УДК 504:620.3

I. Bogdanov, DSc, Professor, Rector
Berdyansk State Pedagogical University
Schmidt str., 4, Berdyansk, Zaporizhia region, Ukraine, 71100
V. Vambol, DSc, Associate Professor, Professor of Department
National University of Civil Protection of Ukraine
Chernishevska str., 94, Kharkiv, Ukraine, 61000
Y. Suchikova, PhD, Associate Professor
National University of Civil Protection of Ukraine
Chernishevska str., 94, Kharkiv, Ukraine, 61000

THE IMPROVEMENT ENVIRONMENTAL SAFETY OF NANOMATERIALS BY MEANS OF ENVIRONMENTAL ASSESSMENT

The article presents the recommendations for environmental assessment of nanoproducts. There have been worked outthe scheme of porous gallium arsenide lifecycle. The method of forming of porous layers of gallium arsenide has been improved. There have been done the expertise of por-GaAs and structures on its base - gallium nitride. It was found that porous gallium arsenide may be health hazardous. Porous gallium nitride is formed by the method of electrochemical etching in the solutions of acids. Such methods of synthesis of nanostructures pose an ecological threat. Understanding these threats will optimize the processes of formation and operation of nanomaterials for ecological safety.

Keywords: ecological safety, nanomaterials, porous gallium arsenide, life cycle.

Problem statement. Nanotechnologies have become strategic industrial and scientific direction. In many areas of science and technology, there is a great interest in the products of nanotechnology, which is associated with the real possibility of practical implementation of their unique properties [1–4].

Nanotechnologies traditionally include designs, in which materials and systems are used that meet three criteria (see fig. 1). The penetration of products of nanotechnologies into the environment can lead to many consequences, which are currently impossible to predict due to the lack of information. However, information about the consequences of the uncontrolled emission of nanoparticles in the environment remains quite scarce.

Exists the need to search for the ways to provide ecological safety of nanotechnology products throughout their life cycle for their further using.

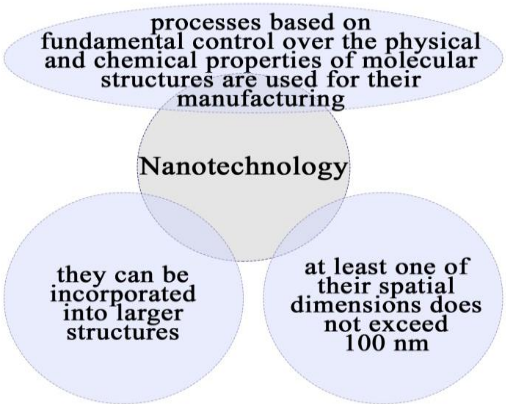

Figure 1 – Nanotechnology criteria

Analysis of the recent researches and publications. Widespread implementation of nanotechnologies in industry is predetermined by a number of factors (see fig. 2). Nanoindustry develops rapidly and, due to this, attraction of investment from government and businesses to this sector is growing around the world.

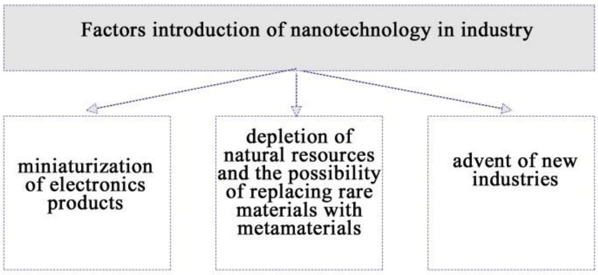

Figure 2 – Factors introduction of nanotechnology in industry

At the same time, more and more researchers acknowledge that the use of nanomaterials may pose a danger to human health and environment [5, 6].

Studies have shown that the quality of nanomaterials, which make them popular, may pose a potential ecological threat [7].

With this in mind, paper [8] proposes to conduct analysis of nanotechnologies with regard to four principles (see fig. 3).

