J. Nano- Electron. Phys.
2 (2010) No3, P. 84-93

PACS number: 64.75.Nx

MODELING OF THE SOLID SOLUTION FORMATION PROCESS IN In_2O_3 - HfO_2 SYSTEM AT HEATING IN THE AIR

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The ionic radiuses for cations, namely, for indium, hafnium, anion, and anion vacancy on the Templiton and Dauben scale, were calculated based on the mathematical models of the solid solution formation in In_2O_3-HfO_2 *system. The phase transition in indium oxide, which is connected with disorder of anion vacancies in the C-type lattice, was revealed. The formation of solid solutions in* In_2O_3-HfO_2 *system occurs based on the disordered* C^1*-type phase of indium oxide. It was established that the limited solid solutions of the subtraction-substitution and subtraction-substitution-intrusion types are formed during the sample sintering at* 1450 °C *and* 1600 °C *in the air medium. The type of solid solution in* In_2O_3-HfO_2 *system depends on the sizes of indium and hafnium cations. The solid solution formation energies in the system were determined. It was found that the conductivity, concentration, and charge carrier mobility depend on the solid solution type and not on the cation valence of dissolved impurity.*

Keywords: *INDIUM OXIDE, HAFNIUM DIOXIDE, SOLID SOLUTION, PHASE TRANSITION.*

(Received 03 September 2010, in final form 28 October 2010)

1. INTRODUCTION

Crystalline structure of Me_2O_3 (Sc_2O_3, In_2O_3, Y_2O_3, Ce_2O_3, Pr_2O_3, Tb_2O_3 R_2O_3 are the rare-earth oxides) oxides belongs to the structure of the *C*-pyrochlore type and contains 25% of naturally ordered anion vacancies, which are the structure elements. Hafnium dioxide has monoclinic, tetragonal, and face-centered cubic (fcc-) ordered structure of the *F*-fluorite type, and based on this modification it is the structural analogue of CeO_2 ,PrO_2, ZrO_2, TbO_2. Conductivity of oxide materials can be ionic, electronic, proton, and mixed one [1] depending on the structure, phase transformations while heating in different mediums, under the action of electric field, etc.

Electronic structure of Me_2O_3 and MeO_2 oxides has the valence band $2P^-$ and different conduction bands. Conduction band of In_2O_3 is a 3*d*-state, of HfO_2 – a 4*d*-state. Materials based on In_2O_3 with additions of HfO_2 are of a practical interest as the materials with electrical conduction. Such materials can be used in different technical and agricultural fields as the solar energy converters, energy sources, solid fuel, materials of radio electronics [2, 3].

Defects, which are the structure elements, can be combined with impurity atoms and form the defect systems in the form of the donor-acceptor pairs. Accumulation of such defects leads to the changes in polymorphic transformation temperatures, physical properties, solid solution dissociation [4].

Thermodynamic calculation of solid solutions based on the pyrochlore structure with structure defects is a complicated process of selection of true models of the solid solution formation, since the model of solid solution defines the form of thermodynamic potential, and the final result as well. Calculation of energy coefficients which determine the change in the internal crystal energy cannot be performed with satisfactory accuracy, and it is reasonable to find them by the comparison with the experiment.

The aim of the present work is to develop the model of the solid solution formation process in In_2O_3-HfO_2 system.

2. INVESTIGATION RESULTS

2.1 Mathematical model of determination of the atomic radiuses in In_2O_3-HfO_2 compounds

To construct the true model of solid solution based on indium oxide with additions of hafnium dioxide, it is necessary to determine the exact values of ionic radiuses of indium and hafnium cations, which form solid solution.

