В Ы В О Д

Результаты исследований показывают, что применение в системах управления нечетких регуляторов, основанных на использовании теории нечетких множеств, позволяет успешно решать задачи обеспечения требуемых динамических свойств системы, так как в этих регуляторах происходит автоматическая подстройка коэффициентов усиления параметров, используемых для управления системой.

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AB-INITIO МОДЕЛИРОВАНИЕ ЭЛЕКТРОННЫХ СВОЙСТВ СВЕРХТОНКИХ ПЛЕНОК ОКСИДОВ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ ДЛЯ СЕНСОРНЫХ НАНОСИСТЕМ

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AB-INITIO SIMULATION OF ELECTRONIC FEATURES OF HYPERFINE RARE EARTH OXIDE FILMS FOR SENSORY NANOSYSTEMS

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Выполнено Ab-Initio моделирование электронных свойств сенсорных наноматериалов на основе редкоземельных оксидов (например, оксида иттрия). Предложен способ моделирования тонких пленок нанометрового масштаба в программном пакете VASP, заключающийся в имитации слоя материала с толщиной, равной размеру элементарной кристаллической ячейки. Разрыв атомных связей в кристалле по одной из координатных осей имитируется путем увеличения расстояния между атомными слоями по этой оси до значений, при которых стабилизируется величина свободной энергии. Установлено, что в сверхтонкой пленке редкоземельного оксида (при толщине пленки, близкой к 1 нм) валентная зона и зона проводимости явно не выявляются, запрещенная зона не формируется. Фактически тонкая пленка оксида редкоземельного элемента в области наномасштаба теряет диэлектрические свойства, которые достаточно отчетливо проявляются в континууме.

Ключевые слова: Ab-Initio, моделирование, сверхтонкие пленки, оксид редкоземельного элемента, сенсорная наносистема.

Ил. 8. Библиогр.: 15 назв.

Ab-Initio simulation of electronic features of sensoring nanomaterials based on rare earth oxides has been made by the example of yttrium oxide. The simulation method for thin films of nanometer scale consisted in the simulation of the material layer of the thickness equal to unit crystal cell size has been proposed within the VASP simulation package. The atomic bond breakdown in the crystal along one of the coordinate axes is simulated by the increase of a distance between the atomic layers along this axis up to values at which the value of free energy is stabilized. It has been found that the valence and conductivity bands are not revealed explicitly and the band gap is not formed in the hyperfine rare earth oxide film (at the film thickness close to 1 nm). In fact the hyperfine rare earth oxide film loses dielectric properties which were exhibited clear enough in continuum.

Keywords: Ab-Initio, simulation, hyperfine films, rare earth oxide, sensory nanosystem.

Fig. 8. Ref.: 15 titles.

Introduction. The technology advancement of sensory nanosystems requires novel materials with sensory properties determined by processes taking place at atomic and molecular levels in nanolayers and nanovolumes. When thin films in sensory nanostructures are of the nanoscale thickness, the change of fundamental properties of substances forming the films takes place. Because of the uncompensated bonds of surface atoms, properties of nanosized particles are similar to atomic surface properties of crystals conditioned by arrangement features of atoms at the phase interface as well as features of atom interaction and their displacements near crystal faces. Mentioned properties of nanoparticles and nanofilms are in particular determined by the breakdown of the translation symmetry of the crystalline structure, smaller number of neighboring atoms, and stronger anisotropy and oscillation anharmonicity. This results in the increase of the adsorbability, capability for ion and atom exchange, and contact interaction of units of sensory nanosystems. However, the analysis of above phenomena and behavior interpretation of nanoparticles in sensoring materials become complicated because of difficulties in the difference of their bulk and surface properties. In the nanosized objects a layer is located at the certain distance from the surface, the elemental composition, atomic and electron structures and so electronic features of which differ drastically from the electronic features of bulk material. The thickness of this layer depends on the nature of material and is defined by the characteristic size inherent to physical phenomenon under consideration.

