characteristic of Gleyther nanostructures [16]. But the size dependence of physical properties is also observed in this area. The surface layer d(II) ≈ 10d is attributed to the size effects of the first kind. Phase size effects (size effects of type II) are observed in the d(I) region. This area is very different from d(II). The phase transition at h = d can be described in the framework of the Landau mean field theory using the order parameter [17].

The rare mineral $PbCu_3(VO_4)_2C_{l2}$, discovered, studied in 1988 and named after the city of Leningrad (now St. Petersburg), has a d(II) surface layer thickness of over 247 nm. This is due, first of all, from equation (4) to a large atomic volume $\upsilon = M/\rho$. This means that the thickness of the surface layer depends on the complexity of the structure of the mineral.

2. Discussion of results

In the present work, we consider a model of the surface layer of atomically smooth crystals, neglecting the roughness of the surface, which at the cleavage surface in the vacuum of semiconductors are of the order of 0.05 nm or slightly more. Using the lattice parameter [18], we calculate the number of monolayers R in the d(I) layer of ferroelectrics.

Table 3. How many atoms are from the surface of ferroelectrics?

Ferroelectric	Number of atoms, R	Ferroelectric	Number of atoms, R
$Ba(NbO_3)_2$	a/c = 30/33	$FeTiO_3$	a/c = 10/5
ТГС	a/b/c = 35/26/57	$LiNbO_3$	a = 10
$PbTiO_3$	a/c = 18/17	$KNbO_3$	a/b/c = 10/14/9
$SrTiO_3$	a = 16	$BiFeO_3$	a/c = 14/6

An analysis of the rounded data of Table 3 shows that the number of monolayers in the d(I) layer for some $Ba(NbO_3)_2$ ferroelectrics and TGS lies in the range of 20-60.

Depending on how the transition from the volume to the surface of a solid body is realized, all surfaces can be divided on the cleavage in vacuum into singular, vicinal and diffusion. On singular surfaces, the transition from the solid to the vapor phase takes place within a single layer, on vicinal surfaces - the transition occurs through several crystallographic planes separated by monoatomic steps, and on diffusion surfaces - the transition from a solid to vapor phase takes place over several atomic layers (Table 3) .

The authors of [19] obtained images of the molecular resolution of the TGS polar surface in the contact mode of atomic force microscopy (AFM). According to their estimates, the width and height of the step of the transition layer in the domain wall were ~ 10 nm and ~ 6.9 nm, respectively. It was also suggested that circular protrusions and depressions, whose dimensions differed in the horizontal direction, and the height or depth, as a rule, was 0.6–0.8 nm, appear due to partial dissolution of the TGS surface by adsorbed water molecules, i.e. they are elements of a surface that degrades after splitting a crystal. One of the results of further research was the

observation of the domain structure of ferroelectrics in the nanometer size range in dynamics: during the transition from the ferroelectric phase to the paraphrase and in the process of depolarization in the switching process [20].

Another important result of TGS research is the observation of domain walls with a resolution close to atomic, which made it possible to measure their width [21]. Atomic force microscopy provides unique opportunities for the study of ferroelectric crystals, allowing you to directly visualize domains and record surface distributions of their characteristics, to which a significant number of publications have been devoted in the last decade (see review [22]). According to the results of [22], the height of the step between the TGS domains of a different sign leaves ~ 1 nm and the width of the DS ~ 30 nm (Table 3). The AFM method was used to study a number of ferroelectrics: barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), ferrite salt ($NaKC4H4O6$ $4H_2O$), aluminum guanidinium sulfate (GASH) $C(NH_2)_3Al(SO_4)_2$ $6H_2O$, and guanidinium aluminum sulphate (GASH) $C(NH_2)_3Al$ $(SO_4)_2$ 6H2O;) and others. [22]. Even in remote times, X-ray studies performed on $BaTiO_3$ crystals by Könzig and co-workers [23] showed that in surface layers with a thickness of about 100 (in our case, this is 131 Å, Table 3), the structure is different from the structure of the thickness. In the Curie region (below 120 °C), differences in the structure of the thickness and surface layer are less pronounced, which indicates some tetragonality of the $BaTO_3$ surface layers above the Curie point. Könzig suggested that these layers can be interpreted as Shotka-depleted ion layers due to impurities having a concentration of 10^{18} cm^{-3} and creating a field of about 10^5 - 10^6 V cm^{-1} (which turned out to be wrong in the light of modern research [22]).

Thus, it can be concluded that both previous and current results of studies of the surface of condensed media (metals, dielectrics, ferroelectrics, etc.) are due to the size effects and the final structures of their existence.

Conclusion

From table 2 it can be seen that the thickness of the surface layer d(I) of ferroelectrics varies from 5 nm for $FeTiO_3$ to 7.8 nm for $BiFeO_3$. Table 2 shows that the surface layer d(II) of some $Ba(NbO_3)_2$ and TGS ferroelectrics exceeds 100 nm, which is characteristic of Gleyther nanostructures.

It was shown that the relation is fulfilled with great accuracy: where T_m is the melting point of a solid (K). The ratio is performed for all metals and for other crystalline compounds. The resulting equation (4) shows that the thickness of the surface layer d(I) is determined by one fundamental parameter — the atomic volume of the element.

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