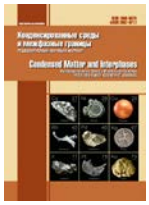

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Аннотации на английском языке

Review

Review article
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Nanoscale semiconductor and dielectric films and magnetic nanocrystals - new directions of development of the scientific school of Ya. A. Ugai “Solid state chemistry and semiconductors” Review

I. Ya. Mittova[1], B. V. Sladkopevtsev[1], V. O. Mittova[2]

[1]Voronezh State University
1 Universitetskaya pl., Voronezh 394018, Russian Federation

[2]Voronezh State Medical University named after N. N. Burdenko
12 Studencheskaya Street, Voronezh 394036, Russian Federation

Abstract

New directions of development of the scientific school of Yakov Aleksandrovich Ugai “Solid state chemistry and semiconductors” were considered for the direction “Study of semiconductors and nanostructured functional films based on them”, supervised by I. Ya. Mittova. The study of students and followers of the scientific school of Ya. A. Ugai cover materials science topics in the field of solid-state chemistry and inorganic and physical chemistry. At the present stage of research, the emphasis is being placed precisely on nanoscale objects, since in these objects the main mechanisms of modern solid-state chemistry are most clearly revealed: the methods of synthesis - composition - structure (degree of dispersion) - properties. Under the guidance of Professor I. Ya. Mittova DSc (Chem.), research in two key areas is conducted: “Nanoscale semiconductor and dielectric films” and “Doped and undoped nanocrystalline ferrites”. In the first area, the problem of creating high-quality semiconductor and dielectric nanoscale films on $A^{III}B^{V}$ by the effect reasonably selected chemostimulators on the process of thermal oxidation of semiconductors and/or directed modification of the composition and properties of the films. They present the specific results achieved to date, reflecting the positive effect of chemostimulators and modifiers on the rate of formation of dielectric and semiconductor films of the nanoscale thickness range and their functional characteristics, which are promising for practical applications.

Nanomaterials based on yttrium and lanthanum orthoferrites with a perovskite structure have unique magnetic, optical, and catalytic properties. The use of various approaches to their synthesis and doping allowing to control the structure and properties in a wide range. In the field of magnetic nanocrystals under the supervision of Prof. I. Ya. Mittova studies of the effect of a doping impurity on the composition, structure, and properties of nanoparticles of yttrium and lanthanum orthoferrites by replacing the $Y(La)^{3+}$ and Fe^{3+} cations are carried out. In the Socialist Republic of Vietnam one of the talented students of Prof. I. Ya. Mittova, Nguyen Anh Tien, performs studies in this area. To date, new methods for the synthesis of nanocrystals of doped and undoped ferrites, including ferrites of neodymium, praseodymium, holmium, etc. have been developed.

Keywords: Semiconductors, Dielectrics, Magnetic nanocrystals, Ferrites, Nanoscale films, Nanocrystals

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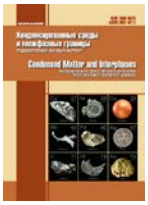
✉ Irina Ya. Mittova, e-mail: imittova@mail.ru



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Review

Review article
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Interaction of metal sulphides in films deposited from solutions of thiourea coordination compounds. Review

V. N. Semenov✉, **A. V. Naumov**

Voronezh State University
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

Metal sulphides are highly important for the technology of semiconductor film materials. The potential of these compounds has not been exhausted yet when it comes to creating optoelectronic devices, solar cells, and luminescent devices based on them. The goal of this work was to determine the nature of interaction of sulphides in polycrystalline layers of CdS–Me_mS_n, where Me are metals of groups I–VII of the periodic table. Cadmium sulphide was chosen as the common component of all studied systems due to the great photoelectric and luminescent properties of this well-studied material.

It was shown that using aerosol spray pyrolysis of the solutions of thiourea complexes, we can obtain solid solutions and chemical compounds of CdS–Me_mS_n at temperatures not exceeding 500 °C. The main electric, optical, and luminescent properties of the layers were described.

