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An obtaining of nanoheteroepitaxial structures with quantum dots for high effective photovoltaic devices, investigation of their properties

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Summary. Experimental results showing of a possibility of an obtaining by a method of liquid phase epitaxy with a pulse cooling of a substrate nanoheteroepitaxial structures with quantum dots for a manufacturing of an one-junction concentrate sun elements are presented. For this purpose an installation and a graphite cassette allowing to obtain many layer structures of high quality have been made. Experiments for an obtaining of structures and complex of investigations of materials under various stages of a technological process have been carried out. Morphology of a structures surface has been learned by a microscope MII-4. Sizes of quantum dots have been found by methods of probe microscopy. Measurements and analysis of photoluminescence spectra of structures have been carried out.

Key words: nanoheteroepitaxial structures, quantum dots, liquid phase epitaxy, substrate, growing.

INTRODUCTION.

Due to the development of modern technologies, investigations in a region of an obtaining of nanoheteroepitaxial structures (NHES) with quantum dots (QD) with a purpose of a creating based on them various devices with improvement properties induce a great interest. One of the important areas for a wide application of those structures is a photovoltaic with a possibility of a creating 3-d generation solar cells with efficiency above 50 % [6]. The creation of such devices will allow better use of electric motors, replacing their internal-combustion engines, which have a number of negative factors [10, 20].

Optimal semiconductor materials for manufacturing one-junction solar cells with maximal efficiency are wide band semiconductor such as gallium phosphide and gallium arsenide. Solar cells, manufactured for example on a base of gallium phosphide, have the efficiency up to 33% whereas maximal efficiency of silicon solar cells does not exceed 27 %. There are theoretical calculations showing that introduction of narrow-band semiconductor QDs in a wide-band solar cell allows to rich the efficiency above 70% due to a summing of an energy of two long-wave light quanta that does not absorbing in wide-band semiconductor material and absorbing by a QD material [2, 7, 18, 23].

At present time QDs basically are obtained by methods of molecular-beam epitaxy and MOCVD. In this case substrates with a lattice constants that significantly different from the lattice constants of materials for QD are used [11]. Despite advances in technology of an obtaining of QD by these methods there are some problems connected with a high cost of technical equipment and specific defects in obtained by these methods materials. All these require a search for alternative methods that can be used for growing of NHES with QD. Such methods must be economically viable and competitive in comparison with applicable today. As such alternative for an obtaining of NHES with QD we use method of a liquid-phase epitaxy (LPE) with pulse cooling of substrate (PCS) [1, 19, 25]. A manufacturing of quantum-sized structures requires not only high technological equipment for their obtaining but a creating new procedures and equipment for a preparation of main and auxiliary materials and also an inspection of raw materials and making structures on various stages of their manufacturing. For a purpose of inspection of morphology of a quantum-sized objects surface at present time it is widely used methods of electron and scanning probe microscopy [8, 12]. Optical properties are investigated by a learning of spectral dependencies of an absorbing, reflection and photoluminescence [11].

PURPOSE

Main purposes of the paper are the description of investigations connecting: with a developing of technological equipment and installations, studying processes of growing and obtaining many layers NGES with QD with reproduced characteristics; with a developing and a justification laboratory technical scheme of a carrying out processes of growing of NGES with QD; with an investigation of a morphology of the surface of obtained structures and structures with open QD by methods of optical and probe microscopy; with an investigation of optical properties of obtained samples.

MAIN MATERIAL

For a carrying out of experiments for the growing of many-layer NGES with QD the laboratory equipment of horizontal type including a heating furnace, a quartz quasi hermetical reactor with a working cassette and installations, a block for a temperature control, a gas distribution system and a vacuum post has been developed, manufactured and established. Constructive features of the equipment provide a possibility of a heating and cooling charged into the reactor of the materials with a velocity up to 30 and 10 grades per minute respectively with a maximal shelf temperature up to 1200°C [4, 14, 15].