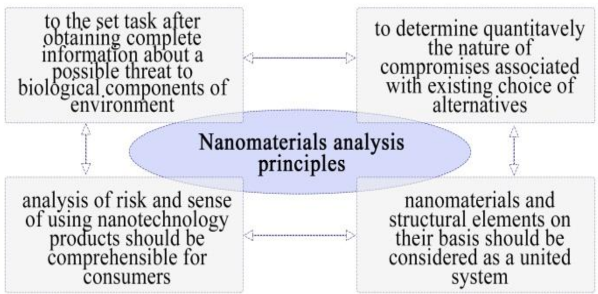

Figure 3 – Nanomaterials analysis principles

In paper [9], authors demonstrate that standard toxicological methods cannot be applied to determine the hazards of nanomaterials: the properties of the latter are caused not by concentration in the volume of material, but rather by its quantodimensional properties.

Many scientists point to potential dangers of nanotechnology products for the environment. However, there is no unified approach to determining the extent of danger of nanomaterials. Methods for detecting this danger at different stages of synthesis and the use of nanoindustry products have not been determined up to now, nor have been explored the problems of ecological safety of nanotechnology application.

Statement of the problem and its solution. Conducted studies were aimed at searching for the ways of providing ecological safety for nanotechnology products throughout their life cycle.

A comprehensive research into the risks of using nanomaterials and controlling their impact on the environment and the human body is a long-lasting and scientifically complicated process. In addition, there are no sufficient data on the toxicity of large quantities of nanomaterials and labeling and passports have not been developed for most of them. That is why we will focus only on general types of nanoindustry influence on the ecosystem and humans.

To do this, one must clearly understand that nanomaterials may pose a danger not only in the course of their usage, but at all stages of their life cycle, the simplified schematic of which is shown in table 1. A manufacturer must provide full information on the nanomaterial according to the procedure shown in table 2.

Table 1 – Schematic of life cycle of nanomaterials

№ Stage	Title Stage	Characteristic
Stage 1	extraction and production of raw materials from nanomaterials	one should consider substances of which the nanoproduct is made
Stage 2	production of nanomaterials	is directly related to the methods of synthesis of nanomaterials
Stage 3	storage and packaging	it is necessary to take into consideration specific features of materials
Stage 4	reclamation and wastes of nanomaterials	testing and identifying the quality and suitability of nano– raw materials for later use is carried out
Stage 5	usage of nanomaterilas	research should be comprehensive, taking into account not only physical and chemical characteristics of substances, but also behavior of the whole product and its components during the operation period
Stage 6	production of nanomaterials products	it should be taken into consideration that nanomaterial exists as a component of the product, which is why its separation is impossible in many cases. Then the reclamation of the entire product is necessary

Table 2 – Recommended procedure to control nanomaterials

1	Product name	product name must correspond exactly to the one indicated on the label; form
2	Usage area	technological purpose (raw material, intermediate product, purpose-oriented product, etc.)
3	Information about manufacturer	full official name, address, telephone, fax, e-mail address, site (if available)
4	Nanoparticles content in material composition	mass or/and number of particles on conversion to mass/ volume unit of product
5	Chemical composition	by systematic or trivial nomenclature, formula, molecular weight
6	Average dimensions of particles	specific surface on conversion to distribution of particles by dimensions
7	Content of cancerogens	according to hygienic norms
8	Impurities	composition, concentration
9	Solubility	in water, lipid and different media
10	Methods of research	provide the proof of existence of nanoparticles in the product or classification as nanomaterial
11	Method of obtaining nanomaterials	by dispersion, by condensation from gas phase, solubility methods, other
12	Hazard class of product	according to GOST (State Standard) 12.1.007–76
13	Possible technogenic risks	if any
14	Toxicological and hygienic characteristics	general toxical and irritation action, allergenity, cancerogenity, mutagenity
15	Impact on environment	migration to ecological objects, stability, biodegradability
16	Rules of handling and storage	which exclude possibility of non-sanctioned influence of product and its components
17	Reclamation	procedure of safe neutralization, utilization and disposal of nanoindustry products
18	Standardizing and legislative provision	information on legislation in field of rules of safe production, circulation and utilization

Specific properties of nanomaterials may vary for each individual case, even with the same chemical formula and method of obtaining. In addition, most indicators are defined not for all substances, and this definition is often impossible because of the lack of necessary equipment or even a method of definition.