The reason is the fact that the values of ionic radiuses cannot be considered as the absolute ones, and it seems that each scale is applicable only for the description of a certain structure type. Linearity of dependence of the lattice parameters of compounds on the cation radius (at fixed anion), presented in the given scale and obtained depending on the geometry of the given structure, at the condition of presence of a dense packing can serve as the validity criterion. Thus, using the ionic radiuses of cations on the Belov-Bokiy scale, which is the most applicable for structures of NaCl-type, the unit cell parameter is determined by formula

$$a_{(k)} = 2(r_k + r_a),\ \Delta a_k/\Delta r_k = 2, \tag{1}$$

where r_k and r_a are the cation and anion radiuses.

Cubic structure of indium oxide of the *C*-pyrochlore type is close to the *F*-fluorite one and differs by the vacancy equal to 1/4 of anion sites and by the doubled lattice parameter. Vacant and filled anion sites appropriately alternate. For an octant of unit cell of the ordered *C*-type structure one can write the lattice parameter of indium oxide using the ionic radiuses

$$0,5a = D_c\left(r_k + 0,75r_a + 0,25r_{v(O)}\right), \tag{2}$$

where a is the lattice parameter; $D_c = 2{,}336$ is the coefficient for cubic structures of rare-earth oxides on the Templiton and Dauben scale; r_a is the ionic radius of oxygen; $r_{v(O)}$ is the radius of anion vacancy. Using this scale it is necessary to find the values of ionic radiuses of indium and hafnium. Cation radius of indium can be determined on this scale if take the value of the lattice parameter of indium oxide (a = 1,0120 nm), which is on the rectilinear dependence plotted using the known values of the lattice parameters for compounds of Me_2O_3-type versus the cation radiuses (Fig. 1) [5]. The cation radius of indium is r_k = 0,0763 nm, the radius of oxygen is equal to $r_{(O)}$ = 0,1374 nm, and the radius of anion vacancy defined by the formula (2) is $r_{v(O)}$ = 0,1380 nm.

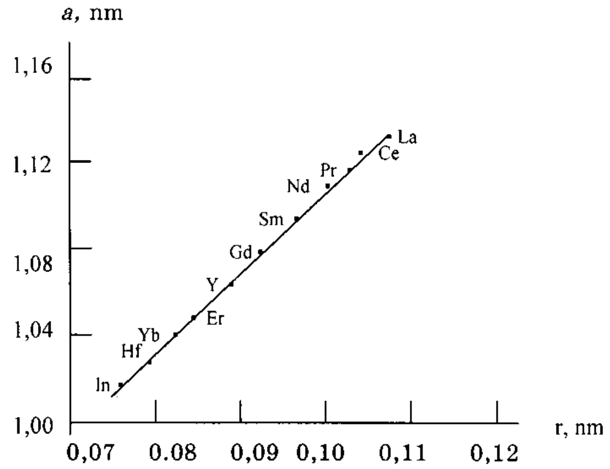

Fig. 1 *– Dependence of the lattice parameter of cubic structures of C-Me_2O_3-type on the cation radius*

Since the interaction between ions in the cubic *C*-type lattice is central, the directions [110], [111], [100] will be the shift directions caused by the difference of the oxygen ion radius and the anion vacancy one.

Consider the atomic packing in the *C*-type structure of the ordered in the plane (110) phase taking into account the defined radius values of indium cation, oxygen, and anion vacancy. It represents the atomic distribution in the form of irregular hexahedron. Oxygen atoms and ordered anion vacancies form the distorted prism consisted of six oxygen atoms and two ordered anion vacancies, which are centered by indium cations or free.

Fcc-structure of hafnium dioxide of the *F*-fluorite type with the unit cell parameter $a = 0{,}53$ nm exists at the temperature 2750 °C, and at lower temperatures it exists in the form of a solid solution with additions of other oxides [6]. Real lattice parameter of hafnium dioxide at the temperature 25 °C is unknown.

