

Deposition by liquid epitaxy and study of the properties of nano-heteroepitaxial structures with quantum dots for high efficient solar cells

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Abstract. The paper presents experimental results showing the possibility of liquid-phase epitaxy with a pulse-cooled substrate nano-heteroepitaxial structures with Ge quantum dots and GaP matrix for production of single-junction solar cells working under sun light concentration. The preparation of the surface of Si wafers suitable for growing of these structures is described. The optimal technological conditions for growing of the of GaP buffer layer on the Si wafer from supersaturated solutions of melts Sn are applied. Structures with Ge quantum dots are grown at different conditions and study of their structural and optical properties is performed. The surface morphology of the grown materials is studied by AFM microscopy. The photoluminescence spectra of nano-heteroepitaxial structures with Ge quantum dots are presented and analyzed.

1. Introduction

Currently 80% of solar cells converting directly (not concentrated) solar radiation efficiency ranging from 12% to 22% are based on monocrystalline, polycrystalline or amorphous silicon. Provided photovoltaics growth at 30% per year until 2030, the need for silicon will increase by more than 200 times that is a problem, both technological and environmental. In this regard the development of solar cells and modules working under high concentration of the solar radiation using single junction solar cells on the basis of nano-hetero-epitaxial (NHE) structures with quantum dots (QDs) arrays offer the possibility for further increasing of the efficiency. The idea launched by A. Nozik [1] to achieve the thermodynamic limit of photovoltaic conversion efficiency (till 84%) using both, short and long wave range of the solar spectrum by applying QDs of narrow gap semiconductors has been confirmed theoretically

Different methods of deposition of high efficiency solar cells using nano-heterojunctions (NHJ) structures with QDs have been experimented. Attempt to use molecular beam epitaxy (MBE) and chemical vapor deposition from organometallic compounds (MOCVD-technology) in the process of preparation of solar cells with high efficiency on the basis of nano-heterojunctions (NHJ) with QDs, where the matrix material used is GaAs, and the QDs material is InAs have been unsuccessful [2].



In this work the method of liquid phase epitaxy (LPE) in the regime of impulse cooling and heating (ICH) of the Si substrate is applied to deposit Ge QDs arrays without elastic - tense "wetting" layer in between QD thus assuring conditions for their formation close to the equilibrium and growing of the structures with reduced carrier recombination and solar cells with efficiency > 35% [3].

It is known that the morphology and the composition of the substrate affect significantly the process of growth of NHE structures with QDs, because it determines the parameters of the crystal lattice of the surface layer and thus the quality of the NHE structures with QDs deposited by LPE method using ICH of the substrate [4]. Therefore, high-quality surface preparation of the substrates plays an important role in applied technology LPE.

The aim of this paper is formation of Ge QDs during the LPE process of crystallization with applying procedure with ICH of the substrate and study of the surface morphology and photoluminescence of p-n nanostructures based on A₃B₅ semiconductors (GaP) on Si substrates obtained in the process of multi-layer epitaxial growth. Using Si substrates which are less expensive than A₃B₅ semiconductors offers advantages concerning decreasing the cost of the solar cells.

2. Experimental

Deposition of the NHE structure with QDs was performed by the LPE method with impulse cooling and heating of the substrate. Special equipment for growing of multilayer NHJ structures with horizontal supplier has been constructed. In this method the front surface of the substrate is stand in a close contact with the saturated melt solution heated to the temperature T. A heat sink which temperature, THS, which is lower than the temperature of the substrate by the amount $\Delta T = T - THS$ is situated on the back surface of the substrate. After some time, which depends on the duration of the cooling impulse $\tau \approx 10^{-3} \div 10^{-1}$ sec, a heat sink takes the temperature of the substrate and nanolayer with QDs arrays is crystallized on the front surface of the substrate [3].

Due to the different in lattice constants of the substrate material (Si) and the material of QDs (Ge), in the initial stage a continuous "wetting" layer by the Stranski-Krastanov's mechanism is formed. With increasing of the thickness of the growing layer the periodic stresses appears at the interface with the substrate. During the process of growing the formation of the Ge QDs takes place in the sites with minimum mechanical stress, i.e. in the positions with perfect structure [5]. The density of the crystallized QDs at optimum conditions is limited mainly by the period of the perfect crystalline structure in the interface.