The features of the atomic structure at the free surface of solid body appear in the relaxation and reconstruction processes. At the relaxation, the structure of atomic planes parallel with the surface remains the same as in the bulk but interplanar spacings at the surface change (usually shorten). The rapidly decreasing change of the interplanar spacing at the surface does not exceed few percent and covers several near-surface layers. The structure reconstruction results in that near the surface the lattice symmetry in the surface region differs sharply from the bulk lattice symmetry. The lattice spacing for such the structure differs from the lattice spacing in the bulk crystal. When the atom interaction is of the anisotropic type, the lattice irregularity results in the radical rearrangement of the atom bond geometry at the surface.

To solve problems of study and fabrication of sensory nanosystems based on thin dielectric films, effective methods for the simulation of physical properties of dielectrics are required. One of such methods for the investigation of dielectrics as active sensory materials is Ab-Initio simulation of their electronic features. Ab-Initio simulation allows characteristics of complex compounds to be predicted, dynamics of the parameter variation under conditions of external and internal (by the incorporation of point defects and their complexes) elastic deformation to be determined, and material composition for the acceptable properties of the sensoring nanostructures to be optimized.

Ab-Initio simulation of the electron properties of rare earth oxides: methodology. Hyperfine films of rare earth compounds (e. g. rare earth oxides) are used as active dielectric materials for quantum sensoring nanosystems [1, 2]. The application of rare earth oxides is conditioned by their high adsorption properties, in particular by the advanced adsorption of oxygen and hydrogen, providing optimal characteristics of sensoring nanosystems. Multilayer nanostructures of metal–dielectric–metal and metal-dielectric-semiconductor types based on thin films of rare earth oxides have been formed and studied for sensoring nanosystems including sensors for the control of multi-component atmospheres [3, 4].

Yttrium is a typical representative of the rare earth group, so rare earth oxides have been studied by the example of the simulation of the Y_2O_3 electronic features. This compound is good dielectric with the 5.8 eV band gap. Satisfactory matching of lattice parameters of yttrium oxide and silicon allows considering Y_2O_3 as a promising dielectric material for the microelectronic sensoring technology. Yttrium oxide has a bixbyite structure, i. e. it forms a body-centered cubic unit cell with 80 atoms and 1a–3 (№ 206) space symmetry group [5–8]. The crystal cell consisted of 6 square faces with 10.5818 Å sides at right angles one to another (Fig. 1). Every face crosses one of crystallographic axes oriented transversely to two others.

VASP (Vienna Ab-Initio Simulation Package) realizing Ab-Initio approach for quantum-mechanical calculations in molecular dynamics (MD) in terms of pseudopotentials with sets of primitive elements of plane waves is used as a modeling tool [9–13]. The above approach realized in VASP is based on a local density approximation (with free energy as a varied value) and a correct estimate of the instant electron ground state in every MD step as well as on the use of efficient matrix diagonalisation techniques and efficient Pulay density mixing schemes.

The interactions between the electrons and ions are described using Vanderbilt ultrasoft pseudopotentials (US–PP), or the projector-augmented-wave (PAW) method. Both methods allow to fulfil a considerable reduction of a required number of plane waves in the transition metal atoms. Moreover, forces needed for the relaxation of atoms to their ground states can be relatively simply calculated with the VASP program. VASP allows carrying out the evolution monitoring of the simulated system as a whole as well as a spatial displacement of single atoms included in the system, calculating their diffusion characteristics, and studying spin-dependent (in particular, magnetic) physical properties of material. VASP availability for the calculation of the dependence of above characteristics on temperature and external and internal elastic deformations is especially attractive to study active sensoring materials [11, 12].

In general the simulation problem of the atomic-structure and electronic properties of rare earth compounds is a selection of optimal calculation algorithms in the VASP program, matching of input parameters of the system simulated to obtain required calculation accuracy, and a selection of a certain method for the adequate determination of sensoring material properties studied. The main methodology used in VASP consists in the solution of the Shrodinger equation for the electron-nuclear subsystem of the structure simulated and in the calculation of the finite total energy, forces and other parameters and values. The projector-augmented-wave (PAW) method of the VASP program that allows lattice parameters to be correctly calculated, spin polarization and physical properties of material to be adequately evaluated is used in this work.