For the structures with the *F*-phase on the Templiton and Dauben scale the following relation takes place:

$$\frac{\Delta a_k}{\Delta r_k} = \frac{4}{\sqrt{3}} = 2,3094 = D_F \, . \tag{3}$$

Parameter of the cubic structure of hafnium dioxide can be found if suggest that the geometric probability $P(a_{\mathrm{Hf}})$ of the lattice parameter of hafnium dioxide is determined on the Templiton and Dauben scale when comparing the lattice parameters of hafnium dioxide and indium oxide

$$P(a_{\mathrm{Hf}}) = \frac{2a_{\mathrm{F}}}{a_{\mathrm{C}}} = \frac{D_{\mathrm{F}}}{D_{\mathrm{C}}} \, ; \; a_F = \frac{a_{\mathrm{C}} D_{\mathrm{F}}}{2D_{\mathrm{C}}} \, . \tag{4}$$

Parameter of the cubic lattice of hafnium dioxide of the *F*-type is equal to $a_{\mathrm{F}} = 0{,}5002$ nm. Using the last value it is possible to find the radius of hafnium cation on the Templiton and Dauben scale and the dependence

$$r_{\mathrm{Hf}} = \frac{a_{\mathrm{Hf}}\sqrt{3}}{4} - r_{(O)} = 0,08\,\mathrm{nm}\,. \qquad (5)$$

If double the value of the cell parameter of hafnium dioxide and add the anion vacancies, we obtain the lattice parameter of hafnium oxide in the *C*-type structure

$$2a_F + 0,25r_{v(O)} = a_0(\mathrm{Hf_2O_3})\,. \qquad (6)$$

It is possible to estimate the radius of anion vacancy in hafnium oxide using the formula

$$r_{v(\mathrm{O})}(Hf) = \frac{a_{\mathrm{F}} \cdot r_{v(\mathrm{O})}(In^{3+})}{a_{\mathrm{C}}} \qquad (7)$$

and obtain the radius value of anion vacancy in the lattice of hafnium oxide, which is equal to $r_{v(O)}$ = 0,1364 nm.

The lattice parameter for Hf_2O_3 in the *C*-type structure determined by the formula (6) is a_{C} = 1,0345 nm. This value of the lattice parameter gets on the linear dependence (Fig. 1) [4, 5]. In accordance with this data one can suggest that the *C*-type structure of hafnium oxide can exist under oxygen evaporation from the lattice of hafnium dioxide at high temperatures in different mediums. Hf_2O_3 compound in the cubic *C*-type structure is not found in publications.

According to the data of [6], along with the solid solutions based on polymorphous modifications of hafnium dioxide, the compounds with cubic phases coexist: below 1900 °C − the *C*-pyrochlore phase; above this temperature − the *F*-fluorite one.

There are structural analogues of the cubic *C*-pyrochlore lattice, such as, Pr_2O_3, Ce_2O_3, Tb_2O_3, the presence of which allows to state the existence of hafnium oxide with the *C*-pyrochlore lattice and Hf_2O_3 composition.

It is known from publications that hafnium dioxide is stable in chemical composition in a wide temperature range, and it exists in monoclinic and tetragonal modifications. Cubic *F*-modification of hafnium dioxide exists as the solid solution HfO_2-R_2O_3 [6, 7].

Obtained values of the radiuses for cations, indium and hafnium, oxygen, anion vacancies allow to construct the model of solid solutions in In_2O_3-HfO_2 system under the condition of the presence of cubic phases, data of oxides, and known phase transformations in the given temperature range.

2.2 Models of the solid solution formation in In_2O_3-HfO_2 system in the temperature range of 25-1600 °C in the air medium

To investigate the interaction in In_2O_3-HfO_2 system samples were prepared from In_2O_3 and HfO_2 powders. Additions were injected into indium oxide in quantity of 0,5-50 mole% of HfO_2. Samples were sintered in the temperature range of 1000-1600 °C in the air medium with further air hardening. Phase composition and the lattice parameters were obtained by the X-ray method. The lattice parameter was determined with error ± 0,0001 nm. The mass loss was ± 0,0002 g. Calculation of the phase transformation energy and the solid solution formation energy was carried out with error ± 0,01 eV. The relative error in the determination of the resistivity ρ, the charge carrier concentration n, and the mobility μ was 3-5%.