It was established that the use of aerosol spray pyrolysis of the solutions of thiourea coordination compounds allows significantly expanding the areas of solubility during the formation of solid sulphide solutions. The specific character of solid-phase interaction and nonequilibrium of the processes occurring during the deposition of layers allow avoiding structural incompatibility of the components expressed in the form of typical factors, such as the non-uniformity of crystal structure, differences in the chemical nature of the components, and discrepancies in sizes of substituting/penetrating atoms.

Under such conditions of deposition of films (the lower threshold of deposition temperatures is determined by the temperature of decomposition of the most thermally stable thiourea coordination compound and does not exceed 250 °C), the solid-phase interactions of most sulphides cannot be achieved. Therefore, the interaction occurs at the moment of thermal destruction of complex compounds due to the emerging valence opportunities of their structural fragments.

Keywords: Metal sulphides, Thiocarbamide coordination compounds, Polycrystalline films, Aerosol spray pyrolysis, Solid-phase interaction

For citation: Semenov V. N., Naumov A. V. Interaction of metal sulphides in films deposited from solutions of thiourea coordination compounds. Review. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(3): 337–352. https://doi.org/10.17308/kcmf.2021.23/3525

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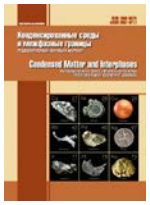
✉ Viktor N. Semenov, e-mail: deanery@chem.vsu.ru



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Review

Review article
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The development of methods for the research and synthesis of solid phases by the scientific school of Ya. A Ugai. Review

G. V. Semenova✉, **A. Yu. Zavrazhnov**

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The scientific school founded by Yakov A. Ugai has existed at Voronezh State University for over fifty years. One of its focus areas has been the development of physics and chemistry for obtaining solid phases in systems with volatile components. This determined the necessity to develop methods for the investigation of vapour pressure (tensimetric methods). This article only focuses on some of the works by the VSU staff dedicated to the study and construction of *P-T-x* diagrams. This review analyses phase equilibria and the nature of the intermediate phases in the $A^{IV} – B^{V}$, $A^{IV} – B^{V} – C^{V}$, and $A^{III} – B^{VI}$ systems. Owing to the special nature of the cation-cation and anion-anion bonds, these compounds have highly specific properties that make them promising materials (2D materials in particular). The article presents an overview of works devoted to the construction of *P-T-x* diagrams and the investigation of defect formation processes in binary and ternary systems based on $A^{IV}B^{V}$ compounds. It should be emphasised that the known techniques needed updating due to the high values of vapour pressure. This allowed conducting experiments at pressures of about 35-40 atmospheres. The study of the A^{III} - B^{VI} systems, on the contrary, is complicated by low values of vapour pressure over indium and gallium chalcogenides and the complex composition of the vapour. For such systems the auxiliary component method was developed. The possibilities of its application are wide and are not limited to $A^{III}B^{VI}$ compounds. A new method for nonstoichiometry regulation was developed and applied using non-destructive selective chemical transport reactions (i.e. with the participation of an auxiliary component). This method is based on the introduction or removal of one of the sample components by means of a selective chemical transport reaction. In conclusion, the development of methods for the research and synthesis of intermediate phases with variable compositions (properties) was analysed based on the example of the discussed systems.

Keywords: Phase equilibria, Tensimetric methods, $A^{IV}B^{V}$ compounds, Indium and gallium chalcogenides, Phase diagrams

For citation: G. V. Semenova, A. Yu. Zavrazhnov The development of methods for the research and synthesis of solid phases by the scientific school of Ya. A Ugai. Review. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases.* 2021;23(3): 353–373. https://doi.org/10.17308/kcmf.2021.23/3526

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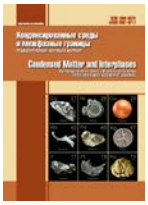
✉ Galina V. Semenova, e-mail: semenova@chem.vsu.ru



