Multicomponent Solid Solutions $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$

Saidov A. S., Usmonov Sn. N. & Rakhmonov U. Kh
Physico-Technical Institute NPO "Physics-Sun", Academy of Sciences of Uzbekistan
100084, 2-B Badamzar yuli str. Tashkent, Uzbekistan
E-mail: amin@uzsci.net; sh_usmonov@rambler.ru

Kurmantayev A. N. & Bahtybayev A. N.
International Kazakh-Turkish University of H. A. Jasavi
Turkistan, Kazakhstan

Received: November 21, 2011 Accepted: December 4, 2011 Published: April 1, 2012
doi:10.5539/jmsr.v1n2p150 URL: http://dx.doi.org/10.5539/jmsr.v1n2p150

Abstract

Epitaxy layers of solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) were grown up from the limited volume of tin solution-melting by method of liquid phase epitaxy. Profiles of distribution of components Ga, P, Zn, Se and Si in grown up epitaxy layers are defined. In spectrum of the photoluminescence of surface of the solid solution at 5 K 2 peaks of radiation are found out. They are probably caused by compounds Si_2 (1.67 eV) and GaP (2.21 eV). It has been shown that covalent coupling Si-Si and Ga-P cause impurity levels laying in the forbidden zone of the solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$. Isotype heterojunction n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) (without luminophor) gives red and yellow luminescence which is caused by electronic transitions from Si-Si and from Ga-P, taking place in tetrahedron lattice of the solid solution.

Keywords: Solid solution, Liquid phase epitaxy, Photoluminescence, Electroluminescence

1. Introduction

Current progress in the development of microelectronics and optoelectronics has aroused considerable interest in the synthesis of materials in the form of thin film substitutional solid solutions, including those based on III–V and II–VI semiconductor compounds. Since the band gap and the lattice constant of these compounds can vary within certain limits, they can be used to synthesize semiconductor materials with a wide variety of electrical and photoelectric properties, to fabricate superlattices with quantum dots, and to design heterojunction structures. The GaInAsSb and AlGaAsSb solid solutions have been used as the basis for the development of effective lightemitting diodes (Baranov, *et al.*, 1986) and high speed photodiodes (Bougnot & De Lannoy, 1988) operating in the spectral range 1.5–4.8 μm, in which there are absorption lines of water vapors, CO_2, nitrogen containing molecules (N_2O, NO_2, NH_3), hydrocarbon molecules, etc.; therefore, they can be used for ecological and technological control of the environment (Mabbit & Parker, 1996).

The GaAs:Cr/ZnS:Cu(Al) structures have been used in the design and fabrication of solid-state image converters operating under excitation of the structure by infrared and X-ray radiations with a brightness corresponding to the threshold values for black white (10–2 cd/m^2) and color (3 cd/m^2) images at doses in the range 0–12 R/s (Kalygina, *et al.*, 2009). These structures can also be used for the development of ionizing radiation detectors with optical reading of information. The use of the ZnTe/CdTe superlattices with a large mismatch of the lattice parameters (6.4%), which were grown by molecular beam epitaxy on a GaAs substrate with ZnTe and CdTe buffer layers, made it possible to produce nanostructures with self organizing quantum dots CdTe (Kozyrev, 2009).

Despite the great success in the investigation and development of various optoelectronic devices based on III–V and II–VI semiconductor compounds, only some of them have now found practical application. This is associated with the relative complexity of their purification and the growth of perfect crystals, which makes them considerably more expensive as compared to elemental semiconductor materials, namely, Ge and Si.

In the given work experimental results of research of growth, photo- and electroluminescence of three-componential solid solution of replacement are presented. As the base component has been chosen wide zone semiconductor ZnSe. Since the band gap of the $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ solid solutions varies as a function of x and y from $E_{g,Si}$ = 1.12 eV to $E_{g,ZnSe}$ = 2.67 eV, these materials can be used in the design and fabrication of optoelectronic devices operating in the near infrared and visible spectral ranges.