The quasi hermetical reactor is provided with a closing device as a flange. For supply and discharge from the quartz reactor working gases and vacuum the flange has technological input and output as well as hermetically sealed holes for inputs of molybdenum or quartz manipulators for a moving of cassette sliders under a process of a growing and shifting of a water-cooled heat sink with built-in thermocouple.

An obtaining of NGES with QD from solution-melt has been carried out by a designed and manufactured graphite cassette that allows to grow high quality NGES with QD by the method of pulse cooling of a substrate on substrates of various diameters and thickness.

One of the purposes of this work was the obtaining of NGES with QD for a manufacturing photoelectrical converter on a base of A^3B^5compounds using as substrates silicon wafers in order to reduce their cost.

For an obtaining NGES with QD by the method LFE with PCS has been developed and justified a laboratory technological scheme of a carrying out of a process. Conventionally, the scheme can be divided into three process steps: a preparing of main materials, technological equipment and installations to the process of the obtaining NGES with QD; the carrying out the process of the obtaining NGES with QD; management of quality and parameters of source materials and grown NGES with QD.

After the preparing main materials with a purpose of a degreasing, a clearing dirt from the surface and a removing oxide and broken (defective) material layer samples was been prepared for a cooking solutions-melts [21, 3, 9, 22, 13, 24]. That subsequently was been loaded to a prepared to the process the cassette. A components mass needing to a cooking saturated solution melts has been calculated on a base of state diagrams of systems Sn-Ga-As, In-Ga-As, Sn-In-As, In-Al-Ga-As, Al-Ga-As, Ga-P-Sn, Sn-Yb for temperature of a carrying out of process of 480°C. A weighing of components has been carried out by a microanalytical scales with a precision of 0,1 mg.

The growing of NGES with QD for solar cells on substrates GaAs or Si of n-type conductivity has been carried out as follows:

1. The growing of a metallic layer of ytterbium of a thickness 10 nm for a case of Si substrate.
2. The growing of a buffer layer of GaAs or GaP of a thickness 100 nm of a n-type conductivity on a substrate GaAs or Si n-type conductivity.
3. The growing of a many layers structure consisting from layers of QD arrays (InAs), seeded by spacer layers from a array materials GaAs or GaP of a n-type conuctivity.
4. The growing of a thick (100 nm) layer GaAs or GaP of n-type conductivity.
5. The growing of a thick (100 nm) layer GaAs or GaP of p-type conductivity.
6. The growing of a many layers structure consisting from layers of QD arrays (InAs), seeded by spaces layers of array materalsGaAs or GaP of p-type conductivity.
7. The Growing of a layer $Al_{0,7}Ga_{0,3}As$ or GaP of p-type conductivity of a thickness of 10-30 nm for an optical window.
8. The growing of under contuct layer GaAs or GaP of p-type conductivity of 100 nm thickness.
9. An infliction of a cooling solution-melt containing over 10 at. % Al for a forming of a quality surface of the under contact layer for a case of GaAs.

Analogical stages are used for a obtaining of NGES with QD on substrates of p-type conductivity.

A main method for management and characterization of parameters of manufacturing NGES are spectral dependence of an absorbing, reflection and photoluminescence. A morphology of grown structures surfaces was been evaluated by methods of an optical microscopy, and morphology of plates surfaces with grown open QD was been evaluated by methods of a probe microscopy.

RESULTS OF RESEARCH

The morphology of surfaces of obtained epitaxial structures and thickness of bulk epitaxial layers (ES) was been measured on a structures cleavage and was been studied by a MII-4 microscope after a treating in etchant $HNO_3:HF:H_20=2:1:5$ and illuminating for 1 minute.

On a Fig.1 a transverse cleavage of gallium arsenide substrate with NGES with QD is represented. A thickness of a layer is approximately 1,5 mkm. ES have an mirror surface morphology. A thickness of microuniformity the surface is not over 0,18 mkm. An investigation of the cleavage has showed an absence of vestige of the corroding: an ES-substrate boundary is planar, ES is solid, inclusions of a solvent on a heteroboundary was not been observed.