As an experimental nanomaterial, we selected porous gallium arsenide (por-GaAs), which was obtained on the substrate of monocrystalline gallium arsenide by the method of photoelectrochemical etching.

Given the general scheme of nanomaterial life cycle, it is expedient to compose LCA of por-GaAs and of the product based on it (see fig. 4). We will accept gallium nitride (GaN/por-GaAs).

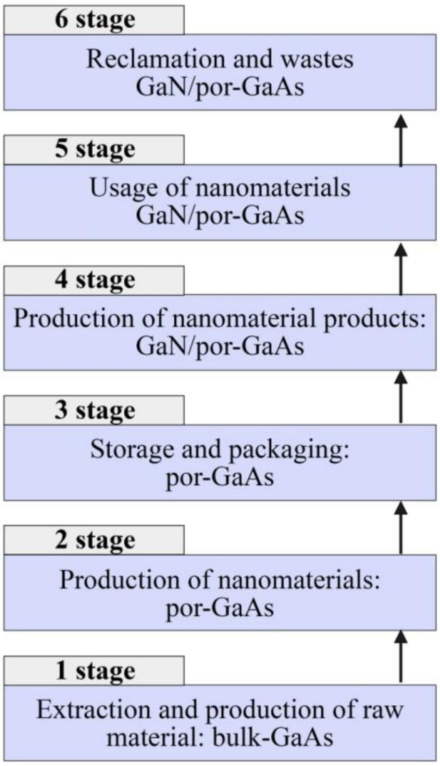

Figure 4 – Life cycle of porous gallium arsenide and gallium nitride based on it

Stage 1 «Extraction and production of raw material bulk-GaAs»

Porous gallium arsenide is made at the surface of monocrystalline gallium arsenide (mono- GaAs or bulk- GaAs). In its turn, monocrystalline gallium arsenide is made by the Chokhralsky.

There are some data on cancerogenity of gallium arsenide: according to the website of U.S. National Library of Medicine, indium phosphide is classified as a substance, probably cancerogenic to humans (Group 2A) [10]. In view of the foregoing, the plates of gallium arsenide should be accompanied by a danger pictogram «Health hazard».

However, it should be taken into account that gallium arsenide is usually presented in the form of crystalline plates that are thermodynamically and electrically stable in the air. So we can assume that the plates themselves do not pose a threat to life and health.

Stage 2 «Production of nanomaterials por-GaAs»

For the experiment, we selected 10 monocrystalline plates of n-type gallium arsenide, alloyed with sulfur. Porous surface was formed in electrochemical cell with solution of hydrochloric acid. Current density during the treatment was selected in the range of 80–180 mA/cm^2, at etching time of 5–10 min.

Given the fact that the solutions of acids are used for the formation of porous layers, it can be argued that this technology is not safe for human health. That is why this experiment should be carried out with the use of means of collective and individual protection. The used electrolyte must be disposed of according to valid legislation requirements.

As a result, a porous layer with tightly packed pores was formed at the surface (see fig. 5). Porous structure is a nanomaterial, consisting of deep cylindrical holes – pores and walls between them – quantum wires.

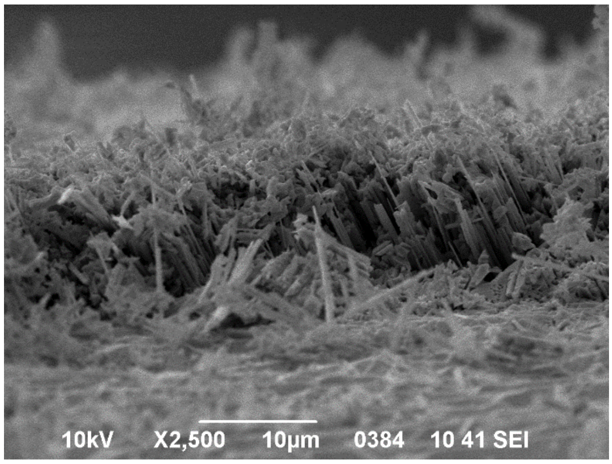

Figure 5 – SEM image of por-GaAs (100): 10 % HCl, j=120 mA/cm^2, t=5m

By the results of scanning electronic microscopy, it is possible to establish that dimensions of pores reach 80 nm on average. This indicates that this structure is mezoporous. Dimensions of walls between the pores are within (20–60) nm (see fig. 6).

