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## Аннотации на английском языке

### Review

Review article

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**Thermodynamics, kinetics, and technology of synthesis of epitaxial layers of silicon carbide on silicon by coordinated substitution of atoms, and its unique properties. A review**

S. A. Kukushkin , A. V. Osipov

*Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences,  
61 Bolshoi Prospekt V.O., St. Petersburg 199178, Russian Federation*

### Abstract

This review covers studies dedicated to the search for and development of sorbents for the extraction of the caesium-137. The review analyses a new method for growing SiC epitaxial films on Si, which is based on the coordinated substitution of some silicon atoms in the Si crystal lattice with carbon atoms. The main idea and theory of the new method is presented. This method significantly differs from classical growth schemes of thin films. The developed method consists in replacing some Si atoms with C directly inside the silicon matrix and not in depositing atoms on the substrate surface. The method allows us to solve one of the main problems of heteroepitaxy, namely, to synthesise low-defect and unstrained epitaxial films with a large difference between the lattice parameters of the film and the substrate. For the first time in the world, a method of the coordinated substitution of atoms of one sort for atoms of another sort has been implemented right inside the original crystal without destruction of the crystal structure. The method resembles the “genetic synthesis” of protein structures in biology. The structural quality of layers obtained by this method significantly exceeds the quality of silicon carbide films grown on silicon substrates by the world’s leading companies. The method is cheap and technologically advanced. The new growth method is compared with classical thin-film growth methods. The thermodynamic and kinetic analysis of the process of substitution of atoms in the solid phase is presented. Using the example of SiC formation, the mechanisms of a wide class of heterogeneous chemical reactions between the gas phase and a solid are described. The review describes a new method for the synthesis of epitaxial SiC layers on single-crystal sapphire substrates, which is based on the method of coordinated substitution of atoms. It is shown that an interface layer with non-standard optical and electrophysical properties appears at the SiC/Si interface formed by this growth method. The unusual properties are caused by a collapse (shrinkage) of the material at which silicon carbide, as a new phase, separates from the silicon matrix. The silicon is subjected to abnormally strong compression. As a result of such shrinkage, every fifth SiC chemical bond is fully consistent with every fourth Si bond, while the remaining bonds are deformed. The latter leads to a change in the structure of the SiC surface zones adjacent to Si and to a transformation of SiC into a “magnetic semimetal”. The epitaxy of SiC films on Si due to the coordinated substitution of half of the Si atoms by C atoms results in absence of lattice misfit dislocations and thus ensures the high crystalline perfection of the SiC films. A description is given for two quantum effects observed in the SiC/Si structures at room temperature in weak magnetic fields: the Meissner–Ochsenfeld effect and the effect of the generation of the Aharonov–Bohm oscillations in the field dependences of the static magnetic susceptibility. A description is given for a discovered phenomenon of phase transition of charge carriers into a coherent state with the simultaneous appearance of a giant value of diamagnetism of the order of  $1/4\pi$  in weak magnetic fields, which has been associated with the appearance of a superconducting state.

**Keywords:** Silicon carbide on silicon, Solid-state reactions, Heterostructures, Epitaxial films, GaN, AlN, ZnO, Spintronics, Wide-bandgap semiconductors, Heat-resistant coatings, Superconductivity, Meissner–Ochsenfeld effect, Aharonov–Bohm effect, LEDs

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## Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/10550>**Influence of pore geometry on the state of bulk pore water in the pressure-temperature phase space**G. S. Bordonskiy<sup>✉</sup>*Institute of Natural Resources, Ecology and Cryology of the Siberian Branch of Russian Academy of Sciences, 16a Nedorezova str., Chita 672002, Russian Federation***Abstract**

In recent years, the existence of a second critical point of the liquid-liquid transition of water has been proven. In the pressure-temperature phase space, this point is located in the temperature range  $-50\text{ }^{\circ}\text{C} \dots -100\text{ }^{\circ}\text{C}$  and at pressure  $\sim 100\text{ MPa}$ . The exact position of this point is not yet known due to experimental difficulties in achieving the deep supercooling of bulk water. The Widom line, the locus of increased fluctuations in entropy and density, is associated with the second critical point. When approaching the Widom line, a sharp increase in a number of physical quantities was established: heat capacity at constant pressure, isothermal compressibility, volume expansion coefficient. However, the practical significance of these features is not clear, since for pressures close to atmospheric, the temperature on it is  $-45\text{ }^{\circ}\text{C}$ . At the same time, it is known that at temperatures below  $-41\text{ }^{\circ}\text{C}$  (homogeneous nucleation temperature), chemically pure supercooled bulk water is unstable due to the very rapid formation of ice crystal nuclei. Nevertheless, supercooling of bulk water to  $-70\text{ }^{\circ}\text{C}$  in nanometre-sized pores is known.