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Original articles

Research article
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Technological features of the method of liquid-phase epitaxy when growing InP/GaInAsP heterostructures

M. G. Vasil'ev✉, A. M. Vasil'ev, A. D. Izotov✉, Yu. O. Kostin, A. A. Shelyakin

Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninsky prospect, Moscow 119991, Russian Federation

Abstract

Semiconductor devices of quantum electronics based on InP/GaInAsP heterostructures require the creation of non-defective chips for emitting devices and photodetectors. The production of such chips is impossible without a thorough technological study of the growth processes of epitaxial structures. One of the important problems in relation to the growth of such structures is the growth defects associated with the process of dissociation of indium phosphide on the surface during their growth. The aim of the work was the investigation of the process and mechanism of destruction (dissociation) of the surface of indium phosphide substrates in the range of growth temperatures of structures, as well as the study of methods and techniques that allow minimize the process of dissociation of surface of indium phosphide.

The work provides studies of the growth processes of InP/GaInAsP heterostructures, from the liquid phase, taking into account the degradation processes of the growth surface and the mechanisms for the formation of dissociation defects. The schemes of the dissociation process of the InP on the surface of the substrate and the formation of the defective surface of the substrate were analysed. At the same time, technological methods allowing to minimize the dissociation of the surface compound during the process of liquid-phase epitaxy were shown. The original design of a graphite cassette allowing to minimize the dissociation of the indium phosphide substrate in the process of liquid-phase epitaxy was proposed.

Keywords: Heterostructures, Growth defects, Laser diodes, Indium phosphide, Buried heterostructures, Channel in the substrate

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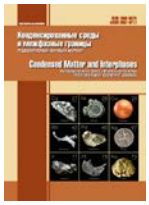
✉ Mikhail G. Vasil'ev, e-mail: mgvas@igic.ras.ru
✉ Alexander D. Izotov, e-mail: izotov@igic.ras.ru



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Original articles

Research article
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A 3D computer model of the CaO-MgO-Al_2O_3 *T-x-y* diagram at temperatures above 1300 °C

V. P. Vorob'eva, A. E. Zelenaya✉, V. I. Lutsyk, M. V. Lamueva

Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences,
6 Sakhianova ul., Ulan-Ude 670047, Russian Federation

Abstract

The research analyses the controversies surrounding the technique for the formation of a CaO-Al_2O_3 binary system and the nature of melting of compounds in it, i.e. whether the 12:7 compound is technically possible and whether the 1:1 and 1:2 compounds are congruently or incongruently melting compounds. It also discusses whether in the CaO-MgO-Al_2O_3 ternary system the following compounds can be formed: a 3:1:1 compound alone or, in addition to it, two more compounds of 1:2:8 and 2:2:14. A 3D model of the *T-x-y* diagram was created for the most common version, with six binary and three ternary compounds. Its high-temperature portion (above 1300°C) consisted of 234 surfaces and 85 phase regions. Ternary compounds were formed as a result of three peritectic reactions. Besides them, six quasi-peritectic and three eutectic invariant reactions occurred in the system with the participation of the melt. The principle of construction for a three-dimensional model involved a gradual transition from a phase reaction scheme (which is transformed into a scheme of uni- and invariant states) presented in a tabulated and then in a graphical form (a template of ruled surfaces and isothermal planes corresponding to invariant reactions) to a *T-x-y* diagram prototype (graphic images of all liquidus, solidus, and solvus surfaces). The design was concluded with the transformation of the prototype into a 3D model of the real system after the input of the base points coordinates (concentrations and temperatures) and the adjustment of curvatures of lines and surfaces. The finished model provides a wide range of possibilities for the visualisation of the phase diagram, including the construction of any arbitrarily assigned isothermal sections and isopleths. The 3D model was designed with the help of the author's software PD Designer (Phase Diagram Designer). To assess the quality of the 3D model, two versions of an isothermal section at 1840 °C were compared: model section and a fragment of an experimental section near Al_2O_3.