2. Growth of Solid Solution of Replacement $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$)

Our approach to possibility of formation of solid solutions of replacement on the basis of Si_2 and binary compounds ZnSe, GaP is connected with conditions of formation of continuous solid solutions of the replacement based on molecular-statistical and crystal-chemical representations. These conditions are offered in works (Saidov, 1997; 1999) as:

$$\Delta z = \sum_{i=1} z_i^m - \sum_{i=1} z_i^n = 0 \quad , \tag{1}$$

$$\Delta r = \left| \sum_{i=1} r_i^m - \sum_{i=1} r_i^n \right| \le 0.1 \cdot \sum_{i=1} r_i^m \, , \tag{2}$$

where z_i^m and z_i^n - valences; r_i^m and r_i^n - covalent radiuses of atoms dissolving m and soluble n of the chemical element or the elements forming molecules of dissolving m and soluble n of compounds accordingly, i = 1, 2, 3, 4. The condition (1) provides electro neutrality of dissolved chemical elements or compounds in dissolving semi-conductor material; it is carried out, when dissolved elements are isovalent for dissolving semiconductor. The condition (2) provides similarity of geometrical parameters of dissolving m and soluble n the compounds excluding occurrence of considerable distortions of the crystal lattice in solid solutions. The less energy of elastic distortions of crystal lattice is the less Δr is; hence, the more crystal perfection of solid solution, the more solubility n in m is. When difference of the sum of covalent radiuses of molecules atoms of forming components is more than 10%, formation of solid solution of replacement for these components is insignificant.

As it is known ZnSe and Si_2, ZnSe and GaP, and also GaP and Si_2 are isovalent and for them the condition of electroneutrality (1) is satisfied:

$$\begin{aligned} z_{Zn} + z_{Se} &= z_{Si} + z_{Si}, \\ z_{Zn} + z_{Se} &= z_{Ga} + z_{P}, \\ z_{Ga} + z_{P} &= z_{Si} + z_{Si}. \end{aligned} \tag{3}$$

Differences between sums of covalents radiuses of atoms of molecules ZnSe, Si_2 and GaP are accordingly

$$\begin{aligned} \Delta r &= |\,(r_{Zn} + r_{Se}) - (r_{Si} + r_{Si})\,| = |\,2.45\ \text{Å} - 2.34\ \text{Å}\,| = 0.11\ \text{Å}, \\ \Delta r &= |\,(r_{Zn} + r_{Se}) - (r_{Ga} + r_{P})\,| = |\,2.45\ \text{Å} - 2.36\ \text{Å}\,| = 0.09\ \text{Å}, \\ \Delta r &= |\,(r_{Ga} + r_{P}) - (r_{Si} + r_{Si})\,| = |\,2.36\ \text{Å} - 2.34\ \text{Å}\,| = 0.02\ \text{Å}. \end{aligned} \tag{4}$$

That it is no more than 4.7 %, hence, they satisfy to the condition of formation of solid solution of replacement (2), their mutual replacement not strongly deforms crystal lattice. Presence at the crystallization front molecular formations IV_2, III–V and II–VI promotes molecular replacement in solid phase, accordingly IV–IV $\rightarrow$ III–V, IV–IV $\rightarrow$ II–VI, III–V $\rightarrow$ II–VI, assuming obligatory existence of pairs IV–IV, III–V, II–VI at any value x (Alfyorov, *et al.*, 1982) as $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$. Replacements of two atoms of molecule ZnSe by two atoms Si-Si or GaP in the crystal lattice causes quantitative change of forces of interaction between the nearest neighbours, but covalent-tetrahedron character of coupling in crystal lattices remains (Figure 1 a, b and c). The solid solution of replacement $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ represents the stable phase. However it is possible appearance of local micro pressure of growhing character and small value of energy of elastic distortions of crystal lattice.