Growing of NHE structures with of QDs of narrow-gap material-Ge, with a surface density < 10¹² cm⁻² on the wider band gap material Si single crystal substrate than used in [2] is performed at 450-500°C temperature of the oven in atmosphere of highly purified hydrogen. Growing of QDs arrays is completed when the temperature of the heat sink becomes equal to the substrate temperature. After that the heat sink is removed and heater with temperature TH above the substrate temperature Ts by an amount $\Delta TH = TH - Ts$ is placed on the back surface of the substrate. The heating impulse leads to the dissolution of the nano-sized "wetting" layer situated between the QDs on the front surface of the substrate. The preliminary experiments show that removing part of the "wetting" layer results in formation of NHE structures with QDs with significantly reduced concentration of generation-recombination centers and in formation of the QDs arrays with parameters close to the "ideal" in the case when the heating impulse amplitude and duration are about 0.3-0.7 of the corresponding values of the cooling impulse. The heating impulse, ΔTH , not only leads to removing the part of the "wetting" layer, but also eliminates the islands of fused quantum dots, where the areas with QDs are slicked in the islands in the place with misfit dislocations, thus it promotes their separation and formation of the QDs with less variation in the size. The process of removing of the part of the "wetting" layer between QDs is terminated when the temperature of the heater becomes equal to the substrate temperature. After that the arrays of the QDs is covered by nano-layer of the matrix material (spacer layer) - GaP. The thickness of the spacer layer should provide tunneling of charge carriers from one QDs arrays located parallel to the surface of the substrate to the other QDs arrays – the vertically coupled QDs.

Location of the superlattices with vertically coupled QDs in the p-n junction, leads to the separation of the generated in QDs carriers by the electrostatic field of the p-n junction.

Multiple repeating steps of growing of QDs arrays and formation of the spacer layers of different type conductivity lead to creation of multi-layer p-n NHE structures with QDs. Monocrystalline Si wafers n-type conductivity with the crystallographic orientation (111), sheet resistance of $20 \Omega/\square$ and diameter of 40 mm are applied as substrates. The solvent used is Sn of high purity. As the matrix material wide-gap A3B5 semiconductor – GaP, is used and narrow-gap semiconductor Ge - for the QDs formation.

The equipment for deposition of NHE structures is designed and manufactured. It consists of a heating furnace, a quartz reactor with a working cassette and snap, a temperature regulator, gas supplier system and vacuum pumps. Heating (to maximum 1200 oC) and cooling are performed with rate of 30oC/min and 10oC/min, respectively. A special graphite cassette-holder is constructed for growing NHE structures from melt-solution on substrate with different diameter and thicknesses.

The surface morphology of the samples is studied by AFM microscope type CMM-2000 (Proton—Zelenograd, Russia) with soft cantilever tip MSCT (Veeco, USA). The spectra of photoluminescence of the grown nano-heteroepitaxial structures with QDs are measured using spectral equipment with monochromator type MDP-4.

3. Results and discussion

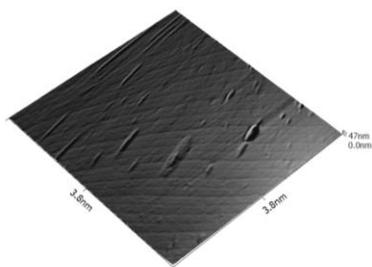
The surface morphology of the Si wafers used for deposition NHE structures is studied before and after dynamic chemical treatment. Figure 1 shows the AFM picture of the pristine silicon substrate before chemical and dynamical processes of preparation. It is observed that the initial silicon wafer has a number of defects - the average surface roughness of the scanned area of 3.7 m length was 3.2 nm and the maximum difference in texture surface - 30 nm. Scratches obtained after the mechanical and chemical polishing are seen. The three-dimensional picture (figure 1 b) reveals the depth of scratches in some places as high as 40 nm and a length of more than 400 nm.