In the present study, we investigated the possibility of reaching the state on the Widom line at negative pressures, for which, theoretically, the temperature of such a state becomes higher than  $-45\text{ }^{\circ}\text{C}$  and can reach its positive values at a pressure of  $-100\text{ MPa}$ . Such a state, in this study, is assumed in the cylindrical hydrophilic pores with a diameter of several nanometres. For the investigation of this possibility and the achievable values of negative pressure (and high temperatures on the Widom line), we measured the low-frequency impedance of a cooled capacitive cell filled with a moistened MCM-41 nanoporous material. In addition, the thermal characteristics were measured in the form of a temperature response of the medium from a pulsed spot heater at a certain distance from it. The position of the Widom line, associated with the second critical point of water, was determined based on the anomalies of the measured physical values in the temperature range  $-50\text{ }^{\circ}\text{C} \dots +10\text{ }^{\circ}\text{C}$ . For MCM-41 with an average pore diameter of  $3.5\text{ nm}$ , dielectric and thermal extrema were found near  $-18\text{ }^{\circ}\text{C}$ , which corresponds to a pressure of about  $-65\text{ MPa}$ .

Thus, the performed experiments have shown the possibility of reaching the state on the Widom line at temperatures characteristic of ordinary conditions. Consequently, a significant change in the physicochemical characteristics of dispersed moistened media in various natural and artificial objects is possible. The study of other sorbents with cylindrical pores in order to achieve positive temperatures on the Widom line is of interest.

**Keywords:** Supercooled water, Second critical point, Widom line, Negative pressure, Nanoporous media**For citation:** Bordonskiy G. S. Influence of pore geometry on the state of bulk pore water in the pressure-temperature phase space. *Condensed Matter and Interphases*. 2022;24(4): 459–465. <https://doi.org/10.17308/kcmf.2022.24/10550>

Research article

<https://doi.org/10.17308/kcmf.2022.24/10551>**Computer model of Cu-Ni-Mn isobaric phase diagram: verification of crystallisation intervals and change of the three-phase reaction type**A. E. Zelenaya<sup>✉</sup>, V. I. Lutsyk, V. D. Baldanov*Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences, 8 Sakhyanovoy str., Ulan-Ude 670047, Russian Federation***Abstract**

The purpose of article was to show the possibilities of spatial computer models of phase diagrams in solving of the problems of digitalization of materials science. The study of the high-temperature part of the isobaric phase diagram for the Cu–Ni–Mn system was carried out taking into account two polymorphic modifications of manganese ( $\delta\text{Mn}$  and  $\gamma\text{Mn}$ ). For a better understanding of the phase diagram structure, at the first stage, its prototype was developed with increased temperature and concentration intervals between binary points with the preservation of topological structure, which is then modified into the model of phase diagram corresponding to the real system. The phase diagram of Cu–Mn–Ni system above  $800\text{ }^{\circ}\text{C}$  was formed by three pairs of liquidus, solidus, and transus surfaces and three ruled surfaces with a horizontal arrangement of the forming segment.

Experimental part: the effect of changing the peritectic equilibrium ( $L + \delta\text{Mn} \rightarrow \gamma\text{Mn}$ ) to the metatectic one ( $\delta\text{Mn} \rightarrow L + \gamma\text{Mn}$ ) was revealed. The crystallisation features at the change of three-phase transformation type were considered, the surface of change of melt mass increment sign and the vertical mass balances for the three-phase region  $L + \delta\text{Mn} + \gamma\text{Mn}$  were constructed. The surface of two-phase reaction, on which the change of three-phase reaction type occurs, is a ruled surface and is determined, using the algorithm for calculating the change in sign of the mass increment of liquid phase. Three-phase region, taking into account the surface of type change of three-phase reaction, is divided into six concentration fields when projecting into the triangle of compositions. Four concentration fields differ in the crystallisation stages and the formed set of microstructures. Isothermal sections were calculated in the temperature range between two minimum points arranged in the Cu–Mn and Mn–Ni systems at zero crystallisation interval between the valleys of the liquidus and solidus surfaces and taking into account the crystallisation interval.