Solid solutions $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ were grown up in technological installation with vertically located quartz reactor. In the graphite cartridge of the reactor located horizontally substrates separated from each other by graphite props installed. The distance between the top substrate and the bottom one was filled by liquid tin solution-melting through lateral cuts of the cartridge. The distance between the top substrate and bottom one was varied - 0.25–2.5 mm by selection of props of different thickness. So we could regulate the volume of the liquid solution-melting. Monocrystal plates GaP of n-type of conductivity with diameter 20 mm, carriers concentration

~ (3–5)·10^{17} cm^{-3} and orientation (111) have been used as substrates. The content of the solution-melting consisting of components Sn, Si, ZnSe and GaP, was calculated on the basis of results of experimental researches of liquid phase system Sn–Si–ZnSe–GaP and literary data (Andreev, 1975; Hansen & Anderko, 1958; Saidov, *et al.*, 1986). Growth of epitaxy films was carried out in the atmosphere of hydrogen cleared by palladium at various values of parameters of technological process: temperature of the beginning of crystallization – T_s, speed of cooling – υ, thickness of the backlash between substrates – h. On the optimum conditions when T_s = 880 °C, υ = 1–1,5 K/min and h = 1 mm, grown up epitaxy layers had mirror-smooth surfaces.

3. Experimental Results and Discussion

3.1 Research of the chemical compound of the solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$

The chemical composition of the surface and the slope of the epitaxial layers of the solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ have been studied by X-ray micro analyzer «Jeol» JSM 5910 LV-Japan (Figure 2). Study of raster pictures of surface layers showed that, when the crystallization begins at temperatures below 800 °C, the films are in the form of dendrite polyhedrons, located on the substrate and connected solidly with it, but at T_s > 800 °C dendrite inclusions are absent. Results of the x-ray microanalysis on the slope have shown that in the transitive area located between the substrate and the epitaxy film, molar content of GaP decreases gradually and that of ZnSe increases; in the epitaxy layer distribution of components ZnSe, Si-Si and GaP on depth is almost homogeneous (Figure 2). On the film surface molar content of gallium was 3.7 at.%, phosphorus - 5.3 at.%, selenium - 42.2 at.%, zinc – 45.8 at.% and silicon 3.0 at.%, that corresponds to the formation of solid solution $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$.

3.2 Research of Photoluminescence of the Solid Solution $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$

Figure 3 shows the spectrum of photoluminescence (PL) of the surface of grown solid solution of $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$. The PL was excited by radiation gallium-cadmium laser (λ_{max} = 325 nm), model GKKL-10UM. Measurements were made in the cryostat "Urteks" at 5 K. PL spectra were recorded at the installation completed on the basis of the double monochromator SDL-1C with the spectral resolution better than 0.2 meV. Signals were registered by photomultiplier with the photocathode S20, operating in photon counting mode. As it is seen from Figure 3, in the PL spectrum a broad band presents that covers almost the entire visible range. The main peak at λ = 440 nm is caused by the basic semiconductor ZnSe (Figure 1 a), its molar content in the surface layer is 88 mol.%. The important result is the appearance of the peaks at λ = 740 nm (E_{ph} = 1.67 eV) and λ = 560 nm (E_{ph} = 2.21 eV) which apparently are connected with formation of isovalent compounds Si_2, GaP in the concentrated solid solution $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$ with great content of ZnSe (Figure 1 b, c). At the absence of the influence of ZnSe on durability of the Si-Si, one might expect the appearance of the peak at E_{ph} = 1.12 eV, equal to the band gap of silicon. It is possible that ZnSe environment with a relatively strong bond (its band gap equal to 2.6 eV) which increases the durability of the Si-Si to 1.67 eV, while at the same time, ZnSe has no significant effect on the position of the peak at 2.21 eV, which is equal to the band gap of gallium phosphate.

Spectra of photoluminescence show that covalent coupling Si-Si and Ga-P in the solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ cause deep impurity energy levels E_{Si2} = 1.67 eV and E_{GaP} = 2.21 eV laying below the ceiling of the zone of conductivity of the solid solution (Figure 4).