The preparation of the Si wafer for deposition of the NHE structures is carried out by applying the chemical-dynamic treatment using two standard procedures for removing the damaged layer as a result of cutting and the chemical mechanical polishing Deshu's [7] and RCA methods [8]. Improvement of the surface morphology of the original Si wafer is achieved.

Figure 2 demonstrates the AFM image of the Si wafer after the chemical-dynamic treatment applying the Deshu's method [6]. The polished Si wafer is degreased, the oxide and damaged layers - removed. It is clearly seen from the AFM image shown in figure 2 a the lack of scratches and the presence of small pits formed during the etching of the material, the maximum size of which is about 300 nm and a depth - 8 nm. The wafer treatment is carried out immediately before starting the process of epitaxy.



a



b

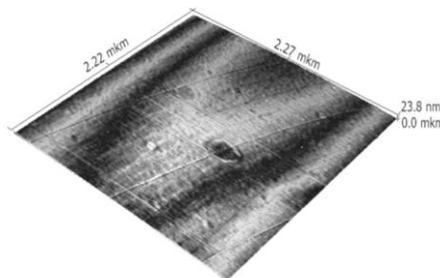


Figure 2. The AFM image (2.22 μm x 2.27 μm) of the Si wafer after treatment by the Deshu's method.

Figure 1. AFM images of the pristine Si substrate: (a) surface view and (b) three-dimensional view. The marker in (a) corresponds to 200 nm.