Keywords: Phase diagram, Computer simulation, Oxides of calcium, magnesium, and aluminium

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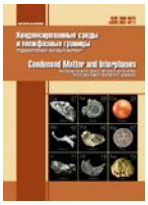
✉ Anna E. Zelenaya, e-mail: zel_ann@mail.ru



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Original articles

Research article
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Synthesis of bulk crystals and thin films of the ferromagnetic MnSb

M. Jaloliddinzoda✉[1], S. F. Marenkin[1,2], A. I. Ril'[2], M. G. Vasil'ev[2], A. D. Izotov[2], D. E. Korkin[2]

[1]National University of Science and Technology MISIS,
4 Leninskiy prospekt, Moscow 119049, Russian Federation

[2]Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninsky prospekt, Moscow 119991, Russian Federation

Abstract

High-temperature ferromagnets are widely used on a practical level. Based on them, magnetic memory for computers and various types of magnetic field sensors are created. Therefore, bulk ingots and thin-film samples of ferromagnet manganese antimonide (MnSb) with a high Curie point are of great interest, both from the practical and fundamental sides. Manganese antimonide films are obtained in hybrid structures using molecular-beam epitaxy. The thickness of the films does not exceed tens of nanometers. Despite their high sensitivity to magnetic fields, their small thickness prevents them from being used as magnetic field sensors. The aim of this work was to synthesise thick bulk ingots of manganese antimonide crystals and films with a thickness of ~ 400 nm on sitall and silicon substrates.

MnSb crystals were synthesised using the vacuum-ampoule method and identified using XRD, DTA, and microstructural analysis. The results of studies of bulk samples indicated the presence of an insignificant amount of antimony in addition to the MnSb phase. According to the DTA thermogram of the MnSb alloy, a small endothermic effect was observed at 572 °C, which corresponds to the melting of the eutectic on the part of antimony in the Mn-Sb system. Such composition, according to previous studies, guaranteed the production of manganese antimonide with the maximum Curie temperature. A study of the magnetic properties showed that the synthesised MnSb crystals were a soft ferromagnet with the Curie point ~ 587 K. Thin MnSb films were obtained by an original method using separate sequential deposition in a high vacuum of the Mn and Sb metals with their subsequent annealing. To optimise the process of obtaining films with stoichiometric composition, the dependences of the thickness of metal films on the parameters of the deposition process were calculated.

The temperature range of annealing at which the metals interact with the formation of ferromagnetic MnSb films was established, the films were identified, and their electrical and magnetic properties were measured.

Keywords: High-temperature soft ferromagnets, XRD, DTA, Thin films, Microstructure analysis, Manganese antimonide (MnSb)

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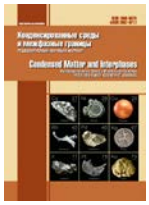
✉ Jaloliddinzoda Muhammadyusuf, e-mail: muhammad.9095@mail.ru



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Original articles

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TSF-MOCVD – a novel technique for chemical vapour deposition on oxide thin films and layered heterostructures

A. R. Kaul[1], R. R. Nygaard✉[1], V. Yu. Ratovskiy[1], A. L. Vasiliev[2,3,4]

[1]*Lomonosov Moscow State University,*
1 Leninskie Gory, Moscow 119991, Russian Federation

[2]*National Research Center "Kurchatov University",*
1 pl. Akademika Kurchatova, Moscow 123182, Russian Federation

[3]*Shubnikov Crystallography Institute of the Russian Academy of Sciences,*
59 Leninskiy prospect, Moscow 119333, Russian Federation

[4]*Moscow Institute of Physics and Technology,*
9 Institutskiy Pereulok, Moscow Region, Dolgoprudny, 141701, Russian Federation