3.3 Research of an Electroluminescence of the Firm Solution $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$

For research of radiating properties of the solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ isotype heterostructures n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) have been manufactured. Silver ohmic contacts to structure were formed by method of vacuum dusting. At reverse voltage, i.e. negative potential is on the substrate n-GaP and positive potential is on the film n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$, beginning at 10 V the luminescence of the heterostructure (Figure 5) was observed visually. It is seen from Figure 5 that spectral content of the luminescence depends on the applied voltage. The analysis shows that at rather low voltage (V < 14 V) radiation of the structure has on the whole red light and at – 16-18 V intensities of red and yellow radiation are comparable, and at V > 19 V red light is again observed. Radiation of red light is probably caused by electron transitions from conductivity zone to the level Si-Si with energy 1.67 eV and radiation of yellow light - to levels Ga-P with energy 2.21 eV.

3.4 Current-voltage Characteristic of Heterostructures n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$)

On the Figure 6 dark current-voltage characteristic of isotype heterostructures n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) is presented. From Figure 6 it is seen that the structure has rectification properties in

the wide interval of voltage. The analysis of current-voltage characteristics shows that at the beginning part of direct branch at voltage from 0.2 to 0.4 V dependence of current (I) from voltage (V) has law of the type $I = I_0 \cdot \exp(qV/ckT)$, with values of parameters I_0 = 4.5 μA and c = 4.3. Further at increase of voltage the current increases under the degree law - $I = A \cdot V^{\alpha}$ where A - the parameter depending on photo-electric properties of heterostructure, α - about 2.

The reverse branch of the current-voltage characteristics can be divided into some parts: at the beginning (till 0.2 V) the ohmic dependence is observed, further at increase of voltage sedate dependences of type $I = B \cdot V^{\alpha}$ is observed. At voltage from 0.2 to 3 V weak dependence of current with $\alpha = 1.5$ is observed, further from 3V till 13 V the square-law with $\alpha = 2$ is observed, at voltage $V > 13$ V strong dependence of the current from voltage with $\alpha > 3$ is observed, that corresponds to intensive radiation of the structure in visible part of spectrum of radiation.

4. Conclusion

Thus new three-component solid solutions of replacement $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) have been grown up on GaP substrates by method of liquid phase epitaxy. Distribution of components of the solid solution on depth and on the film surface is homogeneous. Covalent coupling Si-Si and Ga-P form energy levels 1.67 eV and 2.21 eV laying below the ceiling of the zone of conductivity of the solid solution, which promote radiation of isotype heterostructures n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) red light and yellow light simultaneously. Solid solutions of replacement $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ can be used for working out photodiode structures with integrated radiation without luminophor in visible part of spectrum.

Acknowledgements

Authors are grateful to professor A.Yu. Leyderman for discussion of results and valuable councils.

References

Alfyorov, J. I., Zhingarev, M. Z., Konnikov, S. G., Mokan, I. I., Ulin, V. P., Umanskiy, V. E., & Yavich, B. S. (1982). *Sov. Phys. Semicond.,* N5, 831.

Andreev, V. M., Dolginov, L. M., & Tretyakov, D. N. (1975). Liquid Epitaxy in Technology of Semiconductor Devices. *Moscow: Sov. Radio,* 328.

Baranov, A. N., Dzhurtanov, B. E., Imenkov, A. N., Rogachev, A. A., Shernyakov, Yu. M., & Yakovlev, Yu. (1986). Comparison of the parameters of LED heterostructures with a Ga1 – xInxAsSb (x = 0.09) quaternary solid solution. *P., Sov. Phys. Semicond., 20*(12), 1385.

Hansen, M., & Anderko, K. (1958). *Constitution of binary alloys.* McGRAW-HILL BOOK COMPANY, INC. New York, Toronto, London.