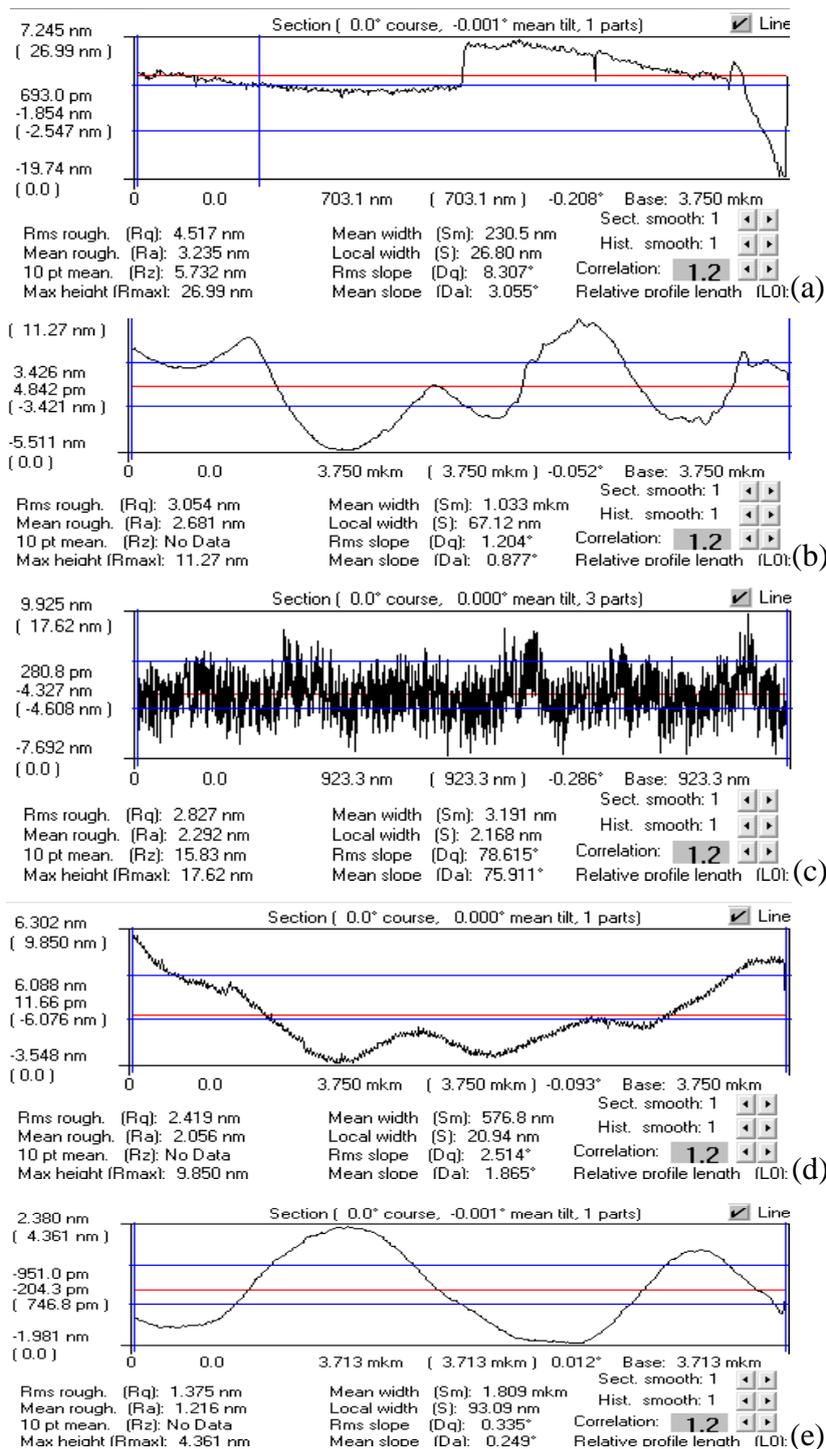


Figure 3. Surface topography of the substrate of Si Si substrates before treatment (a), after treatment by chemical-dynamical method RCA (b), after treatment by Deshus’s chemical-dynamical method (c), with growth buffer layer after Deshus’s method treatment and (d) and with grown buffer layer after RCA treatment (e). The profiles are taken on a segment of 3.7 μm .

Figure 3 shows the surface topography of the Si substrates before treatment (a), after treatment by chemical-dynamical method RCA (b), after treatment by Deshus's chemical-dynamical method (c), after Deshus's method treatment with growth buffer layer and (d) and after RCA treatment with grown buffer layer (e). It is seen that the maximum difference in high of the surface features of 11 nm and 18 nm and the average roughness of 2.6 nm and 2.4 nm in the linear segment of 3.7 μm microns are obtained after treatment by RCA (figure 3 b) and by Deshus's method (figure 3 c), respectively. Both techniques of chemical and dynamic treatment significantly improved the surface morphology of the original Si substrate, the average surface roughness of the samples obtained are practically at the same level within the error of the measurement method, and the maximum difference in the high of the surface features is in favor of techniques RCA. From the figures 3 c and d is observed that the average surface roughness is 2.0 nm and 1.2 nm and difference in the surface texture is 10 nm and 4 nm after formation of the buffer layer on the substrates treated by Deshus's and RCA method, respectively. The results demonstrate that obtained qualities of the buffer layers after RCA treatment is better and can be considered to be suitable for growing of high-quality NHE structures with QDs on Si substrates.

During the process of LPE the optimum technological conditions for epitaxial growth of the buffer Si layer from supersaturated solutions of melt Sn have been established.

A thick GaP layer doped with Sn is deposited on the obtained buffer layer. For growing of the Ge QDs 1 and 3 cooling impulses with difference in the temperature of the heat sick and substrate, $\Delta T_H = 5^\circ\text{C}$ are applied.

The study by AFM demonstrates that the surface roughness of the structure with grown Ge QDs is in the range of $1 \div 5\text{\AA}$. The preliminary study shows that the obtained after one and three pulses are