The spatial model of phase diagram greatly expands the possibilities of computer-aided design of materials. In particular, a solution for the problem of type changing of three-phase reaction was obtained, which cannot be realised either by thermodynamic calculations or by calculations from first principles.

**Keywords:** Phase diagram, Computer simulation, Cu–Ni–Mn system, Change of three-phase reaction type, Crystallisation interval, Microstructure**Funding:** This work was performed under the program of fundamental research IPMS SB RAS, project No. 0270-2021-0002.**For citation:** Zelenaya A. E., Lutsyk V. I., Baldanov V. D. Computer model of Cu–Ni–Mn isobaric phase diagram: verification of crystallisation intervals and change of three-phase reaction type. *Condensed Matter and Interphases*. 2022;24(4): 466–474. <https://doi.org/10.17308/kcmf.2022.24/10551>

Research article

<https://doi.org/10.17308/kcmf.2022.24/10552>**Migration of an incommensurate intercrystalline boundary and boundary self-diffusion**V. G. Kul'kov<sup>✉</sup>*Volzhsk Branch of Moscow Power Engineering Institute,  
69 Lenina prospect, Volzhsky 404101, Russian Federation***Abstract**

Most grain boundaries found in polycrystalline metals are not special. The angle of their mutual disorientation is an arbitrary value, and the axis of rotation is arbitrarily oriented to the plane of the boundary. Periodic atomic structures such as lattices of coincident nodes, alternating polyhedra, and others do not arise within such boundaries. They are called boundaries of a general type, non-special, arbitrary, or incommensurate. The general theory of relaxation processes at such boundaries has not yet been sufficiently developed. The aim of the study was the development of the model of migration of an incommensurate intercrystalline boundary at the atomic level and the description of the process of self-diffusion along it.

A circle called the main region is described around each boundary lattice node of one of the crystallites. If there is an atom in the node, then an atom of another crystallite is excluded from entering it. In the case of a vacant node in the main region, such an atom can be located. An atom in a planar picture means an atomic series in the three-dimensional case. The distribution of vacant nodes of the growing crystallite is uniform over the flat reduced main region. The migration mechanism involves the implementation of the following main processes: local rearrangement of atomic configurations and self-diffusion of atoms in the transverse direction of the slope axis.

The characteristic times of these processes and the expression for the migration rate were found. The migrating boundary contains a large number of delocalised vacancies. This leads to the high diffusion mobility of atoms. Most vacancies in the boundary are not of thermal origin, but are determined only by the geometric atomic structure of the boundary. In this case, the expression for the boundary self-diffusion coefficient does not contain a multiplier depending on the activation energy of vacancy formation. This leads to the fact that the coefficient of self-diffusion along the migrating boundary is significantly higher than in the stationary boundary. The model of an incommensurate boundary allows us to describe its migration and calculate the self-diffusion coefficient.

**Keywords:** Incommensurate intercrystalline boundaries, Delocalised vacancies, Boundary self-diffusion, Migration mobility

**For citation:** Kul'kov V. G. Migration of an incommensurate intercrystalline boundary and boundary self-diffusion. *Condensed Matter and Interphases*. 2022;24(4): 475–482. <https://doi.org/10.17308/kcmf.2022.24/10552>

Research article

<https://doi.org/10.17308/kcmf.2022.24/10553>**Mathematical modelling of vortex structures in the channel of an electro dialysis cell with ion-exchange membranes of different surface morphology**K. A. Lebedev<sup>1✉</sup>, V. I. Zabolotsky<sup>1</sup>, V. I. Vasil'eva<sup>2</sup>, E. M. Akberova<sup>2</sup><sup>1</sup>*Kuban State University,  
149 Stavropolskaya ul., Krasnodar 350040, Russian Federation*<sup>2</sup>*Voronezh State University,  
1 Universitetskaya pl., Voronezh 394018, Russian Federation***Abstract**

One of the ways to obtain membranes with electroconvection as the dominant mechanism of ion transport is to optimise the surface of known brands of commercial heterogeneous membranes by changing their manufacturing technology. For example, the degree of dispersion of the ion-exchanger or the volume ratio of the ion-exchanger to inert binder can be changed. The aim of this study was to determine and theoretically analyse the fundamental correlations between the intensity of electroconvection and the surface morphology of ion-exchange membranes with different ion-exchanger particle content.