2.2.1 Phase transformation in indium oxide

In indium oxide during its heating in the X-ray camera in the temperature range of 25-1000 °C in the air medium while plotting the profile of (211), (222), (400), (622) lines, we discovered their splitting in the temperature range of 500-550 °C. This line splitting corresponds to the phase transformation of the ordered C-type phase into the disordered C^1-type phase. This transition is the first order phase transition and the reversible one, if cool samples from temperatures not higher than 1000 °C. Temperature 550 °C is a critical point for continuous function $y = f(a)$, where this function endures discontinuity of the first order. Transition to the C^1-type phase occurs. New phase is considered to be the disordered one with respect to the initial phase. The lattice parameter of the C^1-type phase, which is determined by the extrapolation of the dependence of the lattice parameters under heating into point at room temperature (the thermal expansion is excluded) (Fig. 2), has the value $a^1_C = 1{,}0115$ nm ± 0,0001 nm.

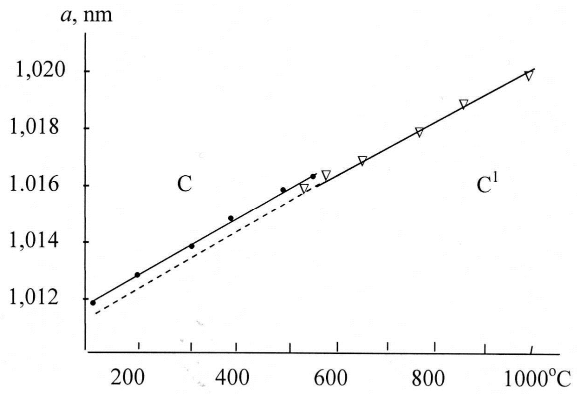

***Fig. 2** – Temperature dependence of the lattice parameter of indium oxide while heating in the air medium: C is the ordered cubic phase; C^1 is the disordered cubic phase*

2.2.2 Mathematical calculation of the phase transformation energy and the solid solution formation energy in In_2O_3-HfO_2 system

C-C^1 transition energy can be estimated using the Boltzmann equation for different states of the system with the probability

$$P[A(T)] = A_0 \exp(-\phi/kT)\,, \qquad (8)$$

where A_0 is the general lattice vibration frequency of initial positions; A is the function of the system physical parameters versus the temperature (the order inversion of anion vacancies in the C-type structure); ϕ is the state energy of the solid. For two states of the solid at the temperatures T_1 and

T_2, the relative probability of finding the state energy of the solid can be obtained by the following relation:

$$\frac{P[A(T_1)]}{P[A(T_2)]} = \frac{\exp(-\phi/kT_1)}{\exp(-\phi/kT_2)}. \tag{9}$$

Energy of the C-C^1 phase transition of indium oxide is equal to $\phi = 0{,}77$ eV obtained by the formula

$$\phi = \left(T_1T_2/\left(T_2 - T\right)_1\right)k\ln\left(V_1/V_2\right), \tag{10}$$

where V_1, V_2 are the volumes of the unit cells of indium oxide at different temperatures.

At high temperatures (1000-1600 °C) the change in the chemical composition (oxygen content) of indium oxide occurs. Additional anion vacancies, which lead to the change of all physical properties of the oxide (increase in the lattice parameter, weight and resistance contraction, change in the sample coloration from yellow to black), appear in the structure.