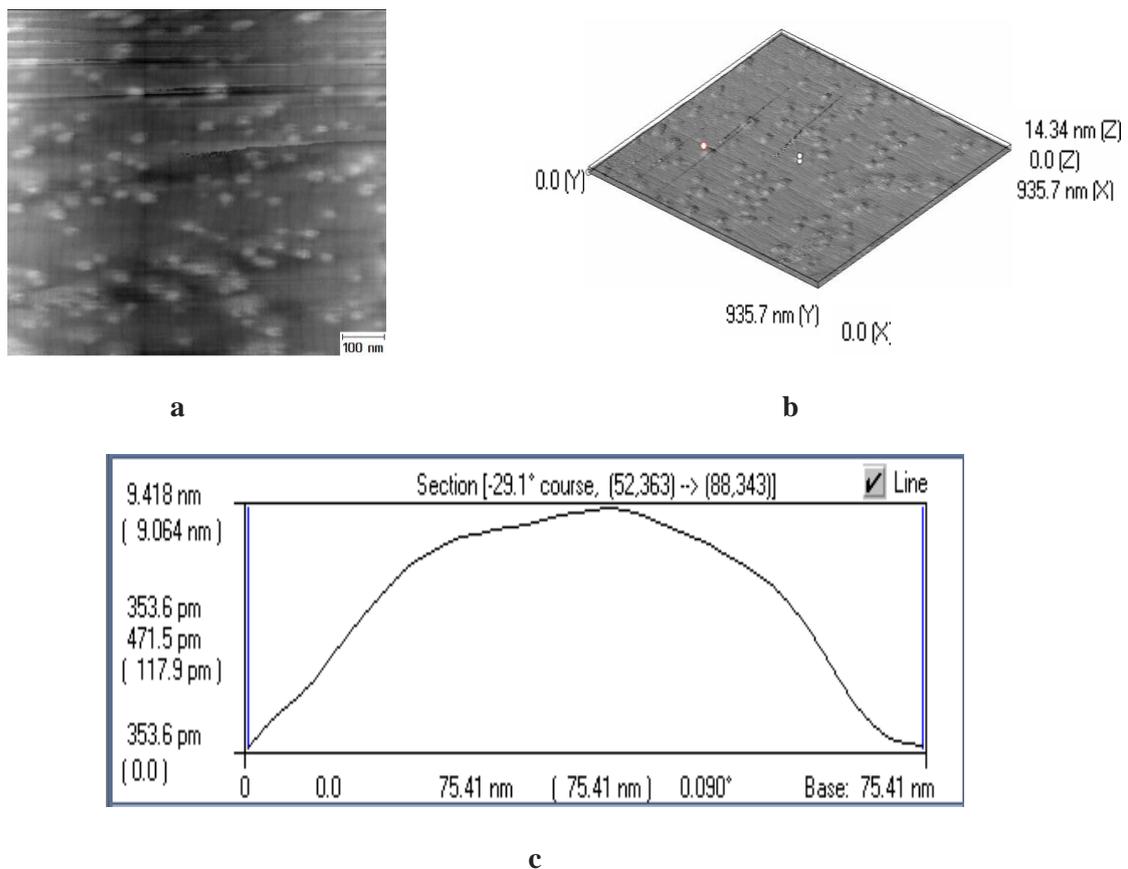


Figure 4. AFM surface view (a), three dimensional image (b) and profile (c) of the Ge QDs in the matrix of GaP on the (111) Si substrate obtained after applying of 3 impulses. The marker in (a) corresponds to 100 nm.

small in size and the QDs with sharp edges corresponding to the crystallographic orientation of the original Si substrate are not seen. Figure 4 shows typical two- and three-dimensional images and the profile, respectively, of the Ge QDs grown after applying of three pulses of cold heat sink. The average height of the QDs is about 8 nm -10 nm and an average width is about 40 nm - 60 nm. The formation of the Ge QDs can be explained by the presence of the stress during the growing of the Ge nano-grains due to the mismatch in the lattice constants of GaP and Ge (3.7%), which results in formation of Ge QDs with $d \leq 10\text{nm}$.

The optical properties of the NHE structures with QDs are investigated on the basis of the photoluminescence spectra. The study of the n-p NHE junction structures with Ge QDs is performed. For comparison the PL spectra of the n-p GaP structures without Ge QDs are presented as well.

Two types of NHE structures are fabricated and their photoluminescence (PL) spectra are measured and compared between them and with PL of the p-n GaP red diode grown on Si substrate. Structure 1 consists of Si substrate treated by RCA method, a buffer layer of GaP doped with Sn, n-p superlattices consisting of Ge QDs arrays separated by spacer layer of n-type GaP (doped with Te) and Ge QDs arrays separated by spacer layer p-type GaP (doped with Zn), and p-type GaP 80 nm thick layer. In between the superlattices are deposited:

- n-type GaP 20 nm thick layer to the n- type superlattice;
- p-type GaP 20 nm thick layer to the p- type superlattice.