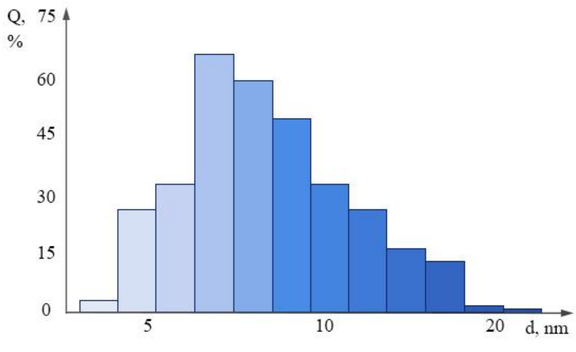

Figure 6 – Distribution of quantum wires by dimensions: Q is the share of particles, %; d – dimensions of particles, nm

Porosity of the obtained layers varies from 30 to 80 %. Fluctuation of surface porosity is caused by uneven concentration non-uniformity of distribution of impurity in the volume of ingot, which occurs during the crystal growth.

Chemical composition of porous samples was assessed using the EDAX method (see fig. 7). Based on results of these data, it may be concluded that the oxide film was not formed at the surface of porous por-GaAs, the existence of elements that make up the etcher was not observed either.

The top layer may shear off even in the contact with hands, forming a nanodispersed powder, which is a real threat to human health – such nanoparticles easily get into the respiratory tract and penetrate the skin.

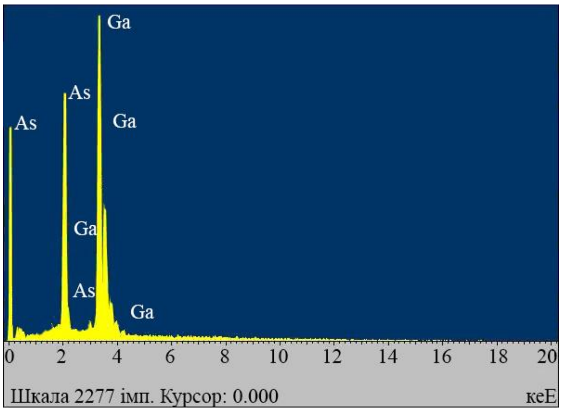

Figure 7 – Chemical composition of elements at the surface of por- GaAs

Stage 3 «Storage and packaging of por-GaAs»

A specific feature of por-GaAs is its ability of "ageing" in the open air. The surface of porous layers of gallium arsenide under normal conditions of storage is covered by the oxide layer. Chemical analysis of the surface of porous GaAs revealed violations of stoichiometry of the original crystal. Oxygen atoms emerged at the surface of the sample (see tab. 3). It indicates creation of proper oxides of GaAs.

Table 3 – Percentage content of elements at the surface of porous n- GaAs, obtained with the help of EDAX method

Spectrum	Component		
	O	As	Ga
Spectrum 1	17.48	22.10	60.42
Spectrum 2	5.76	22.36	71.88
Spectrum 3	13.80	22.10	64.10

Porous surface is characterized by high density of surface states in the forbidden zone, which leads to fixing of the Fermi level, the position of which at the surface practically does not depend on the nature of adsorbed atoms [11]. This circumstance negatively affects the work of many micro– and optoelectronic devices, preventing complete revealing high potential abilities of these semiconductors. To eliminate undesirable surface influence on the properties of devices, the technique called "passivation" is actively developing in technology, within which a variety of methods of surface treatment, related to applying coverings on it, are designed [12].