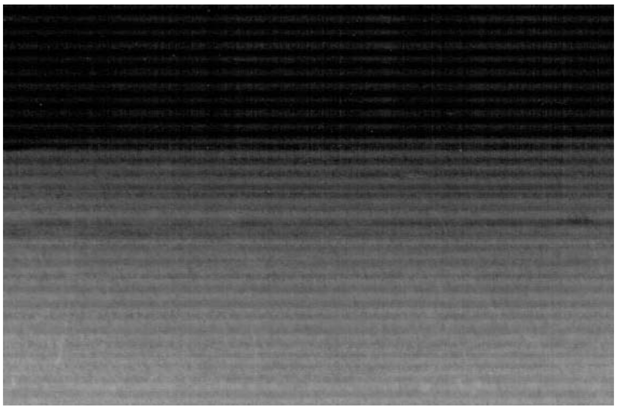

Fig. 1. Transverse cleavage of NGES with QD on a gallium arsenide substrate

A typical morphology of an ES surface grown on a substrate gallium arsenide under growing on substrates (111) and epitaxy temperature 450-500^{o}C are showed on Fig.2.

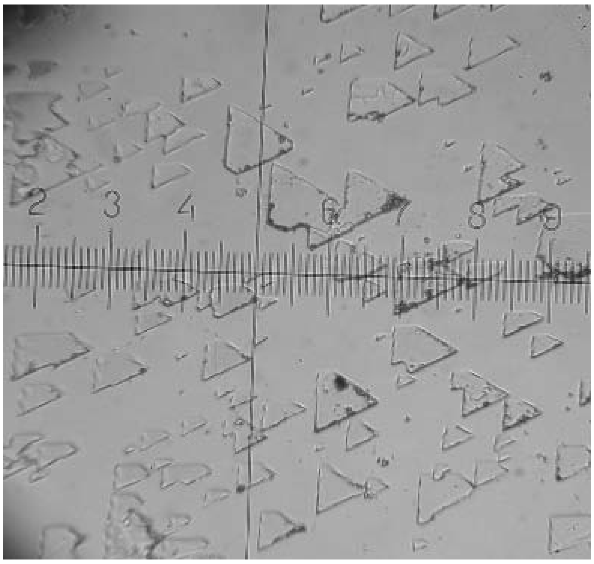

Fig. 2. The morphology of surface of ES grown on gallium arsenide substrates with orientation (111)

On the microscope the silicon and gallium arsenide substrates was been investigated before chemical and dynamical polishing and after it. Before polishing the substrate surface was looked as mirror smooth but under magnification here and there were noticeable roughness in the form of tiny grooves sanding, roughness was R_Z=0,1mkm. After a carrying out of the chemical and dynamical polishing by a method [22] we have seen that scratches disappeared and on the surface the shell etching has been seen, roughness was R_Z=0,08mkm

On Fig.3 grown indium arsenide QD in matrix (buffer layer) gallium phosphide on a silicon substrate with crystallographic orientation (111) picture is shown. The process has been carried out under a temperature 480°C and $\Delta T_F=5$°C under 10 pulse of cooling. A magnification is 500, and scale division ~ 3 mkm. A sample has shells that was been created after chemical and dynamical surface preparation.