Appearance of additional anion vacancies, which distort the atomic oscillations, leads to the local complex deformation interactions between atoms in the lattice. In such areas the energy absorption takes place that is accompanied by the formation of local regions with violated electron neutrality. Surplus charge of anion vacancies is compensated by the formation of color centers. Reduction of indium oxide with the formation of color centers is realized by the following scheme:

$$\mathrm{In_2O_3} \rightarrow \mathrm{In_2O_{3-0,5x}}\, v[\mathrm{F}]_{0,5x} + 0{,}25x\, \mathrm{O_2} \uparrow, \tag{11}$$

where x is the deviation from stoichiometry; v[F] are the color centers formed in accordance with the reaction

$$\mathrm{In}^{2+} + v(\mathrm{O}) \rightarrow \mathrm{In}^{3+} + v[\mathrm{F}]. \tag{12}$$

Change in the free energy connected with the oxide reduction is determined by the following dependence:

$$\Delta\Phi = \left(\frac{\phi_{v(O)}}{2} - \frac{\phi_{v[\mathrm{F}]}}{2} + A - \frac{F}{4}\right)x - T\Delta S, \tag{13}$$

where $\phi_{v(\mathrm{O})}$ is the formation energy of anion vacancy; $\phi_{v[\mathrm{F}]}$ is the formation energy of color center; A is the electron affinity energy; F is the transition energy of oxygen to gaseous phase. Entropy change ΔS during the oxide reduction is defined by the relation

$$T\Delta S = kT\ln x = \gamma kT\ln\frac{\Delta V}{V} = kT\ln\frac{[1{,}5N]!}{[(1{,}5 - 0{,}5x)N]!(N_{0{,}5x})!}, \tag{14}$$

where ΔV is the change in the unit cell volume under formation of additional anion vacancies; γ is some coefficient, which takes into account the volume change around defect and is defined as the ratio of the anion vacancy radius to the oxygen radius.

Using the experimental dependence of $\ln[x/(3-x)]$ on $1/T$, the energy of the indium oxide reduction was determined: $\phi = 1,61$ eV.

The energy of the indium oxide reduction defined by the change in the unit cell volume at different temperatures was found by the formula (10). The values of the defect formation energy in anion sublattice of indium oxide obtained experimentally by the deviation from stoichiometry and by the formula (10) coincide that implies about the correct mathematical model. Using the ionic radiuses of indium and hafnium cations one can suggest that in the given system the formation of limited solid solutions of the substitution-subtraction and substitution-intrusion-subtraction types is possible.

Formation of solid solutions based on indium oxide should be realized by the following scheme: hafnium dioxide is stabilized to the F-type cubic structure, and, probably, to the C-type cubic structure, then it is dissolved in the C^1-type nonstoichiometric phase of indium oxide. Experimental values of the solid solution parameters in the given system at sample sintering are presented in Fig. 3. Breaks at the concentrations of hafnium additions 0,5-5 mole% and 5-15 mole% are observed on this dependence.

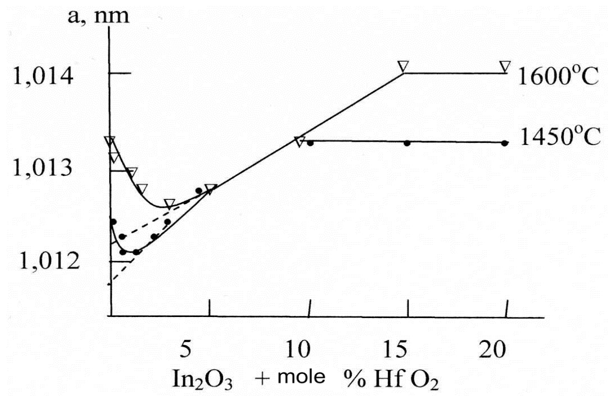

***Fig. 3** – Dependence of the lattice parameters of solid solutions based on indium oxide versus the concentration of hafnium dioxide after sample sintering*

Extrapolation of rectilinear dependence of the lattice parameter of solid solution to zero concentration of hafnium dioxide addition indicates the degree of reduction of pure indium oxide and solid solutions with small additions of hafnium dioxide at different temperatures. Solid solutions are formed based on C^1-type disordered phase. After sample sintering at 1600 °C in the air medium, the same breaks are observed on the dependence of the resistivity in the given concentration range of hafnium dioxide (Fig. 4). The same changes were also observed on the dependence of the charge carrier concentration and their mobility on the solid solution composition (Table 1).