The article presents a mathematical model of ion transport across the ion-exchange membrane/solution interface in the channel of an electro dialysis cell. The phenomenon of electroconvection in electromembrane systems (EMS) was modelled by solving two-dimensional Navier-Stokes equations for an incompressible liquid with no-slip boundary conditions and a set distribution of the electric body force. The body force distribution was set taking into account the real size of ion-exchanger particles and the distance between them that determine the electrical heterogeneity of the surface of experimental ion-exchange membranes with different mass fractions of ion-exchange resin.

It was determined that in the numerical modelling, the most important parameters were the size of the sections of electrical heterogeneity of the membrane surface, the current density, and the length of the space charge region (SCR). Numerical calculations were presented to determine the vortex size depending on the current density and the degree of electrical heterogeneity of the membrane surface.

It was shown that an increase in the mass fraction of ion-exchange resin in the production of heterogeneous sulphocation-exchange membranes resulted in a decrease in the step of electrical surface heterogeneity and promoted the formation of electroconvective vortices interacting with each other. Within the boundary conditions and approximations of the mathematical model, the vortex sizes reach their maximum value in the middle of the heterogeneity section  $L_\sigma$ .

**Keywords:** Mathematical modelling, Electroconvection, Vortex structures, Heterogeneous ion-exchange membrane, Surface morphology, Electrical heterogeneity of surface

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Research article

<https://doi.org/10.17308/kcmf.2022.24/10645>**The effect of solution-combustion mode on the structure, morphology and size-sensitive photocatalytic performance of MgFe<sub>2</sub>O<sub>4</sub> nanopowders**L. A. Lebedev<sup>✉</sup>, M. I. Tenevich, V. I. Popkov

Ioffe Institute,

26 Politekhnicheskaya str., Saint Petersburg 194021, Russian Federation

**Abstract**

Ferrites play a significant role in a number of applications from magnetic ceramic to multifunctional catalytic and antimicrobial material. As a catalytic material, it is crucial to have not only high activity but also be made from abundant elements via energy-efficient techniques, to make it valuable for industrial application. Magnesioferrite nanocrystalline powder series were prepared via solution-combustion route while varying fuel/oxidizer ratio. They were investigated by XRD, BET, SEM, DRS, and Fenton-like photocatalytic activity. Temperature-time profiles were measured for the combustion reaction of all mixtures. Results show a strong correlation between fuel content and temperature, structure, and morphology. But despite average surface area and crystallite size, the sample synthesized with excess fuel showed high dye adsorption capacity and catalytic activity.

**Keywords:** Photocatalyst, Ferrites, Spinel, Solution-combustion synthesis, Fenton-like process**Acknowledgments:** The XRD and SEM studies were performed on the equipment of the Engineering Center of Saint Petersburg State Institute of Technology.**For citation:** Lebedev L. A., Tenevich M. I., Popkov V. I. The Effect of solution-combustion mode on the structure, morphology and size-sensitive photocatalytic performance of MgFe<sub>2</sub>O<sub>4</sub> nanopowders. *Condensed Matter and Interphases*. 2022;24(4): 496–503. <https://doi.org/10.17308/kcmf.2022.24/10645>

Research article

<https://doi.org/10.17308/kcmf.2022.24/10554>**The influence of acid activation of bentonite in the composition of a bipolar membrane on the characteristics of the electro dialysis conversion of sodium sulphate**S. I. Niftaliev<sup>1</sup>, O. A. Kozaderova<sup>1</sup>, K. B. Kim<sup>1✉</sup>, P. E. Belousov<sup>2</sup>, V. V. Krupskaya<sup>2</sup>, A. V. Timkova<sup>1</sup><sup>1</sup>Voronezh State University of Engineering Technologies,

19 Revolutsii pr., Voronezh 394036, Russian Federation

<sup>2</sup>Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences,

35 Staromonetny per., Moscow 119017, Russian Federation

**Abstract**

The effect on the characteristics of the electro dialysis process of the acid activation of bentonite included in the cation-exchange layer of an experimental bipolar membrane obtained by applying a liquid LF-4SK cation-exchange layer containing bentonite particles onto an anion-exchange membrane-substrate MA-41 was studied.

