

# Effect of Diatomic Silicon Molecular Impurities on the Luminescent Properties of Semiconductor Solid Solutions

A. S. Saidov<sup>a</sup>, Sh. N. Usmonov<sup>a, b, \*</sup>, D. V. Saparov<sup>a</sup>, and A. M. Akhmedov<sup>c</sup>

<sup>a</sup>Physico-Technical Institute, Scientific Production Association Physics–Sun, Academy of Sciences of Uzbekistan, Tashkent, 100084 Uzbekistan

<sup>b</sup>Chirchik State Pedagogical Institute, Chirchik, 111700 Uzbekistan

<sup>c</sup>Tashkent Institute of Irrigation and Agriculture Mechanization Engineers, Tashkent, 100000 Uzbekistan

\*e-mail: sh\_usmonov@rambler.ru

Received July 5, 2019; revised November 4, 2019; accepted February 7, 2020

**Abstract**—One of the urgent problems of materials science in the field of photovoltaics is obtaining promising novel photoactive semiconductor materials with predetermined photoelectric parameters to provide an efficient manifestation of photovoltaic, thermovoltaic, and emitting effects in the visible and near-infrared regions of the radiation spectrum. In this aspect, it is of great practical and fundamental interest to clarify the effect of diatomic molecular impurities on the electrophysical and photoelectric properties of semiconductor materials, as well as to reveal the energy levels of impurity molecules depending on the parameters of the base material. For this purpose, several semiconductor substitutional solid solutions based on elemental semiconductors such as Si and Ge, as well as III–V isoperiodic binary compounds such as GaAs and GaP, and II–VI isoperiodic binary compounds such as ZnSe and ZnS with Si<sub>2</sub> molecular impurities have been obtained and studied. (Si<sub>2</sub>)<sub>1-x-y</sub>(Ge<sub>2</sub>)<sub>x</sub>(GaAs)<sub>y</sub>, (ZnSe)<sub>1-x-y</sub>(Si<sub>2</sub>)<sub>x</sub>(GaP)<sub>y</sub>, (Si<sub>2</sub>)<sub>1-x</sub>(GaP)<sub>x</sub> and (Si<sub>2</sub>)<sub>1-x</sub>(ZnS)<sub>x</sub> solid solutions have been grown on silicon Si (111) substrates from a limited volume of tin and lead solution-melt by means of liquid-phase epitaxy. The grown epitaxial layers have a monocrystalline structure with mirror-like smooth surfaces. The photoluminescence spectrum of solid solutions has been studied. The spectrum covers the photon energy range from 1.18 to 1.55 eV for (GaAs)<sub>0.95</sub>(Ge<sub>2</sub>)<sub>0.05</sub>(Si<sub>2</sub>), from 1.38 to 3.1 eV for (GaP)<sub>0.98</sub>(Si<sub>2</sub>)<sub>0.02</sub>, from 1.55 to 3.1 eV for (ZnSe)<sub>0.88</sub>(Si<sub>2</sub>)<sub>0.03</sub>(GaP)<sub>0.09</sub>, and from 1.55 to 3.2 eV for (ZnS)<sub>0.97</sub>(Si<sub>2</sub>)<sub>0.03</sub>. It has been found that Si<sub>2</sub> molecules in the case of (GaAs)<sub>0.95</sub>(Ge<sub>2</sub>)<sub>0.05</sub>(Si<sub>2</sub>) solid solution form deep impurity energy levels lying at 1.33 eV below the bottom of the conduction band, in the case of (GaP)<sub>0.98</sub>(Si<sub>2</sub>)<sub>0.02</sub>, it is 1.47 eV, in the case of (ZnSe)<sub>0.88</sub>(Si<sub>2</sub>)<sub>0.03</sub>(GaP), 1.67 eV, and in the case of (ZnS)<sub>0.97</sub>(Si<sub>2</sub>)<sub>0.03</sub>, 1.82 eV. It is shown that in solid solutions with Si<sub>2</sub> molecular impurities, an increase in the dissociation energy of the covalent bond in Si–Si impurity molecules is observed with increasing band gap and with decreasing crystal lattice parameter of the base semiconductor. Change in the dissociation energy of the Si–Si covalent bond in the tetrahedral crystal lattice of different semiconductors is caused by a change in the length of the Si–Si covalent bond, as well as by a change in the hybridization of the atomic electron shells of Si<sub>2</sub> impurity molecules and base material molecules. The studied (Si<sub>2</sub>)<sub>1-x</sub>(GaP)<sub>x</sub> and (Si<sub>2</sub>)<sub>1-x</sub>(ZnS)<sub>x</sub> solid solutions can be used as a photoactive material for the development of photoconverters operating in the visible and near-infrared regions of the radiation spectrum.