At chemical passivation, an oxide layer is removed from the surface of semiconductor, instead of which a thin crystalline film of chemically inert material is formed. This film can perform the functions of a superfine buffer layer and protect surface of the semiconductor from contact with aggressive components of the environment [13].

The layers of porous GaAs were kept in the Na_2S solution for 20 min. During chalcogenide por-GaAs passivation the oxide layer is removed, a thin crystalline film of chemically and electrically inert material is formed instead of it. These nanomaterials may be stored under normal conditions in a special container, avoiding contact with aggressive substances.

Stage 4 «Production of nanomaterial products GaN/por-GaAs»

Thin films of gallium nitride on the substrate of porous gallium arsenide were obtained by the method of ray-radical epitaxy. The main difference of this method from the traditional epitaxy is that one component comes with gas phase (atomic nitrogen), and the other (gallium) is obtained from the volume of the crystal [14]. As atomic nitrogen, especially pure ammonia is used, which passes through the high-frequency discharge, resulting in atomic nitrogen, which is a chemically active. A stream of atomic nitrogen gets on the crystal of gallium arsenide. It results in the process of conversion of surface layers. At the surface of porous GaAs, thin GaN films emerge (see fig. 8). A film of gallium nitride is formed with the violation of stoichiometry toward gallium.

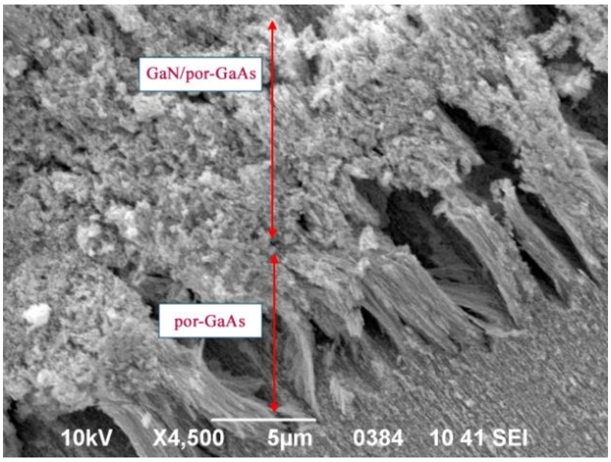

Figure 8 – GaN film is formed at the surface of por-GaAs by the method of radical-beam epitaxy

Gallium nitride may cause irritation of skin and eyes, pain in joints and bones, tooth decay, nervous and gastrointestinal disorders, pain in the heart and the overall weakness [15]. Acute and chronic toxicity of this substance are not known enough. Given high thermodynamic, electrical and chemical stability of indium nitride, it can be argued that its crystals may be considered conditionally safe under normal conditions.

Stage 5 «Usage of nanomaterials»

The structures, based on nitrides of the third group, have a predicted operation life of about 5 years [16, 17]. In this context, we imply retaining all electro-physical indicators at the output level. This is followed by a slow degradation of the structure surface. GaN/GaAs is used as a raw material for solar cells whose operation life is 20 years.

Stage 6 «Reclamation and wastes»

As was noted above, the original nanomaterial is used as a raw material for products and devices, the reclamation of which is recommended to conduct with the "hazardous wastes" label [18, 19]. Currently, there is a limited number of studies, devoted to the recycling of nanomaterials, and, until sufficient data are collected, such materials should be treated as hazardous [20].

The analysis, presented above, of quality control of gallium arsenide at all stages of the life cycle allows making up a control card of por-GaAs (see fig. 9) according to the procedure, presented in table 2. To identify the possible danger of nanoproduct, it is necessary to evaluate its indicators from its design stage to the reclamation stage. This approach might be applied in the analysis of other nanomaterials, taking into account their specific features.

Methods of measurement of parameters and properties of nanostructures is a fixed set of operations and regulations, compliance with which provides obtaining measurement results with guaranteed accuracy according to the adopted method. One may say that the method of measurement is the technology of measurement process. However, most methods are still at the stage of development and do not allow providing full control of quality and safety of nanomaterials.