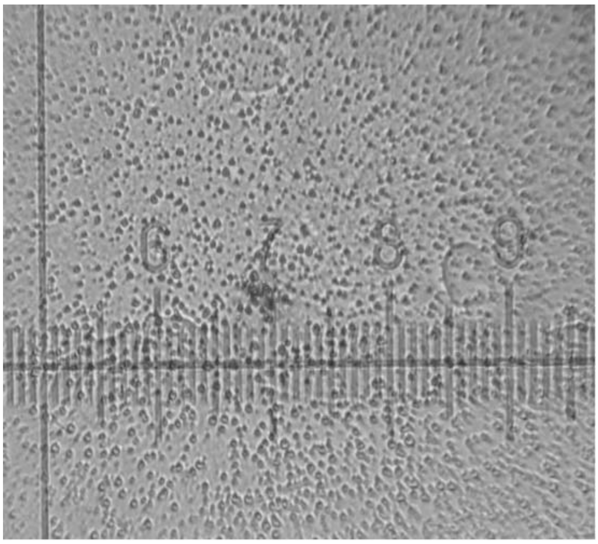

Fig. 3. A seeding of grown QD of indium arsenide in a matrix of gallium phosphide, a surface orientation is (111)

Obtained samples was been investigated also by the probe microscopy methods on a multimicroscope SMM-2000 in a regime of atomic and force microscopy [12]. An investigated sample was been put out from plates under investigation. By the method we investigated plates with obtained by LPE with PCS structures with not seeded QD, and plates of source materials before and after chemical treating. Chipped sample was been attached by two-side scotch on a sample holder of the microscope [16, 5, 17].

A scanning was been carried out by soft cantilevers of MSCT mark of Veeco, USA, firm by a highest console with smallest rigidity with a nominal pressure of 20 units with a speed of approximately 4 mkm per second and with a number of averages in point 16, that allows to us to obtain acceptable results with enough high speed of the scanning.

On Fig.4 a primary frame of the source substrate of silicon before chemical and dynamical preparation to epitaxy process is shown. There are scratches left by grinding grain on the silicon substrate after chemical and mechanical polishing on the picture. The presentation of the frame in 3D (Fig.5) contrast visualize the structure. It shows that deep of scratches in some places riches 40 nm and a length is over 400 nm.

Fig. 4. A primary frame of a source silicon substrate

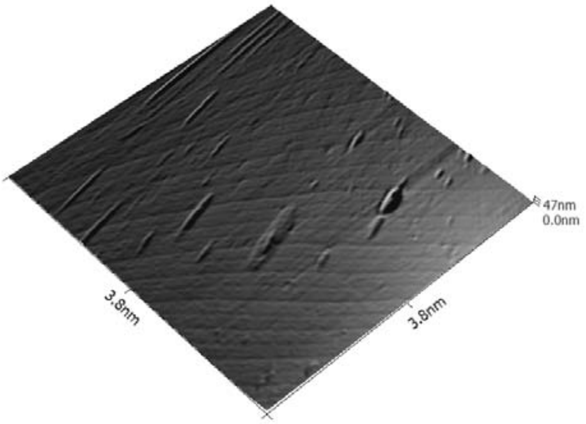

Fig. 5. 3D frame of source silicon substrate

On a Fig.6 a source silicon substrate that was held a chemical and dynamical polishing by method described in [22] is shown. The polishing of plates has the following goals: a degreasing, a cleaning the surface from contaminations and a removing an oxide and defect layer of the material. One can see an absence of scratches from a grinding grain and a presence of small pits that was been formed in process of treatment of the material. A maximal size of pits is over 300 nm and depth is 8 nm. A processing of plates was been carried out immediately prior to the process of epitaxy and a cassette layout.

On Fig. 7 and Fig. 8 primary and 3D frames of grown QD of gallium arsenide in a matrix (buffer layer) of gallium phosphide on a silicon substrate with crystallographic orientation (111) is shown. The process was been carried out under temperature of 480°C and ΔT_F=5°C under 10 pulses where ΔT_F is temperature difference between substrate and heat absorber (cooling pulse).