**Keywords:** solid solution, liquid-phase epitaxy, molecular impurity, energy level, covalent bond, photoluminescence

**DOI:** 10.3103/S0003701X20030093

## INTRODUCTION

The revealing of patterns for correlation between the photoelectric and electrophysical properties of binary compounds and multicomponent solid solutions (SSs) depending on the parameters of the molecules of the components and impurities involved in the system [1, 2], as well as establishing patterns for interrelations between the energy characteristics of impurities and components inherent in semiconductor SSs promote solving a number of practical problems in the technology of semiconductor devices [3, 4].

The isovalent molecular impurities that satisfy the conditions for the formation of substitutional solid solutions with the base material, depending on the relationship between the dissociation energy of covalent bonds inherent in dissolved molecules and inherent in solvent molecules, can form deep energy levels localized in the band gap or in the valence band of the solvent. Such impurity levels in semiconductors are determined by interaction between the atoms of impurity molecules and the atoms of the base material, as well as by structural and electrophysical parameters of

the solvent and dissolved molecules [5–9]. They are the crystal lattice parameter of the base material, covalent radii inherent in the atoms of the impurity molecules and in the base material, the band gap of the base material, and the energy of breaking the covalent bonds of atoms of impurity molecules.

The accumulation of experimental data concerning interactions between the impurity and solvent molecules, revealing the energy parameters of dissolved molecules depending on the fundamental parameters of the solvent should make it possible to purposefully use features of impurity molecules for developing a wide range of optoelectronic devices, in particular, for extending the spectral sensitivity range of photodetectors and for increasing the efficiency of photo converters.

## MATERIALS AND METHODS

In this study, we present the results for studies on the ionization energy of  $\text{Si}_2$  impurity molecules depending on the band gap and the crystal lattice parameter of semiconductor SSs based on elemental semiconductors such as Si, Ge, and III–V isoperiodic binary compounds such as GaAs, GaP, as well as II–VI isoperiodic binary compounds such as ZnSe and ZnS. For this purpose, we studied the photoluminescence spectra of such SSs  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}(\text{Si}_2)$ ,  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$ , and  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$ ,  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$ .

Epitaxial layers of the  $(\text{Si}_2)_{1-x-y}(\text{Ge}_2)_x(\text{GaAs})_y$ ,  $(\text{Si}_2)_{1-x}(\text{GaP})_x$ ,  $(\text{ZnSe})_{1-x-y}(\text{Si}_2)_x(\text{GaP})_y$ , and  $(\text{Si}_2)_{1-x}(\text{ZnS})_x$  SSs were grown by means of liquid-phase epitaxy from a limited volume of the molten metal solution described in [10, 11].  $(\text{Si}_2)_{1-x-y}(\text{Ge}_2)_x(\text{GaAs})_y$  SSs were grown from a lead solution-melt (Si–Ge–GaAs–Pb), the composition of which was determined based on data published in [12], and on the results of preliminary studies. The epitaxial layers were grown on *n*Si (111) substrates. The films with mirror-like surfaces were obtained at a temperature of crystallization onset amounting to 850°C and at a forced cooling rate of the solution-melt amounting to 1 deg/min. The grown layers had a single-crystal structure, p-type conductivity with a resistivity of ~0.5 Ohm cm and a thickness of ~20 μm. The analysis of the results of X-ray microanalysis of the chip and the surface of epitaxial films has shown that a surface layer up to 8 μm thick represents a  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}$  SS, and the molar content of Si in this layer is lower than 0.8%, i.e., Si is an impurity in the SS.

The epitaxial layers of the  $(\text{Si}_2)_{1-x}(\text{GaP})_x$  SS were grown on silicon *p*Si (111) substrates under the following conditions of liquid-phase epitaxy: the crystallization temperature ranging within 980–830°C, the solution-melt cooling rate amounting to 1 deg/min and the thickness of the solution-melt being 1 mm [13]. The composition of the tin solution-melt consisting of Si, GaP, and Sn was determined from the state dia-

gram for the Si–Sn binary alloy taking into account the solubility of GaP in Sn (Sn 100 g, GaP 2.5 g, Si 1.8 g). The epitaxial layers exhibited a single crystal structure, *n*-type conductivity and a thickness of 25 μm. The analysis of the results of X-ray microanalysis for the chips and the surface of the films has shown that the concentration of Ga and P atoms in the  $(\text{Si}_2)_{1-x}(\text{GaP})_x$  epitaxial layer monotonically increases in the direction of film growth reaching 48 mol % of Ga and 52 mol % of P, whereas the content of Si decreases to zero on the film surface.