Acid activation of bentonite was carried out with nitric acid ( $C = 1$  and  $4 \text{ mol/dm}^3$ ) for 6 hours at temperatures of 20 and 90 °C. The conversion of sodium sulphate ( $C = 0.5 \text{ mol/dm}^3$ ) was carried out in a six-section electro dialysis apparatus with experimental bipolar membranes containing bentonite in its original form and after acid activation. It has been shown that the addition of bentonite treated with nitric acid ( $C = 4 \text{ mol/dm}^3$ ,  $t = 90 \text{ °C}$ ,  $\tau = 6 \text{ h}$ ) to the cation-exchange layer of a bipolar membrane leads to an increase in productivity, current efficiency and a decrease in energy costs compared to a membrane containing bentonite in its original form.

Experimental bipolar membranes made on the basis of MA-41 and a liquid sulphonic cation exchanger containing acid-activated bentonite clays make it possible to obtain an acid and alkali performance comparable to that of the MB-3 bipolar membrane.

**Keywords:** Electro dialysis, Bipolar membrane, Acid activation, Bentonite, Sodium sulphate, Acid, Alkali**Funding:** The work was carried out within the framework of the grant of the President of the Russian Federation for state support of young Russian scientists - candidates of science (MK-685.2021.1.3).**For citation:** Niftaliev S. I., Kozaderova O. A., Kim K. B., Belousov P. E., Krupskaya V. V., Timkova A. V. The influence of acid activation of bentonite in the composition of a bipolar membrane on the characteristics of the electro dialysis conversion of sodium sulphate. *Condensed Matter and Interphases*. 2022;24(4): 504–510. <https://doi.org/10.17308/kcmf.2022.24/10554>

Research article

<https://doi.org/10.17308/kcmf.2022.24/10555>**Photosensitisation of reactive oxygen species with titanium dioxide nanoparticles decorated with silver sulphide quantum dots**O. V. Ovchinnikov, M. S. Smirnov, A. S. Perepelitsa<sup>✉</sup>, S. V. Aslanov<sup>✉</sup>, A. P. Gureev, V. N. Popov, F. A. Tsybenko, A. M. H. Hussein

Voronezh State University,

1 Universitetskaya pl., Voronezh, 394018, Russian Federation

**Abstract**

At present, the development of methods for sensitisation to the visible and IR spectral regions of systems for the photocatalytic production of reactive oxygen species based on titanium dioxide nanoparticles is of great interest. The purpose of this work was to establish the regularities of the photogeneration of reactive oxygen species during the formation of TiO<sub>2</sub> nanoparticle – Ag<sub>2</sub>S quantum dots nanoheterosystems under the action of radiation in visible and near-infra-red spectral regions.

The paper analyses the photocatalytic properties of anatase nanoparticles 10–15 nm in size decorated with colloidal Ag<sub>2</sub>S quantum dots with an average size of 2.5 nm passivated with thioglycolic and 2-mercaptopropionic acids. Selective sensor dyes were used to estimate the effectiveness of sensitisation of various reactive oxygen species with the studied photocatalysts under excitation in the UV and visible region. It was shown that decorating TiO<sub>2</sub> nanoparticles with quantum dots leads to an increased efficiency of the production by the system of hydroxyl radical, superoxide anion, and hydrogen peroxide under photoexcitation in the TiO<sub>2</sub> absorption region (UV range). Sensitisation of the production of reactive oxygen species by nanosystems was detected during excitation by radiation in the visible spectral region (outside the intrinsic TiO<sub>2</sub> absorption band). It was also found that there is an increase in the efficiency of the production of reactive oxygen species (up to 1.5 times) when thioglycolic acid is replaced with 2-mercaptopropionic acid as a passivator of Ag<sub>2</sub>S quantum dots.

The obtained data were used to develop a schematic diagram of photoprocesses in the system.

**Keywords:** Reactive oxygen species, Photocatalysis, Nanoparticles, Titanium dioxide, Quantum dots, Silver sulphide, Photosensitisation

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Research article

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### Study of the proteolytic activity of ficin associates with chitosan nanoparticles

S. S. Olshannikova<sup>1</sup>, Yu. A. Redko<sup>1</sup>, M. S. Lavlinskaya<sup>1,2</sup>, A. V. Sorokin<sup>1,2</sup>, M. G. Holyavka<sup>1,2</sup>, N. E. Yudin<sup>1</sup>, V. G. Artyukhov<sup>1</sup>