Abstract

A new principle for supplying volatile precursors to MOCVD gas-phase chemical deposition systems is proposed, based on a two-stage evaporation of an organic solution of precursors from a soaked cotton thread, which passes sequentially through the zones of evaporation of the solvent and precursors. The technological capabilities of TSF-MOCVD (Thread-Solution Feed MOCVD) are demonstrated based on examples of obtaining thin epitaxial films of CeO_2, h-LuFeO3 and thin-film heterostructures β-Fe_2O_3/h-$LuFeO_3$. The results of studying the obtained films by X-ray diffraction, energy dispersive X-ray analysis, and high- and low-resolution transmission microscopy are presented. Using the TSF module, one can finely vary the crystallisation conditions, obtaining coatings of the required degree of crystallinity, as evidenced by the obtained dependences of the integral width of the h-$LuFeO_3$ reflection on the film growth rate. Based on the TEM and XRD data, it was concluded that β-Fe_2O_3 grows epitaxially over the h-$LuFeO_3$ layer. Thus, using TSF-MOCVD, one can flexibly change the composition of layered heterostructures and obtain highly crystalline epitaxial films with a clear interface in a continuous deposition process.

Keywords: Thread-solution feed, TSF, MOCVD, Epitaxy, Thin films, Heterostructures

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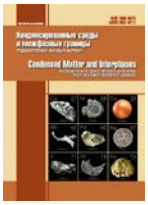
Для цитирования: Кауль А. Р., Нигаард Р. Р., Ратовский В. Ю., Васильев А. Л. TSF-MOCVD – новый способ осаждения оксидных тонких пленок и слоистых гетероструктур из газовой фазы. *Конденсированные среды и межфазные границы*. 2021;23(3): 396–405. https://doi.org/10.17308/kcmf.2021.23/3531

✉ Roy Nygaard, e-mail: rnygaard@mail.ru



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Original articles

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Creation of thin films on the surface of InP with a controlled gas-sensitive signal under the influence of PbO + Y_2O_3 compositions

V. F. Kostryukov✉, D. S. Balasheva, A. S. Parshinav

Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

Thin-film objects with a reproducible temperature dependence of the resistance, thermally stable, and easy to obtain can be used as the sensitive elements in semiconductor gas sensors. The aim of this study was to create thin films on the InP surface under the influence of an oxide chemostimulator + inert component (PbO + Y_2O_3, respectively) compositions and to determine their gas-sensitive properties and their dependence on the formula of the composition.

Thin films were synthesised on the InP surface by the method of chemically stimulated thermal oxidation under the influence of various PbO + Y_2O_3 compositions. The thickness of the formed films, their elemental and chemical composition were determined (by laser ellipsometry, X-ray phase analysis, and infra-red spectroscopy). A number of experiments were carried out to establish the gas-sensitive properties of the obtained films with respect to ammonia with concentrations of 120, 100, and 80 ppm.

By chemically stimulated thermal oxidation, we obtained thin films with semiconductor properties on the InP surface. It was determined that the samples had n-type conductivity. A gas-sensitive response was detected in the presence of ammonia in the atmosphere. The ability to create thin films with a predetermined value of sensory response was demonstrated.

Keywords: Semiconductors, Indium phosphide, Thin films, Gas sensitivity, Thermal oxidation

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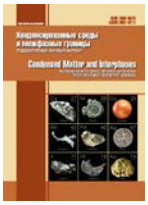
✉ Victor F. Kostryukov, e-mail: vc@chem.vsu.ru



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Structure and chemical composition of grain boundaries in the magnetic semiconductor GaSb<Mn>

V. P. Sanygin, O. N. Pashkova, A. D. Izotov✉

Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninsky prospekt, Moscow 119991, Russian Federation

Abstract

The structure and chemical composition of grain boundaries in GaSb<Mn> magnetic semiconductors have been investigated. We determined that quenching of the GaSb melt with 2% Mn results in the formation of a textured polycrystal (111). The grain boundaries of the texture are formed by split 60 degree dislocations with <110> dislocation lines. Microinclusions based on the ferromagnetic compound MnSb are located on the stacking faults of split dislocations. The chemical compositions of microinclusions differ, but their average composition is close to $Mn_{1.1}Sb$. The synthesized GaSb<Mn> is a soft ferromagnet with a coercive force of 10 Oe and a magnetic state approaching superparamagnetic.