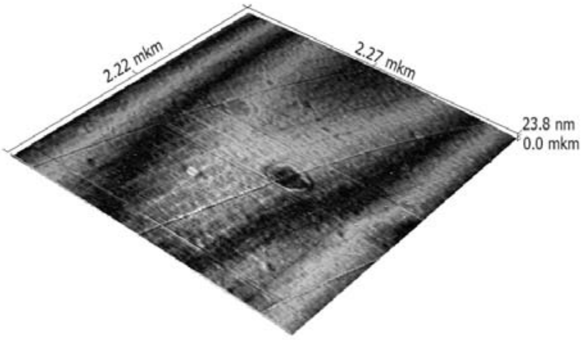

Fig. 6. 3D frame of a source silicon substrate after chemical dynamical treatment

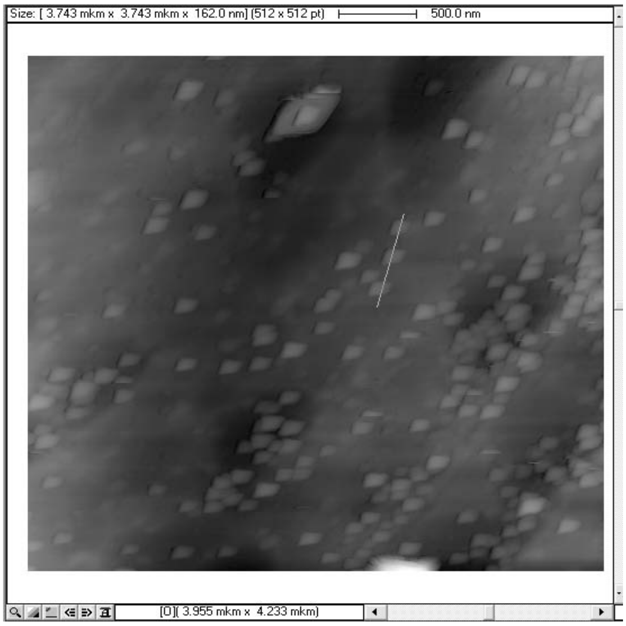

Fig. 7. Source frame of grown QD of gallium arsenide in a matrix of phosphide gallium, substrate orientations (111)

On Fig. 9 a profile of QD emphasized by a line on Fig.7 is shown. As one can see from the profile the average size of QD grown under presented above technological parameters is in width of the order 100 nm and in height of the order 20 nm.

On Fig. 10-12 primary, 3D and profile of QD of indium arsenide in a matrix (buffer layer) gallium phosphide on a silicon substrate with crystallographic orientation (111) with a disorientation of 4-angle grades are shown. The process was been carried out under temperature of 480^{o}C and ΔT_F=5° C under 10 pulses. As one can see from pictures, a density of the seeding of QD is higher that is connected with a presence of stairs on a disoriented substrate. The same is caused by the presence of various size QD: a big ones with a size approximately 150 nm in width and up to 70 in height and small ones (that is occupied on stairs situated under an angle) with size up to 120 nm in width and 40 nm in height.

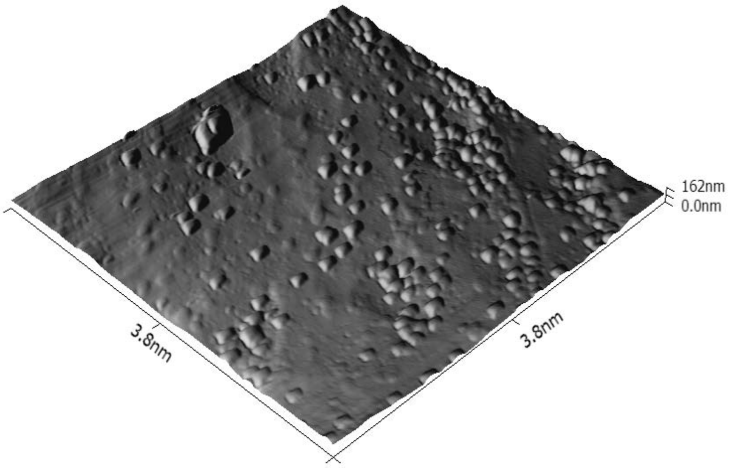

Fig. 8. 3D frame of grown QD of indium arsenide in matrix of gallium phosphide, a substrate orientation is (111)