Kalygina, V. M., Tyazhev, A. V., & Yaskevich, T. M. (2009). Solid-state image converters on the basis of the GaAs/ZnS structures. *Semiconductors, 43*(7), 943. http://dx.doi.org/10.1134/S1063782609070239

Kozyrev S. P. (2009). IR spectroscopy of lattice vibrations and comparative analysis of the ZnTe/CdTe quantum-dot superlattices on the GaAs substrate and with the ZnTe and CdTe buffer layers. *Semiconductors, 43*(7), 911. http://dx.doi.org/10.1134/S1063782609070161

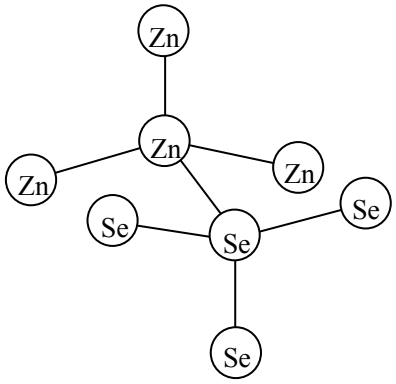
Mabbit, A., & Parker, A. (1996). Methane and carbon dioxide detection using LED sources. *Sens. Rev., 16*(3), 38. http://dx.doi.org/10.1108/02602289610123558

Ougnot, G., & De Lannoy, F. (1988). *J. Electrochem. Soc., 135*, 783.

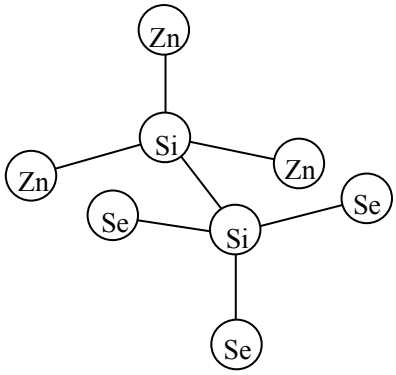
Saidov, A. S., Saidov, M. S., & Koshchanov, E. A. (1986). Liquid Epitaxy compensated layers of gallium arsenide and solid solutions based on it. Tashkent: “Fan”, p.127.

Saidov, M. S. (1997). *Applied Solar Energy, 33*(5), 48.

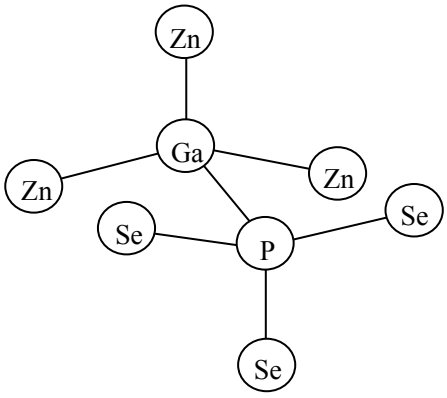
Saidov, M. S. (1999). *Applied Solar Energy, 35*(3), 48.



a)



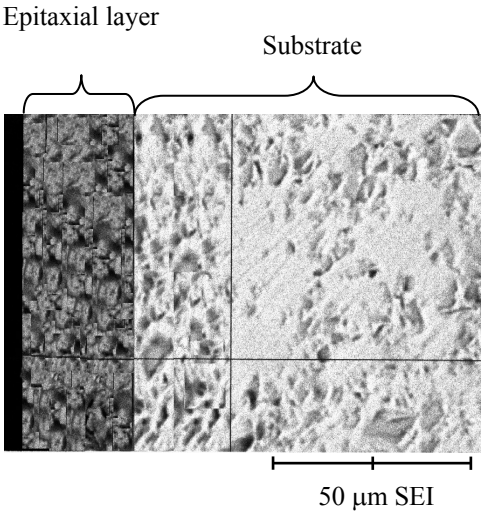
b)



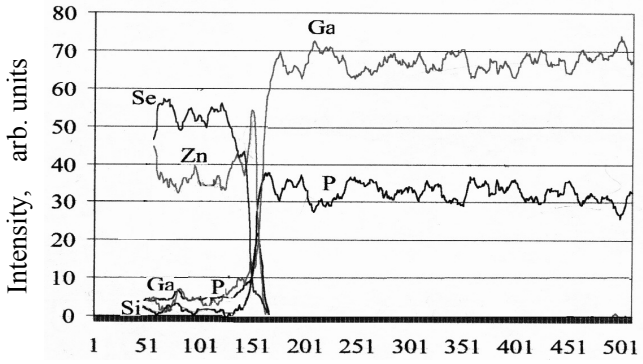
c)