Conclusions. A scheme of the life cycle of por-GaAs was developed, which should be considered as a multi-stage process from the preparation of source material to the reclamation. The methods for controlling quality and safety of porous gallium arsenide and GaN based on them were presented. It is necessary to exercise control at every stage of the lifecycle using appropriate techniques and methods of research. It was found that porous gallium arsenide is dangerous for health material.

Acknowledgement. Present study was conducted within the framework of the scientific state-funded research «Nanostructured semiconductors for power efficient ecologically friendly technologies that increase power efficiency and ecological safety of the urbosystem» (State registration number 0116U006961).

Figure 9 – Control card of quality and ecological safety of porous gallium arsenide

References

1. Khrypunov G. Increasing the efficiency of film solar cells based on cadmium telluride / G. Khrypunov, S. Vambol, N. Deyneko, Y. Suchikova // Eastern-European Journal of Eenterprise Technologies. – 2016. – № 6/5 (84) – P. 12–18.

2. Suchikova Y. Provision of environmental safety through the use of porous semiconductors for solar energy sector / Y. Suchikova // Eastern-European Journal of Eenterprise Technologies. – 2016. – № 6/5 (84) – P. 26–33.

3. Bremus-Koebberlinga E. A. Nano structures via laser interference patterning for guided cell growth of neuronal cells / E. A. Bremus-Koebberlinga, S. Beckemper, A. Gillner // Journal of laser applications. – 2012. – Vol. 24, №. 4. – P. 042013-1– 042013-6.

4. Beckemper S. Generation of periodic micro- and nanostructures by parameter-controlled three-beam laser interference technique / S. Beckemper, J. Huang, A. Gillner, K. Wang, // J. Laser Micro/Nanoeng. – 2011. – № 6 (1). – P. 49–53.

5. Sengul H. Toward sustainable nanoproducts: An overview of nanomanufacturing methods / H. Sengul, T. L. Theis, S. Ghosh // J. Ind. Ecol. –2008. – № 12. – P. 329–359.

6. Meyer D.E. An examination of existing data for the industrial manufacture and use of nanocomponents and their role in the life cycle impact of nanoproducts / D. Meyer, M. Curran, M. Gonzalez // Environ. Sci. Technol. – 2009. – № 43. – P. 1256–1263.

7. Dhingra R. Sustainable Nanotechnology: Through Green Methods and Life-Cycle Thinking / R. Dhingra, S. Naidu, G. Upreti, R. Sawhney // Sustainability. – 2010. – V. 2. –P. 3323–3338.

8. Theis T. L. A life cycle framework for the investigation of environmentally benign nanoparticles and products / T. L. Theis, B. R. Bakshi, D. Durham, V. M. Fthenakis, T. G. Gutowski, J. A. Isaacs, T. Seager, M. R. Wiesner // Phys. Status Solidi RRL. – 2011. – P. 1–6.

9. Seager T. P. Coupling Multicriteria Decision Analysis and Life Cycle Assessment for Nanomaterials / T. P. Seager, I. Linkov // Journal of Industrial Ecology. – 2008. – V. 12, № 3. – P. 282–285.

10. U.S. National Library of Medicine [Electronic resource]. – Mode of access : https://pubchem.ncbi.nlm.nih.gov/compound.

11. Liu Y. Chemical passivation processes for biofunctionalization schemes on semiconductor surfaces / Y. Liu, J. Chen, A. V. Teplyakov // Langmuir. – 2012. – № 6/28 (44). – P. 15521-8.

12. Bessolov V. N. Chalcogenide passivation of III–V semiconductor surfaces / V. N. Bessolov, M. V. Lebedev // Semiconductors. – 1998. – № 32. – P. 1141.

13. Vambol S. Analysis of the ways to provide ecological safety for the products of nanotechnologies throughout their life cycle / S. Vambol, V. Vambol, Y. Suchikova, N. Deyneko // Eastern-European Journal of Eenterprise Technologies. – 2017. – № 1/10 (85) – P. 27–36.