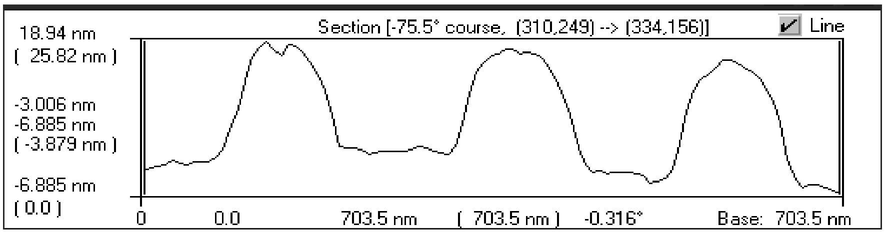

Fig. 9 A profile of QD of indium arsenide in a matrix of gallium phosphide under emphasizing on the Fig. 7

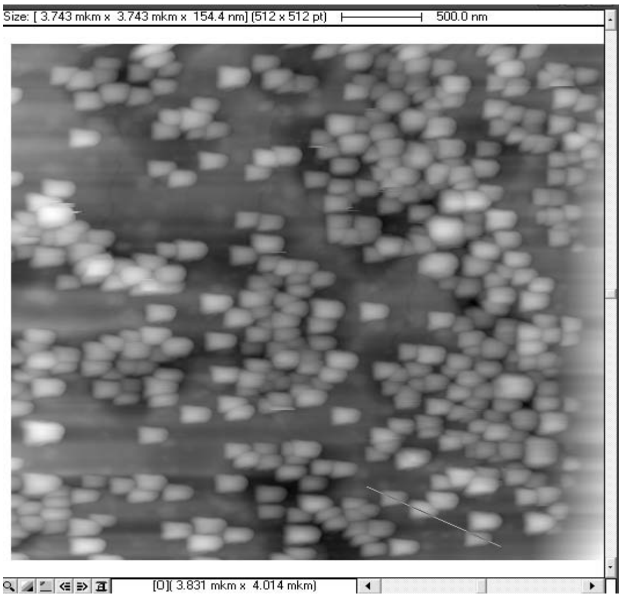

Fig. 10. A primary frame of grown QD of indium arsenide in a matrix of gallium phosphide, a substrate orientation is (111) with a disorientation in 4^{o}

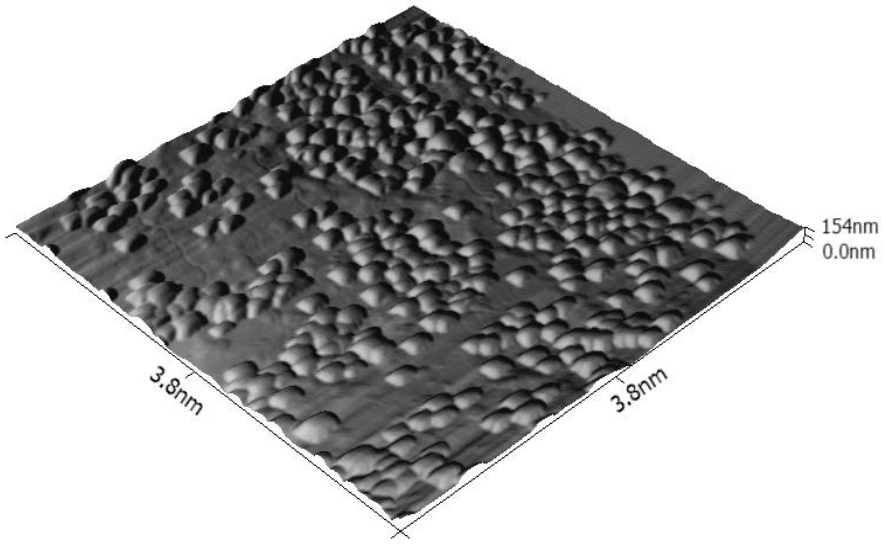

Fig. 11. 3Dframeof grown QD of indium arsenide in a matrix of gallium phosphide, a substrate orientation is (111) with a disorientation in 4^o