Keywords: Magnetic semiconductors, Gallium antimonide, Crystal lattice defects, Magnetic clusters

Acknowledgements: The work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the state order to Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. The authors are grateful to the Centre for Collective Use of Physical Research Methods of IGIC RAS.

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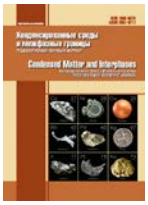
✉ Alexander D. Izotov, e-mail: izotov@igic.ras.ru



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Original articles

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Double molybdates of silver and monovalent metals

T. S. Spiridonova[1]✉, S. F. Solodovnikov[2], Yu. M. Kadyrova[1,3], Z. A. Solodovnikova[2], A. A. Savina[1,4], E. G. Khaikina[1,3]

[1]*Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, 6 ulitsa Sakhyanovoy, Ulan-Ude, Republic of Buryatia 670047, Russian Federation*

[2]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Akademika Lavrentieva prospekt, Novosibirsk 630090, Russian Federation*

[3]*Banzarov Buryat State University, 24a ulitsa Smolina, Ulan-Ude, Republic of Buryatia 670000, Russian Federation*

[4]*Skolkovo Institute of Science and Technology, 30, bld. 1 Bolshoy Boulevard, Moscow 121205, Russian Federation*

Abstract

The Ag_2MoO_4–Cs_2MoO_4 system was studied by powder X-ray diffraction, the formation of a new double molybdate $CsAg_3(MoO_4)_2$ was established, its single crystals were obtained, and its structure was determined. $CsAg_3(MoO_4)_2$ (sp. gr. $P\bar{3}$, Z = 1, a = 5.9718(5), c = 7.6451(3) Å, R = 0.0149) was found to have the structure type of $Ag_2BaMn(VO_4)_2$. The structure is based on glaserite-like layers of alternating MoO_4 tetrahedra and $Ag1O_6$ octahedra linked by oxygen vertices, which are connected into a whole 3D framework by $Ag2O_4$ tetrahedra. An unusual feature of the Ag2 atom environment is its location almost in the centre of an oxygen face of the $Ag2O_4$ tetrahedron. Caesium atoms are in cuboctahedral coordination (CN = 12).

We determined the structures of the double molybdate of rubidium and silver obtained by us previously and a crystal from the solid solution based on the hexagonal modification of Tl_2MoO_4, which both are isostructural to glaserite $K_3Na(SO_4)_2$ (sp. gr. $P\bar{3}m1$). According to X-ray structural analysis data, both crystals have nonstoichiometric compositions $Rb_{2.81}Ag_{1.19}(MoO_4)_2$ (a = 6.1541(2), c = 7.9267(5) Å, R = 0.0263) and $Tl_{3.14}Ag_{0.86}(MoO_4)_2$ (a = 6.0977(3), c = 7.8600(7) Å, R = 0.0174). In the case of the rubidium compound, the splitting of the Rb/Ag position was revealed for the first time among molybdates. Both structures are based on layers of alternating MoO_4 tetrahedra and AgO_6 or (Ag, Tl)O_6 octahedra linked by oxygen vertices. The coordination numbers of rubidium and thallium are 12 and 10.

Keywords: Double molybdates, Silver, Monovalent metals, Binary systems, X-ray diffraction study, Structure, Glaserite

Acknowledgements: the authors are grateful to PhD Irina A. Prodan (Gudkova) and Ms Oksana A. Gulyaeva for recording and processing the X-ray diffraction data of the crystals on a Bruker X8 Apex CCD automated diffractometer. This research was supported by the Ministry of Science and Higher Education of the Russian Federation, projects No. 0273-2021-0008 (Baikal Institute of Nature Management, SB RAS), and No. 121031700313-8 (Nikolaev Institute of Inorganic Chemistry, SB RAS).