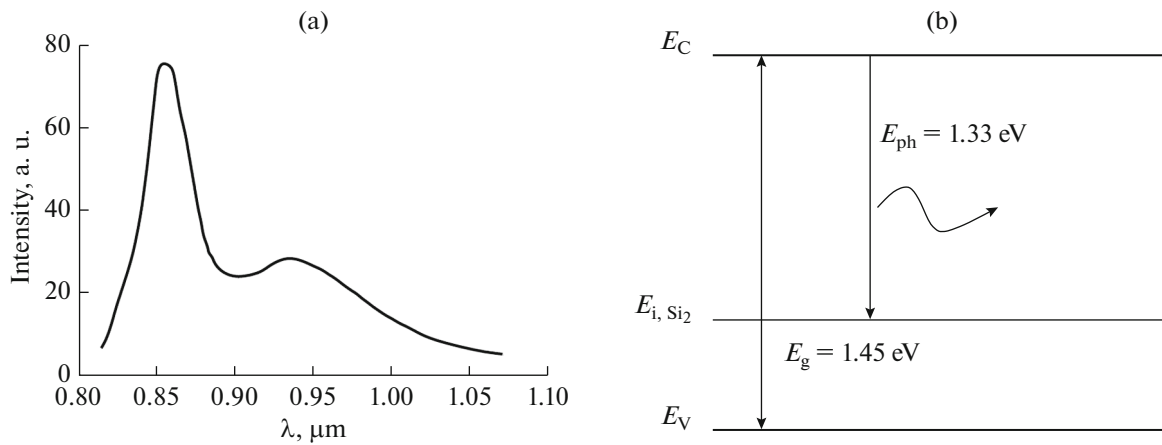
The epitaxial layers of the  $(\text{ZnSe})_{1-x-y}(\text{Si}_2)_x(\text{GaP})_y$  SS were grown on *p*Si (111) silicon substrates made of tin solution-melt (Sn–Si–ZnSe–GaP) [14]. The composition of the solution-melt was calculated based on the results of preliminary experiments concerning the state diagram of the Sn–Si binary alloy taking into account the solubility of ZnSe and GaP in Sn at different temperature values (above 700°C). Perfect single-crystal layers of SSs with (111) orientation were obtained at a crystallization onset temperature amounting to 880°C, at a cooling rate of the solution-melt amounting to 1 deg/min, and at a thickness of the solution-melt amounting to 1 mm. In this case, the epitaxial films exhibited an electronic type of conductivity and mirror-smooth surfaces. The results of X-ray microanalysis throughout the surface and throughout the chip have shown that within the epitaxial layer the distribution profile for the atoms of  $\text{Si}_2$ , GaP and ZnSe components is uniform in depth. At the same time, on the film surface the content of Ga amounts to 3.7 at %, the content of P was 5.3 at %, Se was 42.2 at %, Zn was 45.8 at %, and the content of Si amounts to 3.0 at %, which corresponds to the formation of  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS.

The epitaxial layers of  $(\text{Si}_2)_{1-x}(\text{ZnS})_x$  SS were obtained on silicon *p*Si (111) substrates from tin solution-melt (Sn–Si–ZnS) in the temperature range of 1000–840°C (upon cooling). Single-crystal films with (111) orientation and mirror-smooth surfaces were grown at a cooling rate of the solution-melt ranging from 0.7 to 1.0 deg/min and at a solution-melt thickness amounting to 1 mm. The epitaxial films exhibited an electronic type of conductivity. X-ray microprobe analysis of the surface and chips of epitaxial films has shown that the surface area of the film represents a  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$  SS.

## RESULTS AND DISCUSSION

The energy levels of  $\text{Si}_2$  molecules in various semiconductor SSs have been estimated based on the results from the spectral dependence of the photoluminescence (PL) of the surface of grown epitaxial films at low temperatures [15–17].

PL excitation in the epitaxial  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}(\text{Si}_2)$  layer has been carried out by red laser radiation in the fundamental absorption region of the wide-gap com-



**Fig. 1.** Photoluminescence spectrum for the epitaxial layer of a  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}\langle\text{Si}_2\rangle$  SS at a temperature of 77 K (a) and an energy band diagram for the solid solution with the impurity energy level ( $E_{i,\text{Si}_2}$ ) of the atoms composing  $\text{Si}_2$  molecules (b).

ponent of the  $(\text{GaAs})$  solid solution at a temperature of liquid nitrogen (77 K). Figure 1a shows the PL spectrum of the epitaxial layer. In the studied SSs, Si atoms behave as impurity atoms.