<sup>1</sup>Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

<sup>2</sup>Sevastopol State University,

33 Universitetskaya ul., Sevastopol 299053, Russian Federation

#### Abstract

The purpose of the research was to develop and study biocatalysts based on ficin associates with chitosan nanoparticles. We obtained medium and high molecular weight chitosan nanoparticles with the addition of ascorbic acid and without it. The zeta potential of all types of nanoparticles was 0 mV. The associates of ficin and chitosan nanoparticles formed with the addition of ascorbic acid exhibited higher proteolytic activity. While determining the stability of the associates of chitosan and ficin nanoparticles, we noticed a decrease in the proteolytic activity of the samples within seven days. Medium and high molecular weight chitosan nanoparticles obtained using ascorbic acid differed significantly in size from the nanoparticles produced without ascorbic acid. The proposed biocatalysts have high prospects for use in cosmetology, biomedicine, and pharmacy.

**Keywords:** Nanoparticles, Ficin, Chitosan, Association

**Funding:** The study was founded by the Priority-2030 programme of Sevastopol State University, strategic project No.3 (production of chitosan nanoparticles), and by the Ministry of Science and Higher Education of the Russian Federation in the framework of the government order to higher education institutions in the sphere of scientific research for years 2020-2022, project No. FZGU-2020-0044 (complexation of nanoparticles with enzymes).

**For citation:** Olshannikova S. S., Redko Yu. A., Lavlinskaya M. S., Sorokin A. V., Holyavka M. G., Yudin N. E., Artyukhov V. G. Study of the proteolytic activity of ficin associates with chitosan nanoparticles. *Condensed Matter and Interphases*. 2022;24(4): 523–528. <https://doi.org/10.17308/kcmf.2022.24/10556>

Research article

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### Deposition of zinc sulphide films from thiourea complexes and a study of their optical properties

T. V. Samofalova<sup>✉</sup>, V. N. Semenov, P. V. Seredin, D. L. Goloshchapov, N. S. Buylov

Voronezh State University,

1 Universitetskaya pl., Voronezh 394018, Russian Federation

#### Abstract

This work presents the results of a study of zinc sulphide films deposited by aerosol pyrolysis from aqueous solutions of thiourea complex compounds  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Cl}_2]$  and  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Br}_2]$  in the temperature range of 350–500 °C.

The IR and Raman spectra of zinc complexes were studied. It was determined that in the studied complexes, the thiourea molecule was coordinated to the metal cation through the sulphur atom. In the low-frequency Raman region ( $\nu < 400 \text{ cm}^{-1}$ ), we recorded the bands characterising the vibrations of the zinc-sulphur and zinc-chlorine (bromine) bonds of the studied complex compounds in the Raman scattering spectra. The optical properties of zinc sulphide films were studied using optical spectrophotometry. Based on the absorption spectra, the optical band gap of ZnS films was determined. It was 3.67–3.74 eV and 3.63–3.70 eV for the samples deposited from  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Cl}_2]$  and  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Br}_2]$  complexes, respectively. We recorded a decrease in the band gap of the synthesised layers upon an increase in the deposition temperature. It is due to changes in their defect structure.

One of the main types of defects in the ZnS films deposited from  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Cl}_2]$  and  $[\text{Zn}(\text{N}_2\text{H}_4\text{CS})_2\text{Br}_2]$  complexes is a halogen atom in the anion sublattice of the sulphide ( $\text{Cl}_s^-$ ,  $\text{Br}_s^-$ ). As the deposition temperature increases, the content of these defects in the films decreases due to the complete destruction of Zn–Cl and Zn–Br bonds and volatilisation of halogen during the thermolysis of the complexes. Oxygen ( $\text{O}_s^{2-}$ ) occupies the vacated places of  $\text{Cl}_s^-$ ,  $\text{Br}_s^-$ . The films contained oxygen as they were synthesised in an oxidising atmosphere and due to partial hydrolysis of the initial zinc salt. An increase of oxygen content in the samples upon an increase of the deposition temperature results in a decrease of the optical band gap of the ZnS films.