Structure 2 is different from the structure 1 by the lack of 20 nm n- and p- type GaP layers between the superlattices with Ge QDs.

Figure 5 demonstrates the PL spectra of the structures 1 excited by two laser radiation with $\lambda = 4880\text{\AA}$ (curves 1 in figure 5 (a) and $\lambda = 5145\text{\AA}$ (curve 1 in figure 5 ((b)). For comparison the PL spectra of the p-n GaP red diode without Ge QDs are shown as well (curves 2 in figures 5 (a) and (b)). The PL spectrum of the structure 1 with Ge QDs (Figure 5 (a) excited by laser with $\lambda = 4880\text{\AA}$ shows a broad band with a maximum at 1.49 eV. The PL maximum position of the p-n diode without Ge QDs is observed at higher energy – 1.77 eV. The intensity of the PL in the structures with Ge QDs is stronger than the intensity of PL of the junction without QDs. Under excitation with laser radiation with the larger wave length, $\lambda = 5145\text{\AA}$ (figure 5 b), the position of the PL maximum does not change however the intensity of maximum the PL band of the structure 1 with Ge QDs decreases about 3 times and it become less intensive than the intensity of PL of the n-p GaP structures without QDs. The

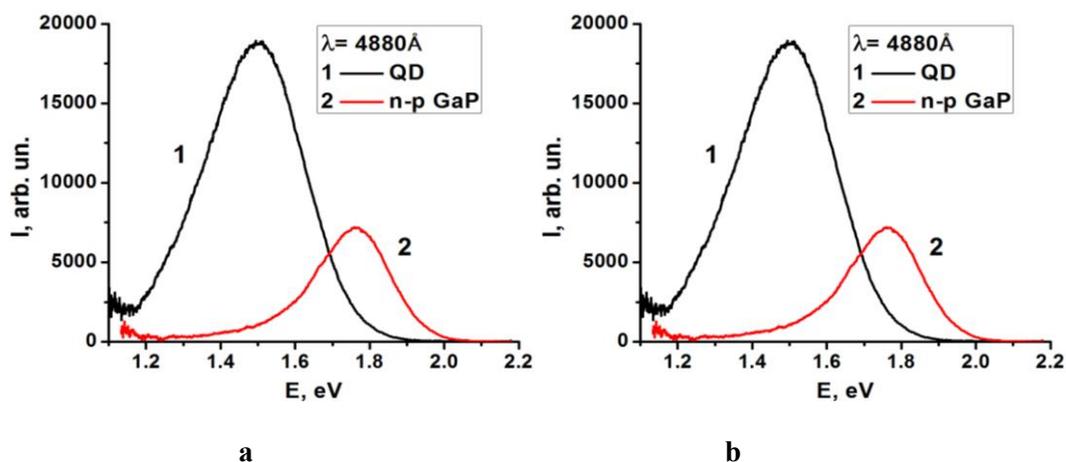


Figure 5. Photoluminescence spectra of NHE structures 1 with Ge QDs in the matrix of GaP (a) under excitation with wave lengths: $\lambda=4880\text{\AA}$ (a) and $\lambda=5145\text{\AA}$ (b) (curves 1). For comparison the PL spectra of the n-p GaP structures without Ge QDs are shown as well (curves 2).

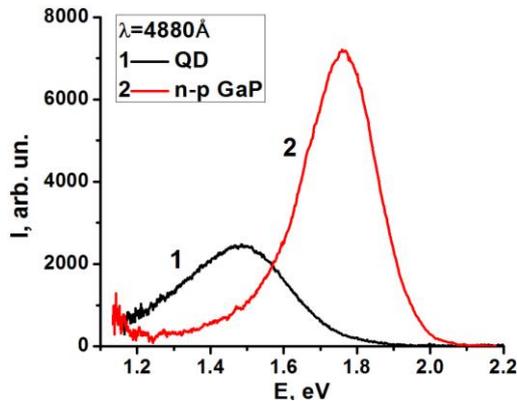


Figure 6. Photoluminescence spectra of NHE structures 2 with Ge QDs, without GaP layer between the superlattices measured under excitation with wave lengths $\lambda=4880\text{\AA}$ (curve 1). For comparison the PL spectra of the n-p GaP structures without Ge QDs are shown as well (curves 2).