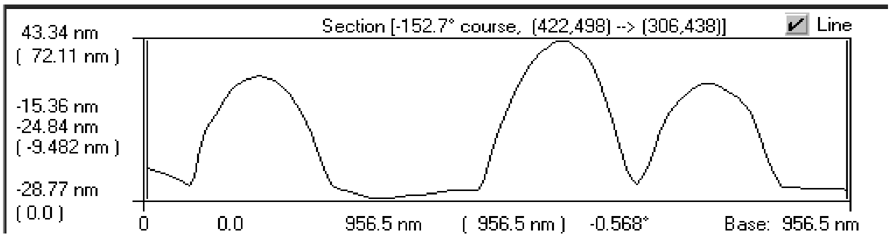

Fig. 12. A profile of QD of gallium arsenide in a matrix of gallium phosphide under a emphasizing on a Fig. 10

A studying of spectral dependencies of an absorption, a reflection and a photoluminescence was been carried out by a set of spectral apparatus on a base of monochromators MDR-41.

In photoluminescence spectra of samples, obtained by a mentioned above method, an investigated radiation of the photoluminescence was been led out both from the sample surface as from a butt of the sample. Emission bands in intervals 1,05-1,35 eV was been observed in photoluminescence spectra of all investigated samples. We connect this fact with a radiation of QD of indium arsenide in a matrix of gallium arsenide.

On Fig. 13 and Fig. 14 typical photoluminescence spectra under a RT obtained from butts of samples of NGES with QD in a system InAs-GaAs that have been grown under 480^{o}C (sample 1) and 500^{o}C (sample 2) respectively on a substrates of gallium arsenide with orientation (111) is presented. The first sample differs from the second sample by less quantity of layers with QD. Remain parameters of technological process of an obtaining of samples is the same. From the investigation of the obtained spectra, we believe that short wave bands under $h\nu \geq 1,4$ eV are connected with a radiation of the substrate of gallium arsenide, and long wave bands is connected with a radiation of QD of indium arsenide.

A shift to a long wave region of a radiation band of sample 2 versus band of sample 1 that one can see from pictures, can be connected with the difference of the temperature under the obtaining of structures (a difference of QD sizes), or, maybe, with a difference of quantity of QD layers. In work [11] it is shown that with an increasing of quantity of QD layers photoluminescence spectra shift to long wave region that is connected with a forming of a system of vertically connected QD. The same phenomenon we observe in our photoluminescence spectra.

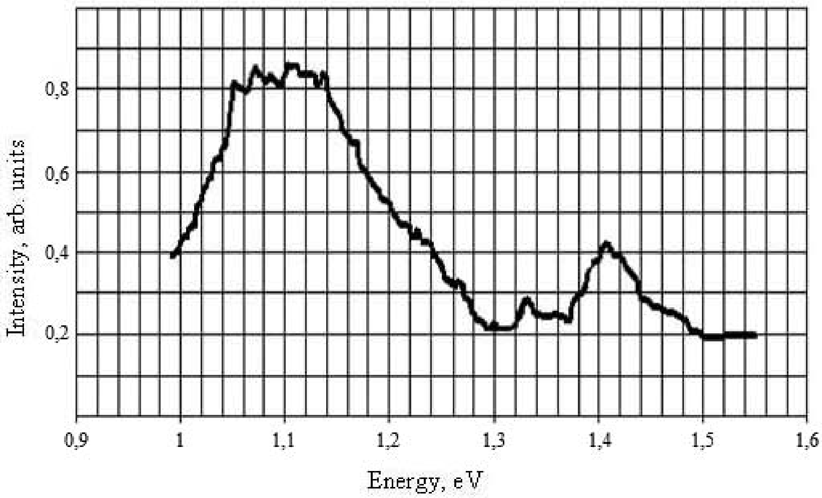

Fig. 13. A photoluminescence spectrum under RT obtained from a butt of sample with NGES with QD in s system InAs-GaAs, grown under 480°C on substrates of gallium arsenide with orientation (111)