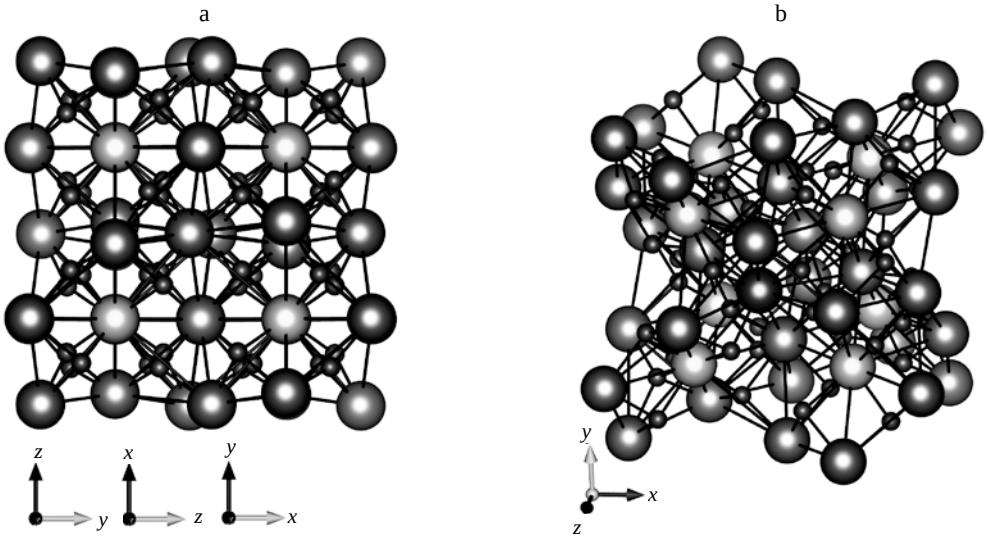

Fig. 1. Y_2O_3 three-dimensional cubic cell: a – view along Cartesian coordinates; b – spatial orientation; – yttrium atom; – oxygen atom

The idea of the simulation algorithm used consists in that the calculation begins from the relatively small number of atoms in the model crystallite and then the structure translation upto the required size is made on the basis of results obtained. So, in the framework of the VASP package an opportunity is given to simulate structures with low atom count where the temperature dependence of the atom motion is neglected. In another algorithm block, data resulted from the calculation of every single layer merge into one system. Then withdrawal/addition of atoms is performed to obtain lattice defect of specified type (vacancy, interstitial, or their complexes). At the next stage of the simulation algorithm realization, the selection of the procedure for the atom addition to the array simulated is made. For example, if a point defect (pictured as a sphere) is considered, the increase of its impact takes place on the principle of the sphere enlargement. Previously series of tests is made; in particular the calculation of optimal number of points that determine a degree of reciprocal space partition (*k*-points) is made as well as minimal energy of the system simulated is defined. Accuracy of the atoms coordinates determination in the system simulated depends on the number of *k*-points. For dielectrics it is enough ten points per unit cell.

Atomic structure and electronic properties of the bulk rare earth oxides. When the relaxation of the system simulated is made, parameters for the calculation of forces, as well as for the volume and shape changes of the crystalline cell are determined. The density of states and the energy-band structure of yttrium oxide were been calculated [14, 15]. The calculated densities of states are shown at the Fig. 2. The calculation of the density of states allowed the Fermi level equal to 1.5515 eV to be determined.

When the energy-band structure is calculated, the first Brillouin zone of the lattice which is considered as a unit cell of a reciprocal lattice having point symmetry of this lattice is determined. All Brillouin zones are replicas of the first zone: they are obtained by translating points pertinent to the first zone on the reciprocal lattice vectors. Fig. 3 shows the first Brillouin zone of Y_2O_3. Principal points of high symmetry in the first Brillouin zone are denoted as following: Γ is a center of the Brillouin zone; M, A, X are points located on directions (110), (111), (100) correspondingly.