ratio of the intensity of the maximum of PL bands under excitation with $\lambda = 4880\text{\AA}$ is about 2.5 and under excitation with $\lambda = 5145\text{\AA}$ - about 0.86. The observed dependence of the PL intensity on the energy of the exciting radiation can be explained by the effect of excitation splitting of the high-energy quant of the radiation. In this case of the presence of the quantum dots, two or more electron-hole pairs can be generated when of the photon energy exceeds about two time the energy of formation of electron-hole pairs (Nozick's effect) [1].

Figure 6 shows the PL spectrum of the structure 2 measured under 4880 nm laser excitation. PL band due to the Ge QD is observed at the same energy 1.49 eV however its intensity is lower about 6 times than PL intensity of the structure 1 with 20 nm GaP layer between the superlattice. The ratio in the intensity of the PL of the structure with QDs and that of the p-n GaP diode without QDs is about 0.35. This observation demonstrates that the 20 nm GaP layer between the superlattices with Ge QDs leads to decreasing in the nonradiative recombination of nonequilibrium carriers. It is possible to conclude that to increase the radiative recombination in the NHE structures it is necessary to create arrays of QDs not in the depletion region (structure 2) but in the volume of p- n junction as it is in the case of the structure 1 which is more favorable case for application into solar cells. Applying the effective mass approximation using the Schrödinger equation at different values of the size of the Ge QDs is possible to calculate the energy spectrum of charge carriers in Ge QDs between the GaP layers:

$$E_n = \frac{\pi^2 \hbar^2}{2m^* d^2} \left(n - \text{arctg} \sqrt{\frac{U_0}{E_n}} - 1 \right)^2 \quad (1)$$

where E_n is the energy of the mini-gap of the QDs material with quantum number n , measured from the bottom of the conduction band (for electrons) or valence band (for holes); U_0 - potential barriers for the carriers; d - the width of the quantum hole (pit) m^* - effective mass of the charge carriers.

If the size of the Ge QDs is assumed to be $d \leq 13$ nm the calculated values for the energy are comparable with the energy of the PL peak position in figures 5 and 6 (curves 1). The slight difference in the size of the Ge QDs between the values of the size of the Ge QDs (~ 10 nm) observed in the AFM images and the used for the theoretically estimation by eq.1 ($d \leq 13$ nm) could be explained with not perfect control of the temperature during the growing of the superlattices Ge QDs/GaP layers. It should be noted that our results about the size and density of the Ge QDs reported here are close to the obtained and with the published by the other authors [9].

4. Conclusions

Equipment has been designed and used for LPE growing of hetero-epitaxial structures with Ge quantum dots from molten solution in p-n junction GaP solar cells on Si substrate. The technological conditions for preparation of the surface of Si substrate suitable for growing of buffer layer from

supersaturated solutions of melt Sn are established and applied for deposition of NHE structure with Ge QDs. The Ge QDs are grown by the method of LPE with applying of impulse cooling and heating of the substrate. The study of the structural properties by AFM of the substrate after applying different treatment reveals the morphology, surface roughness, the linear dimensions of quantum dots and their density. It is observed that the structure with Ge quantum dots has more intensive bands of PL than that without QDs due to the increasing of the radiative recombination of the carriers, e.g. in the presence of the Ge QDs the nonradiative recombination is reduced. It is possible to conclusion that in order to increase the radiative recombination in multilayer p-n NHE structures it is necessary to create arrays of QDs in the volume regions with p-and n- GaP. The work is in progress to apply the method of LPE growing of the nano-heteroepitaxial A3B5 structures with Ge QDs in p-n junction GaP on Si substrates for high efficient low cost solar cells.

Acknowledgement

The work has been supported by the NSF- of Bulgaria - grant DNTS/Ukraine - 01/0005.

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