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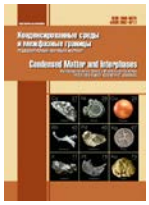
✉ Tatyana S. Spiridonova, e-mail: spiridonova-25@mail.ru



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Activation of film growth on indium phosphide by pulsed photon treatment

E. V. Tomina[1,2]✉, B. V. Sladkopevtsev[2], D. V. Serikov[3], I. Ya. Mittova[2]

[1]Morozov Voronezh State Forest Engineering University,
8 Timiryazeva ul., Voronezh 394087, Russian Federation

[2]Voronezh State University,
1 Universitetskaya pl., Voronezh 394018, Russian Federation

[3]Voronezh State Technical University,
14 Moskovsky prosp., Voronezh 394026, Russian Federation

Abstract

Photon activation of various physicochemical processes by the radiation of powerful pulsed xenon lamps (radiation range of 0.2-1.2 μm) is one of the promising areas of material science. The aim of this study was to determine the effect of pre-oxidative pulsed photon treatment on the process of thermal oxidation of indium phosphide with a nanosized layer of V_2O_5 on the surface, as well as its effect on the composition and morphology of the formed films.

We determined the optimal mode of pre-oxidative pulsed photon treatment of magnetron-formed V_2O_5/InP heterostructures with a radiation density of 15 J/cm^2. By laser and spectral ellipsometry methods, photon activation of V_2O_5/InP before thermal oxidation was found to increase the thickness of the formed films practically twofold. X-ray diffraction analysis confirms the intensification of the phosphate formation process. The morphological characteristics of the films were determined by atomic force microscopy.

Pre-oxidative pulsed photon treatment with an optimal radiation density of 15 J/cm^2 activates the thermal oxidation of V_2O_5/InP heterostructures. It is associated with the formation of new active centres and accelerated rearrangement of chemical bonds in the intermediate complexes of the V_2O_5 catalyst with semiconductor components.

Keywords: Indium phosphide, Vanadium (V) oxide, Thermal oxidation, Thermal oxidation, Pulsed photon treatment

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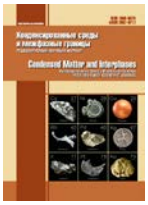
✉ Elena V. Tomina, e-mail: tomina-e-v@yandex.ru



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An integral feature of porous silicon and its classification

A. M. Khort✉, **A. G. Yakovenko, Yu. V. Syrov**

MIREA – Russian Technological University. Institute of Physics and Technology,
78 Prospekt Vernadskogo, Moscow 119454, Russian Federation

Abstract

Porous silicon is currently one of the most studied materials which is used both in the areas traditional for silicon, such as electronics and optoelectronics, and in completely unconventional ones, such as catalysis, energetics, biology, and medicine. The multiple possibilities of the material are revealed due to the fact that its structure can be radically different depending on the properties of the initial silicon and the methods of obtaining porous phases. The use of any material inevitably leads to the need to classify its various forms. The purpose of the article was to find the most significant parameter that can be used as the basis for the classification of porous silicon.

Historically, the terminology defined by the IUPAC pore size classification has been used to classify porous silicon. Due to the authority of IUPAC, many researchers have considered this terminology to be the most successful and important, and the radial pore size has often been regarded as a main parameter containing the most important properties of porous silicon. Meanwhile, the unique properties and practical application of porous silicon are based on its developed inner surface. The method of nitrogen porosimetry, which is simple in its practical implementation, is often used in scientific literature to determine this value.

The most suitable integral parameter for the classification of porous silicon, regardless of its structure and morphology, is the total specific internal surface (cm^{-1}) that can be relatively easily established experimentally and is of fundamental importance for almost all applications of porous silicon. The use of this value does not exclude the use of other parameters for a more detailed classification.

Keywords: Porous silicon, Classification, Radial pore size, Nitrogen porosimetry, Ttotal specific internal surface area

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✉ Andrei M. Khort, e-mail: poristsil@yandex.ru