Figure 1. Spatial configuration of the tetrahedral bonds of the multicomponent solid solution $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ – atoms of the molecule ZnSe (a), two atoms of the molecule ZnSe with two atoms of Si-Si (b) and two atoms of ZnSe molecule with two atoms of the molecule GaP (c)

 ISSN 1927-0585 E-ISSN 1927-0593



a)



b)

Figure 2. Raster image of slope (a) and distribution profile of the components Ga, P, Zn, Se and Si (b) in the epitaxial alloy layer$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$

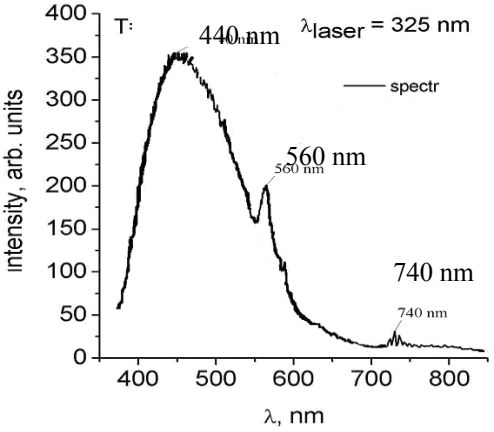


Figure 3. Photoluminescence surface of the epitaxial layer $(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) at T = 5 K

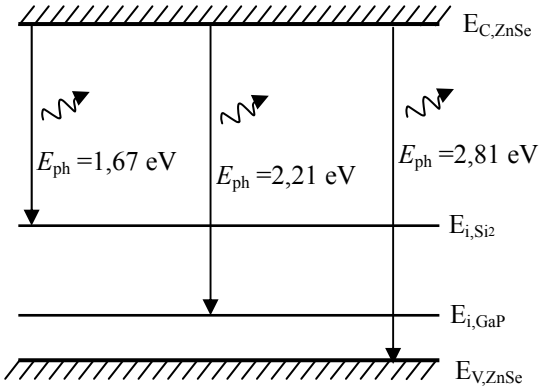


Figure 4. The energy band diagram of ZnSe with isovalent impurities Si_2 and GaP

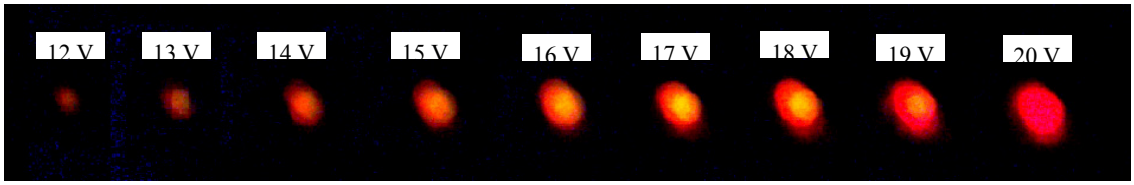


Figure 5. Luminescence of isotype heterojunction n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$) at reverse voltage

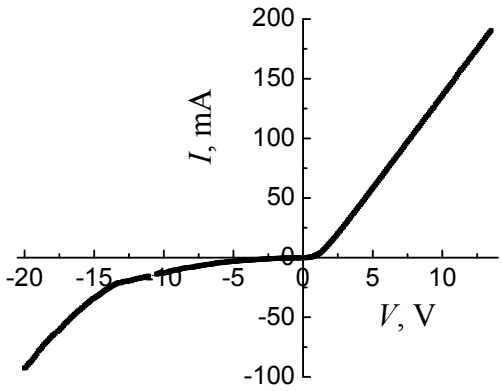


Figure 6. Dark current-voltage characteristic of isotype heterostructures n-GaP–n^+-$(ZnSe)_{1-x-y}(Si_2)_x(GaP)_y$ ($0 \le x \le 0.03$, $0 \le y \le 0.09$)

ISSN 1927-0585 E-ISSN 1927-0593