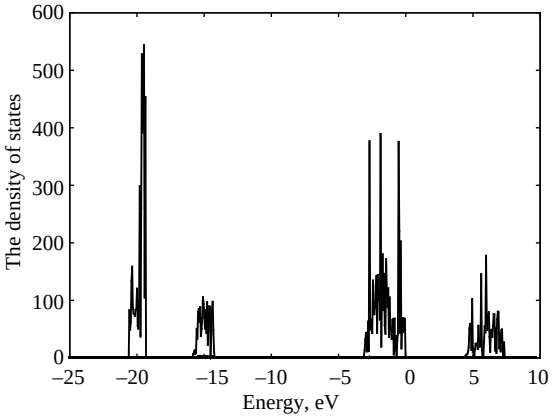

Fig. 2. Density of states of Y_2O_3
(the Fermi level is superposed with 0 eV energy value)

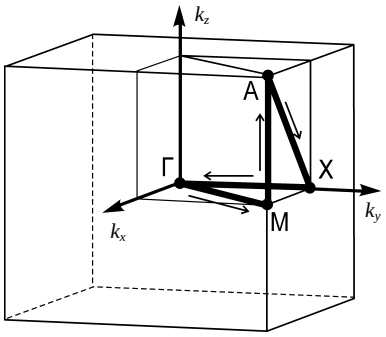

Fig. 3. Brillouin zone of Y_2O_3 rare earth compound

The construction of the first Brillouin zone enables defining a contour by which the energy-band structure should be calculated. The analysis of the structure and physical-chemical properties of rare-earth oxides showed that the Γ–M–A–X–Γ contour of the unit cell is of the greatest interest in the studies of Y_2O_3 compound. Analysis of the energy-band structure (Fig. 4) show that yttrium oxide is indirect dielectric with band gap E_g = 4,439 eV.

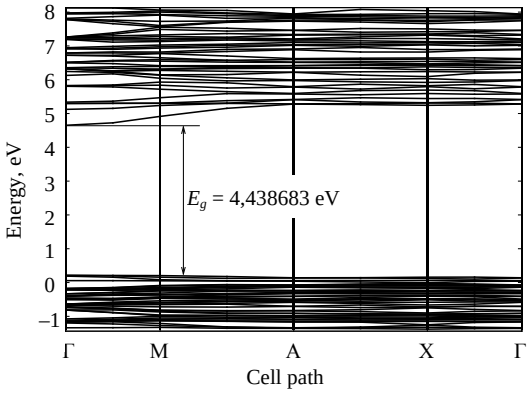

Fig. 4. Energy-band structure of bulk yttrium oxide
(the Fermi level is superposed with 0 eV energy value)

It can be assumed that the increase of the exchange energy results in the appearance of splits in the energy-band structure, and the indirect transition between the conduction band and valence band results in the polarization interaction near points X ((100) direction) and Γ (center of the Brillouin zone). The parameter "effective mass" (dynamical mass of a particle when it moves in the periodic field of crystal) for Y_2O_3 is $0{,}068m_e$ (m_e is effective mass of electron). It should be noted that the difference between simulated values of the Fermi level and band gap and reference values is a characteristic property of the majority of models. In the case in question the above difference relates to the use of certain approximations on the solution of the Shrodinger equation.

Ab-Initio simulation of electronic properties of thin films of rare earth oxides. The simulation of electronic properties of studied materials with the imitation of the crystal structure limited along one of the coordinate axes, e. g. along *Z*-axis, is of particular interest. Such the representation approximates the model of rare-earth oxide lattice to the state of analysis of a thin film, the thickness of which is equal to the crystal cell size along *Z*-axis. Moreover, in this case the crystal free surface the presence of which is provided for in the technology of sensory control to provide an interaction of active sensoring material with monitored substance is considered.

To study electronic properties of thin films of rare earth oxides, in particular yttrium oxide, the unit cell translation is performed along *X* and *Y* axes to obtain a plane, and then along the *Z* axis to obtain the needed crystal structure. Then the crystal cell spacing along *Z* axis sufficient for the breakdown of all atomic bonds along the investigated direction is specified to implement a physically adequate conversion of the thin film. This procedure can be conventionally interpreted as a wave function interruption along the investigated axis. A need for this procedure is conditioned by the fact that VASP does not provide possibility for wave functions truncation (attenuation or limitation) along single directions. The determination of minimal distance between the atomic layers at which the value of free energy is stabilized is a sufficient condition for the correct representation of the atomic bond breakdown. For material under investigation the optimal value of an amendment which should be added to atomic spacing along the *Z* axis is equaled 10 Å (Fig. 5).