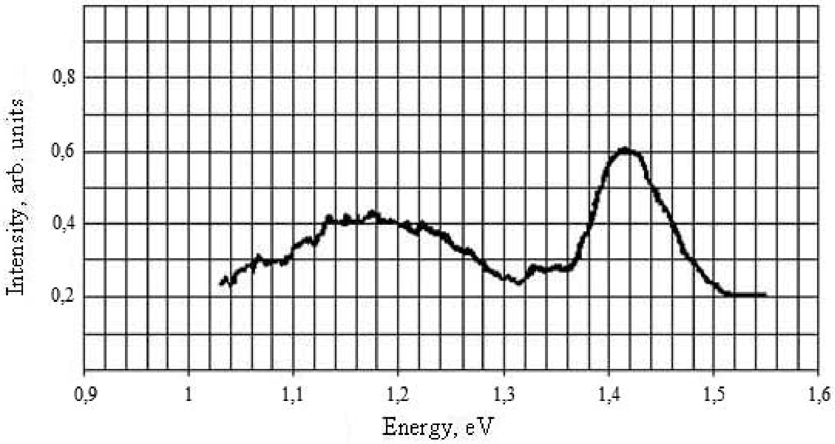

Fig. 14. A photoluminescence spectrum under RT obtained from a butt of sample with NGES with QD in system InAs-GaAs, grown under 500°C on substrates of gallium arsenide with orientation (111)

CONCLUSIONS

In progress of project performance, we obtain the follow main results.

1. A special installation of horizontal type has been developed, manufactured and tuned.
2. A graphite cassette for a growing of nanoheterostructures of semiconductor compounds from solutions-melts has been developed and manufactured. It allows to obtain many layers NGES with QD by the method of PCS of higher quality and on substrates of various diameters and thickness.
3. A laboratory technology for an obtaining of NGES with QD on a base A^3B^5 compounds has been developed. Experimental samples have been obtained.
4. A complex of investigations of materials under various stages of technological process has been carried out. A morphology of surface has been studied by an interference microscope MII-4. Investigations of obtained structures with open QD have been carried out by a methods of atomic and force microscopy. Sizes of QD is detected. Measurements and analysis of photoluminescence spectra of obtained samples has been carried out on a set spectral equipment on a base of monochromators MDR-41.

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ПОЛУЧЕНИЕ НАНОГЕТЕРОЭПИТАКСИАЛЬНЫХ СТРУКТУР С КВАНТОВЫМИ ТОЧКАМИ ДЛЯ ВЫСОКОЭФФЕКТИВНЫХ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ, ИССЛЕДОВАНИЕ ИХ СВОЙСТВ

Игорь Марончук, Сергей Быковский,
Степан Бондарец, Анна Вельченко

Аннотация: В работе представлены экспериментальные результаты, показывающие возможность получения методом жидкофазной эпитаксии с импульсным охлаждением подложки наногетероэпитаксиальных структур с квантовыми точками для изготовления однопереходных концентраторных солнечных элементов. С этой целью была изготовлена установка и графитовая кассета, позволяющая получать многослойные структуры высокого качества. Проведены эксперименты по получению структур и комплекс исследований материалов при различных стадиях технологического процесса. Морфологию поверхности структур изучали на микроскопе МИИ-4. Размеры квантовых точек, определяли методами зондовой микроскопии при исследованием образцов структур с открытыми квантовыми точками. Проведены измерения и анализ спектров фотолюминесценции структур.

Ключевые слова: наногетероэпитаксиальные структуры, квантовые точки, жидкофазная эпитаксия, подложка, выращивание.