In In_2O_3-HfO_2 system one can suggest the formation of solid solution of the subtraction-substitution type on basis of nonstoichiometric indium oxide of the C^1-type with 0,5-5 mole% of hafnium dioxide using the mathematical model

$$(1-y)\,\mathrm{In_2O_{3-0,5x}}\,v[\mathrm{F}]_{0,5x} + y\,\mathrm{HfO_2} \rightarrow (\mathrm{In}^{3+}_{1-y}\,v[\mathrm{F}]_{0,5x}\,\mathrm{Hf}^{4+}_{y})_2\,\mathrm{O}_{3-0,5x+0,5y} + 0,25x\,\mathrm{O_2}\uparrow, \quad (15)$$

where y is the HfO_2 addition.

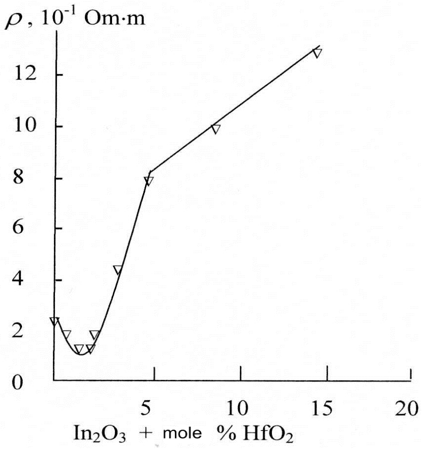

***Fig. 4** – Dependence of the sample resistivity on the concentration of hafnium dioxide additions after sintering at 1600 °C*

***Table 1** – Experimental values of the charge carrier concentration and mobility in the samples containing the single-phase solid solution based on indium oxide with HfO_2 additions after sintering at 1600 °C*

mole% of HfO_2 in solution	n 10^{-19}, cm^{-3}	μ, cm^2/v_c
0,5	9,8	52
1,0	9,5	51
1,5	9,3	50
2,0	9,2	48
3,0	8,9	42
5,0	7,7	30
10,0	6,7	18
15,0	6,0	10

Change in the free energy of the solid solution formation of the subtraction-substitution type based on nonstoichiometric indium oxide of the C^1-type with 0,5-5mole% of hafnium dioxide is determined by the formula:

$$\Delta\Phi(x,y) = [0,5\phi_{v(O)} - 0,5\phi_{v(F)} + A - 0,25F](x) + \phi_{subst}(y) - T\Delta S(x,y)\,, \quad (16)$$

where $\phi_{v(\mathrm{O})}$ is the free energy of the anion vacancy formation; $\phi_{v(\mathrm{F})}$ is the free energy of the color center formation; A is the electron affinity energy; F is the transition energy of oxygen to gaseous phase; $\phi_{subst}(y)$ is the free energy of substitution of In^{3+} cations on Hf^{4+}; $\Delta S(x, y)$ is the entropy change of the solid solution formation.

In the limited region of solid solution of the subtraction-substitution type during sintering of the samples with In_2O_3 + 0-1,5 mole% of HfO_2 composition at the temperatures 1450 °C and 1600 °C, the decrease in the lattice parameter, resistivity, deviation from stoichiometry, and slight decrease in the charge carrier concentration and mobility takes place.

In the samples of In_2O_3 + 2-5 mole% of HfO_2 composition the increase in the lattice parameter and resistivity, and the decrease in the charge carrier concentration and mobility occurs. Such changes in the properties of the samples containing solid solution of the subtraction-substitution type can be explained by the fact that the increase in the hafnium dioxide concentration in solution leads to the decrease in the defect concentration and stabilization of the solution. The solution formation energy defined by the formula (10) is equal to $\phi = 1{,}17$ eV.

In the samples of $In_2O_3 + 5\text{-}15$ mole% of HfO_2 composition during sintering at the mentioned temperatures the further increase in the lattice parameter and resistivity, and the decrease in the charge carrier concentration and mobility takes place. For these compositions the slopes of the single-phase solid solution are changed on the dependences of the lattice parameter and resistivity. Such changes in the properties of the solution indicate the formation of a new type of solid solution, namely, subtraction-substitution-intrusion.