**Keywords:** Thiourea complex compounds, Aerosol pyrolysis, Zinc sulphide, Films, Optical band gap

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## Research article

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### The conditions for the solid state synthesis of solid solutions in zirconia and hafnia systems with the oxides of rare earth elements

P. P. Fedorov<sup>✉</sup>, E. V. Chernova

Prokhorov General Physics Institute of the Russian Academy of Sciences,  
38 Vavilova str., Moscow 119991, Russian Federation

#### Abstract

The goal of this work was to study the specific features of obtaining  $(\text{Zr,Hf})_{1-x}\text{R}_x\text{O}_{2-0.5x}$  solid solutions through solid-phase sintering and to analyse the correctness of the existing variants of phase diagrams for  $(\text{Zr,Hf})\text{O}_2\text{-R}_2\text{O}_3$  zirconia and hafnia systems with the oxides of rare earth elements.

We analysed the existing data on the duration of annealing used to study phase equilibria in zirconia and hafnia systems with the oxides of rare earth elements. The “annealing time logarithm – reciprocal temperature” dependences were constructed. It was shown that the effective diffusion coefficient upon annealing was at least 200 kJ/mol. The time of annealing required for the achievement of equilibrium at 1300 °C was no less than 6 months. The annealings for one year did not allow receiving reliable information on phase equilibria in these systems with temperatures lower than 1250 °C. All the data on phase diagrams presented in earlier studies for lower temperatures did not characterise the equilibrium state of systems. Apart from low-temperature phases of variable compositions presented in phase diagrams, among the characteristics of non-equilibrium states there were violations of the Hume-Rothery rule and observations of diffusionless processes of ordering of solid solutions, including those occurring upon “fluorite-pyrochlore” solid state transitions. Probable schemes of low temperature phase equilibria in the  $\text{ZrO}_2\text{-Er}_2\text{O}_3$  and  $\text{HfO}_2\text{-Eu}_2\text{O}_3$  systems were presented taking into account the third law of thermodynamics.

The obtained results are fundamental and will be useful for the assessment of the stability of thermal barrier coatings and fuel cells based on zirconium and hafnium oxides with the oxides of rare earth elements.

**Keywords:** Zirconia, Hafnia, Zirconium oxide, Hafnium oxide, Oxides of rare earth elements, Solid solutions, Ordering, Phase diagrams, Sintering

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## Research article

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### Modelling optical polarization processes on laser modified titanium with a polyvinyl alcohol film

A. V. Tsibulnikova<sup>✉</sup>, A. A. Khankaev<sup>1</sup>, D. A. Artamonov<sup>1</sup>, I. G. Samusev<sup>1</sup>, V. A. Slezhkin<sup>2</sup>, I. I. Lyatun<sup>1</sup>, V. V. Bryukhanov<sup>1</sup>

<sup>1</sup>Immanuel Kant Baltic Federal University,  
14 A. Nevskogo ul., Kaliningrad 236016, Russian Federation

<sup>2</sup>Kaliningrad State Technical University,  
1 Sovetsky pr., Kaliningrad 236022, Russian Federation

#### Abstract

The article presents the results of research of optical spectra of surface plasmon polaritons on laser modified titanium with a deposited micron polymer polyvinyl alcohol (PVA) film.

The metasurface of titanium was created by means of femtosecond laser treatment with  $\lambda = 1.035 \mu\text{m}$  and the duration  $\tau = 280 \text{ fs}$  with linear and circular radiation polarization. Sets of laser pulses were applied pointwise to the surface with a step of 100  $\mu\text{m}$  with the interval  $t_i = 25\text{--}750 \text{ ms}$ . In the case of linear radiation polarization, tracks of ripple structures with a line density of up to  $N \sim 1,200 \text{ mm}^{-1}$  appeared on the scribed titanium surface. It was found that when titanium is exposed to circular polarization radiation, occasional ablation cavities with lobed circular ripple nano-microstructures appear along the line of beam pulse propagation.

Mathematical modelling of real  $\text{Re}(\epsilon)$  and imaginary  $\text{Im}(\epsilon)$  permittivity established that the spectral parameters in the reflectance spectra of polarized radiation almost fully matched. The analysis of the spectra also established that the maximum absorption was in the IR region due to the presence of a PVA film.

**Keywords:** Plasmon resonance, Laser structuring, Circular polarization, Metasurface, PVA film

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## Research article

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### Growth kinetics of anodic oxide layers on cobalt silicides in sulphuric acid solutions

A. B. Shein<sup>✉</sup>, V. I. Kichigin

Perm State National Research University,  
15 Bukireva ul., Perm 614990, Russian Federation

#### Abstract

The aim of this research was to study the growth kinetics of anodic oxide films on cobalt silicides in sulphuric acid solutions under potentiostatic conditions with various pretreatment of the electrode surface. For the study, we used low and high silicon silicides ( $\text{Co}_2\text{Si}$  and  $\text{CoSi}_2$ ) in 0.05 and 0.5 M  $\text{H}_2\text{SO}_4$ .