14. Suchikova Y. A. Synthesis of indium nitride epitaxial layers on a substrate of porous indium phosphide / Y. A. Suchikova // Journal of Nano- and Electronic Physics. – 2015. – Vol. 7, Is.3. – P. 03017-1 – 03017-3.

15. Sato T. Electrochemical formation of N-type GaN and N-type InP porous structures for chemical sensor applications / T. Sato, X. Zhang, K. Ito, S. Matsumoto, Y. Kumazaki // Browse Conferences SENSORS, 2016 IEEE (30 Oct.-3 Nov). 2016.

16. Suchikova Y. A. Usage of porous indium phosphide as substrate for indium nitride films / Y. A. Suchikova, V. V. Kidalov, A. A. Konovalenko, G. A. Sukach // ECS Transactions. – 33(38). – 2011. – P. 73–77.

17. Singh P. Degradation Physics of High Power LEDs in Outdoor Environment and the Role of Phosphor in the degradation process / P. Singh, C. M. Tan // Scientific Reports. – 2016. – № 6. – P. 24052.

18. Tan C. M. Time Evolution Degradation Physics in High Power White LEDs Under High Temperature-Humidity Conditions / C. M. Tan, P. Singh // IEEE Transactions on Device and Materials Reliability. – 2014. – № 14. – P. 742–750.

19. Amoabediny G. H. Guidelines for safe handling, use and disposal of nanoparticles / G. H. Amoabediny, A. Naderi, J. Malakootikhah, M. K. Koohi, S. A. Mortazavi, M Naderi, H. Rashedi // J. Phys. : Conf. – 2009. – № 170. – P. 012037.

20. Rajendran V. Development of Nanomaterials from Natural Resources for Various Industrial Applications / V. Rajendran // Advanced Materials Research. – 2009. – Vol. 67. – P. 71–76.

The article received by the editorial board 06.03.2017

І. Т. Богданов, В. В. Вамболь, Я. О. Сичікова

ПІДВИЩЕННЯ ЕКОЛОГІЧНОЇ БЕЗПЕКИ НАНОМАТЕРІАЛІВ ШЛЯХОМ ПРОВЕДЕННЯ ЕКОЛОГІЧНОЇ ЕКСПЕРТИЗИ

У статті представлено рекомендації щодо проведення екологічної експертизи нанопродуктів. Розроблено схему життєвого циклу поруватого арсеніду галію. Удосконалено методику формування поруватих шарів арсеніду галію. Проведено експертизу por-GaAs і структури на його основі – нітриду індію. Встановлено, що поруватий арсенід галію може бути небезпечним для здоров'я. Поруватий арсенід галію формується методом електрохімічного травлення у розчинах кислот. Такі методи синтезу наноструктур становлять екологічну загрозу для навколишнього середовища. Розуміння цих загроз дозволить оптимізувати процеси формування та експлуатації наноматеріалів для забезпечення екологічної безпеки.

Ключові слова: екологічна безпека, наноматеріали, поруватий арсенід галію, життєвий цикл.

И. Т. Богданов, В. В. Вамболь, Я. А. Сычикова

ПОВЫШЕНИЕ ЭКОЛОГИЧЕСКОЙ БЕЗОПАСНОСТИ НАНОМАТЕРИАЛОВ ПУТЕМ ПРОВЕДЕНИЯ ЭКОЛОГИЧЕСКОЙ ЭКСПЕРТИЗЫ

В статье представлены рекомендации по проведению экологической экспертизы нанопродуктов. Разработана схема жизненного цикла пористого арсенида галлия. Усовершенствована методика формирования пористых слоев арсенида галлия. Проведена экспертиза por-GaAs и структуры на его основе – нитрида индия. Установлено, что пористый арсенид галлия может быть опасным для здоровья. Пористый арсенид галлия формируется методом электрохимического травления в растворах кислот. Такие методы синтеза наноструктур представляют экологическую угрозу для окружающей среды. Понимание этих угроз позволит оптимизировать процессы формирования и эксплуатации наноматериалов для обеспечения экологической безопасности.

Ключевые слова: экологическая безопасность, наноматериалы, пористый арсенид галлия, жизненный цикл.