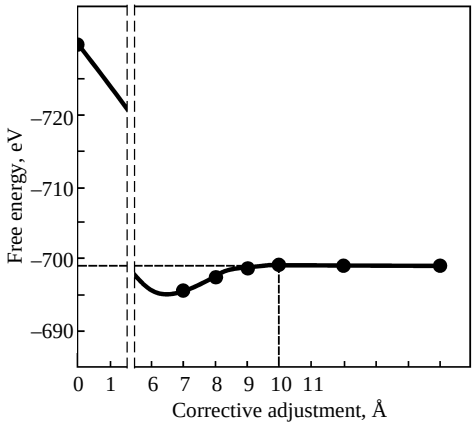

Fig. 5. Determination of optimal distance for the analysis of bond breakdown between the atomic layers

A next step in the simulation of electronic properties of the thin film is a transformation of a vector value along the *Z* axis and coordinates of atoms of unit Y_2O_3 cell defined in the crystal bulk taking into consideration the value of the amendment calculated. For that the *Z* vector of the translational cube is increased to the value equal to the ratio of the sum of the lattice spacing and correcting amendment (10 Å) to the lattice spacing. This value was found to be equaled 1,945 Å. Since the change of the translational cube size results in the atom displacement (prescribed in arbitrary units) from initial coordinates, atom coordinates along the *Z* axis of the unit cell defined in the crystal bulk are normalized relatively to the vector value along the *Z* axis obtained for the thin film. The view of the crystal cell transformed by above methodology to represent the Y_2O_3 hyperfine film is presented in Fig. 6.

The calculation of the density of single-electron states (Fig. 7) allows concluding the following. A wider range of the energy values by which electrons are distributed in the thin yttrium oxide film than in the crystal bulk is formed. It is explained by the fact that the geometrical discretization of nanosized structures is responsible for the discreteness of the quantum-sized energy spectrum. In accordance with the uncertainty principle, the electron confinement at least in one direction results in the increase of its pulse by the value h/L where h is Planck's constant and L is the length of the structure confining the electron moving. Kinetic energy of electrons, respectively, increases by the value $\Delta E = h^2k^2/2m = (h^2/2m)(\pi^2/L^2)$ where $k = 2\pi/\lambda$ and m is electron mass.

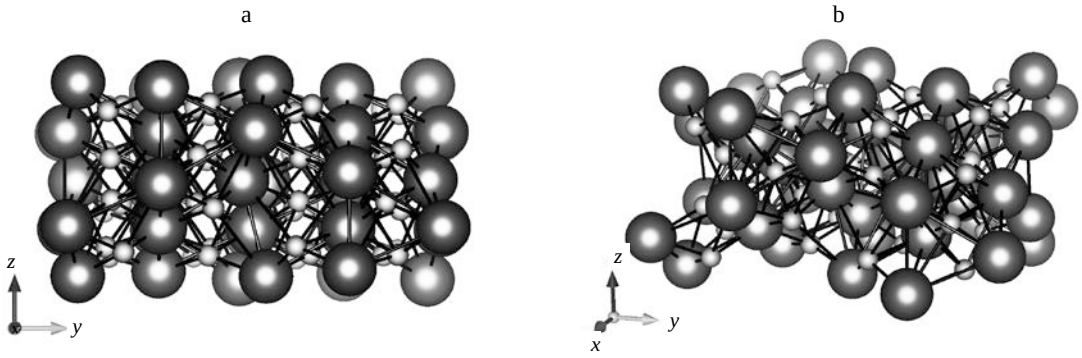

Fig. 6. Yttrium oxide crystal cell view as a result of the Y_2O_3 hyperfine film simulation:
a – is a *Z–Y* plane view; b – is a spatial orientation; – yttrium atom; – oxygen atom