We obtained the chronoamperograms in the time interval  $t = 0.3\text{--}3000 \text{ s}$  with the oxide formation potentials of  $E_f = 0.2, 0.5, \text{ and } 1.0 \text{ V (SHE)}$ . It was determined that the kinetics of the growth of oxide layers on cobalt silicides in acidic solutions greatly depends on the method of the silicide surface pretreatment (mechanical polishing; cathodic pre-polarisation in a  $\text{H}_2\text{SO}_4$  solution; exposure to  $\text{H}_2\text{SO}_4$  solution at the open circuit potential; exposure in a 2 M KOH solution; and exposure to 2% HF solution). In most cases, at low  $t$  (up to 30–50 s), the

oxide films grew due to the ion migration in the strong electric field generated in the film during anodic polarisation.

In some cases ( $\text{Co}_2\text{Si}$  silicide with higher cobalt content; pretreatment of  $\text{Co}_2\text{Si}$  in alkaline solution, further enriching the silicide surface with cobalt; and the region of high values of  $t$ ), the point defect model seemed to be executed.

**Keywords:** Cobalt silicide, Passivity, Oxide film, Growth kinetics, High field model, Point defect model

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Research article

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### Anodic oxide coatings with a hierarchical micronanostructure on sintered titanium powders

N. M. Yakovleva<sup>1✉</sup>, A. M. Shulga<sup>1</sup>, I. V. Lukianchuk<sup>2</sup>, K. V. Stepanova<sup>1</sup>, A. N. Kokatev<sup>1</sup>, E. S. Chubieva<sup>1</sup>

<sup>1</sup>Petrozavodsk State University,

33 Lenina prospekt, Petrozavodsk 185910, Russian Federation

<sup>2</sup>Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences,

159 100-Letiya Oktyabrya ul., Vladivostok 690022, Russian Federation

#### Abstract

$\text{TiO}_2$  nanotubes formed by electrochemical anodising of Ti (titanium foil) are normally X-ray amorphous. To improve their functional properties, they are usually converted into crystalline nanotubes by annealing at  $T \approx 400\text{--}500$  °C. What is more, under certain conditions, oxide films with a hierarchical micronanostructure can be formed on titanium foil by anodising in fluorine-containing electrolytes. Such films contain nanostructured microcones whose atomic structure corresponds to anatase ( $\alpha\text{-TiO}_2$ ). It is interesting to find out whether it is possible to form anodic oxide coatings with a hierarchical micronanostructure on the surface of sintered powders of titanium sponge, which should have much larger specific surfaces and a wider range of applications. This paper is aimed at the study of the process of anodising porous samples of sintered powders of titanium sponge in an aqueous electrolyte (1 M  $\text{H}_2\text{SO}_4$  + 0.15 wt % HF).

The object of our study were sintered titanium powders in the form of samples of porous powder materials with a specific area of  $S_{sp} = 1,350$   $\text{cm}^2/\text{g}$ . Anodising was conducted in a 1 M  $\text{H}_2\text{SO}_4$  + 0.15 wt % HF electrolyte at various values of current density ( $j_m$ ). Surface morphology before and after anodising was investigated by scanning electron microscopy and atomic force microscopy. X-ray diffractometry was used to study the phase composition.

The research involved the study of the influence of conditions for the galvanostatic anodising of samples of porous powder materials made from titanium sponge on the growth, morphology, and atomic structure of anodic oxide coatings. For the first time, it was shown that anodising at the values of current density  $j_m = (230 \div 1,890)$  mA/g leads to the appearance of nanostructured  $\alpha\text{-TiO}_2$  microcones (with base diameters and heights of up to 4  $\mu\text{m}$ ) in an amorphous nanoporous/nanotube oxide matrix (with an effective pore/tube diameter of about 50 nm). Since such coatings have a high specific area and a hierarchical micronanostructure, they are promising for the design of devices for photocatalytic environment purification and production of superhydrophobic surfaces.

**Keywords:** Sintered powders, Porous powder materials, Titanium sponge, Anodic oxide coatings, Structure hierarchy, Microcones, Crystalline, Nanostructured titanium dioxide, Scanning electron microscopy, Atomic force microscopy

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