In the samples containing more than 15 mole% of HfO_2 in the solution after sintering at 1600 °C, presence of the following phases was observed: C^1-type indium oxide and cubic F-type hafnium dioxide. Excess hafnium cations can penetrate into nonstructural positions and form the Frenkel pairs. These defects are additional sources of the decrease in the charge carrier concentration and mobility. Such solid solution of the subtraction-substitution-intrusion type can be presented by the mathematical model

$$(1-y)\,In_2O_{3-0,5x}\,\upsilon[F]_{0,5x} + y\,HfO_2 \rightarrow (In^{3+}_{1-y}\,\upsilon[F]_{0,5x}\,Hf^{4+}_{y-u}[Hf^{4+}]\upsilon(k)_u)_2\,O_{3-0,5x+0,5y}\,, \qquad (17)$$

where u is the concentration of interstitial Hf^{4+} cations; $\upsilon(k)$ are the Frenkel pairs. Dependence of u on the temperature T and composition y of the solid solution is determined by the minimum of the free energy using the formula

$$\Delta\Phi(x,y,u) = [0{,}5\phi_{\upsilon(O)} - 0{,}5\phi_{\upsilon(F)} + A - 0{,}25F](x) + \phi_{subst}(y-u) + \phi_{intr}(u) - T\Delta S(x,y,u)\,, \qquad (18)$$

where $\phi_{subst}(y-u)$ is the free energy of substitution of In^{3+} cations on Hf^{4+}; $\phi_{intr}(u)$ is the free energy of intrusion of Hf^{4+} cations into nonstructural positions of the indium oxide lattice; $\Delta S(x, y, u)$ is the entropy change of the solid solution of the subtraction-substitution-intrusion type.

The solid solution formation energy of the subtraction-substitution-intrusion type based on indium oxide with additions of hafnium dioxide is equal to $\phi = 0{,}87$ eV. Decrease of the solid solution formation energy is compensated by the energy gain due to the formation of the solid solution of the subtraction-substitution type. The substitution energy of hafnium cations into nonstructural positions (the Frenkel pairs) is 0,3 eV.

The total energy of the solid solution formation in $In_2O_{3\text{-}x}$ - HfO_2 system is equal to

$$\phi = \phi_{(C\rightarrow C^1)} + \phi_{S.s.(subtr-subst)} + \phi_{S.s.(subtr-subst-intr)} = 2{,}81\,\text{eV}\,. \qquad (19)$$

In the given system the specified defect concentrations control the solid solution formation of different types that leads to the changes in the structural and physical properties of the samples based on indium oxide with additions of hafnium dioxide.

3. CONCLUSIONS

1. While modeling the solid solution formation process, the complex dissolution mechanism of hafnium cations in the indium oxide lattice is discovered in In_2O_3 – HfO_2 system.
2. The mathematical model of the radius determination for In^{3+} and Hf^{4+} cations, oxygen, and anion vacancy on the Templiton and Dauben scale is developed, and the possibility of existence of hafnium oxide Hf_2O_3 with the *C*-type lattice under the reduction of hafnium dioxide is calculated.
3. $C \to C^1$ phase transformation in indium oxide is experimentally discovered, and the calculation model of the phase transformation energy is proposed.
4. The mathematical models of the solid solution based on indium oxide of the subtraction-substitution and subtraction-substitution-intrusion types are constructed.
5. Based on the studied models of interaction in In_2O_3 –HfO_2 system and experimental data, the anion vacancy formation energies and the solid solution formation energies (for the subtraction-substitution and subtraction-substitution-intrusion types) are determined.
6. According to the obtained data, one can suggest that the sample conductivity depends on the type of solid solution formed in the given system, but not on the valence of dissolved cations in the indium oxide lattice.

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