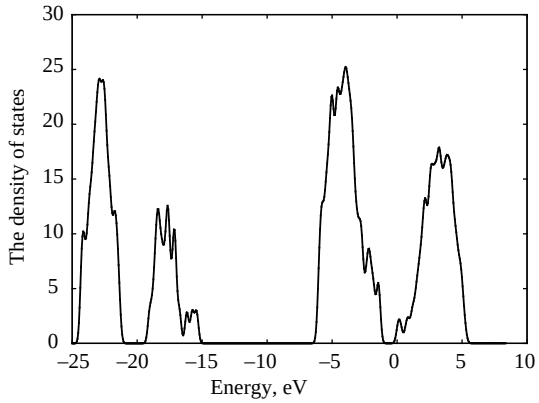

Fig. 7. Density of states of the thin yttrium oxide film
(the Fermi level is superposed with 0 eV energy value)

Thus, quantum confinement is accompanied by the change of the electron energy and the formation of the discrete energy spectrum $E_n = (h^2\pi^2/2mL^2)n^2$ where $n = 1, 2, 3, \ldots$ As this takes place, the energy spectrum of the crystal cell considered is characterized by the density of states $g(E)$ that is a number of possible physically nonequivalent energy states in the certain range ΔE: $g(E) = \lim \Delta j(E)/\Delta E$ where $\Delta j(E)$ is a number of states with the energy in the range from E to $E + \Delta E$. When the thin-film nanostructure is simulated as a crystal confinement along one of the axes, it shows up as an increase of the number of levels of the energy spectrum not only in the valence and conductivity bands characteristics for continuum but in the band gap as well. So the valence and conductivity bands for electrons in the thin film are not revealed explicitly and the band gap is not formed (Fig. 8).

In fact the hyperfine yttrium oxide film loses dielectric properties which were exhibited clear enough in continuum. The study and use of this phenomenon opens new possibilities for the formation of nanoelectronic devices including nanosensors due to the development of new methods for the electron flow control in the films under investigation.

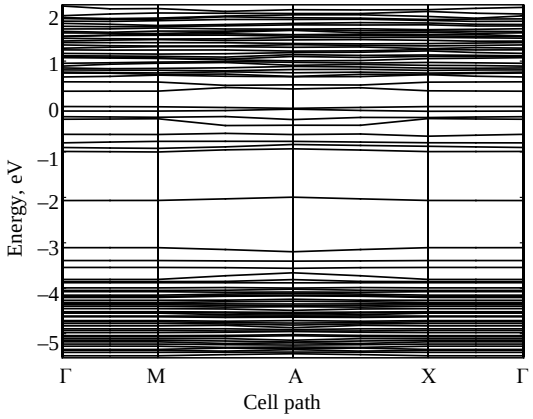

Fig. 8. Energy-band structure of the thin yttrium oxide film
(the Fermi level is superposed with 0 eV energy value)

CONCLUSIONS

Ab-Initio simulation of electronic features of sensoring nanomaterials based on rare earth oxides has been made with the example of yttrium oxide. The VASP simulation package with the description of the electron-nuclear interaction in the system under investigation by the projector-augmented-wave (PAW) method that allows the density of states and energy-band structure to be calculated correctly enough has been used as a modeling tool. Yttrium oxide has been shown to be indirect dielectric with the band gap E_g = 4,439 eV and Fermi energy E_F = 1,552 eV. It is assumed that the increase of the exchange energy results in the appearance of splits in the energy-band structure, and

the indirect transition between the conduction band and valence band results in the polarization interaction near points X ((100) direction) and Γ (center of the Brillouin zone). The calculation strategy for thin films of nanometer scale consisted in the simulation of the material layer of the thickness equal to unit crystal cell size has been proposed within the VASP simulation package.

The atomic bond breakdown in the crystal along one of the coordinate axes is simulated by the increase a distance between the atomic layers along this axis up to values at which the value of free energy is stabilized. It has been ascertained that in the hyperfine rare earth oxide film (at the film thickness close to 1 nm) the valence and conductivity bands are not revealed explicitly and the band gap is not formed. In fact the hyperfine rare earth oxide film loses dielectric properties which were exhibited clear enough in bulk oxide.

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