The PL spectrum of the  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}\langle\text{Si}_2\rangle$  SS (Fig. 1a) covers the near infrared range of the emission spectrum from 0.81 to 1.08  $\mu\text{m}$  with a maximum at a wavelength of 0.855  $\mu\text{m}$ , which corresponds to photon energy  $E_{\text{ph}} = 1.45$  eV. The photons with such energy at a temperature of 77 K are produced in the course of the radiative band-gap recombination of electron-hole pairs located in the near-surface epitaxial layer ( $\sim 3$   $\mu\text{m}$  thick) of the  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}\langle\text{Si}_2\rangle$  SS, whose band gap ( $E_{g,\text{TPSS}} = 1.45$  eV) is lower than the  $E_g$  of GaAs ( $E_{g,\text{GaAs}} = 1.51$  eV) and higher than  $E_g$  of silicon ( $E_{g,\text{Si}} = 1.16$  eV) and that of germanium ( $E_{g,\text{Ge}} = 0.73$  eV).

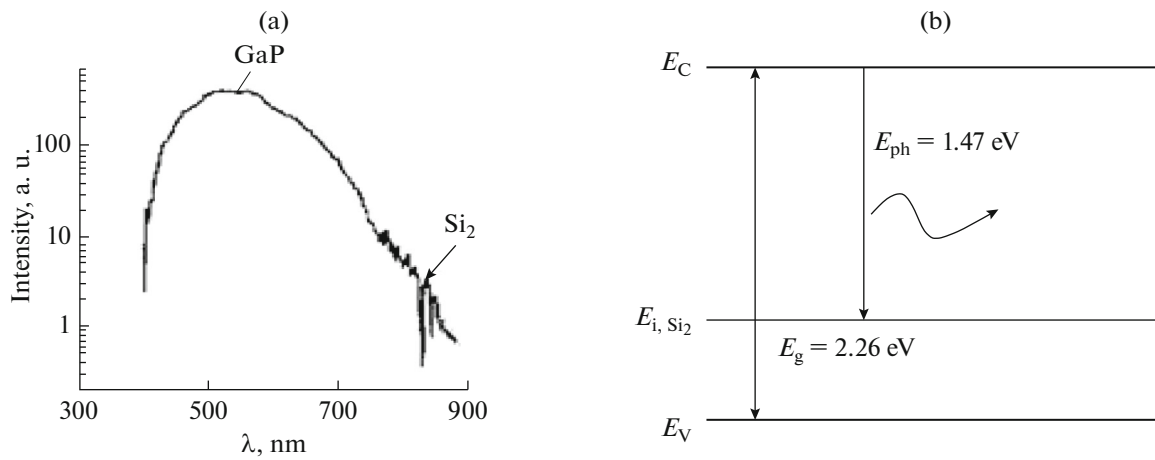
As it can be seen from Fig. 1a, in the long-wavelength region of the PL spectrum at a wavelength of 0.933  $\mu\text{m}$  there is a small but rather wide maximum of radiation intensity, which corresponds to photon energy  $E_{\text{ph}} = 1.33$  eV. In all appearance, the radiative transition of electrons from the conduction band to the impurity levels of  $\text{Si}_2$  molecules located in the band gap of the  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}\langle\text{Si}_2\rangle$  SS (Fig. 1b) could be, responsible for this peak. The author of [18], in order to take into account the effect of the atoms of the base semiconductor surrounding  $\text{A}_2$  or CD molecules exerted on the A–A or C–D covalent bond, have studied the photoluminescence spectrum of gallium arsenide doped with Ge at a temperature of 77 K, wherein a radiation peak at photon energies amounting to about 0.85 eV has been observed. This peak is caused by the transition of electrons from the conduction band to impurity levels of  $\text{Ge}_2$  molecules. The author of this study has concluded that  $\text{Ge}_2$  in GaAs creates an impurity level located at 0.85 eV below the bottom of the conduction band (at a temperature of 77 K).

The content of Si in the near-surface region of the film is lower than 0.8 mol %, and, as a result, the energy level at  $E_{\text{ph}} = 1.33$  eV could be caused by a radiative recombination of charge carriers with the participation of Si–Si covalent bond surrounded by a GaAs-enriched sublayer of the tetrahedral crystal lattice of the  $(\text{GaAs})_{1-x}(\text{Ge}_2)_x\langle\text{Si}_2\rangle$  SS.

As it is known, the dissociation energy of the Si–Si covalent bond located in the tetrahedral crystal lattice of intrinsic silicon at 77 K amounts to 1.16 eV [19]. However, when  $\text{Si}_2$  molecules are surrounded by relatively strongly bound atoms of GaAs molecules, owing to the hybridization of the electron shells of  $\text{Si}_2$  molecules and GaAs atoms, the Si–Si covalent bond energy increases up to  $E_{i,\text{Si}_2} = 1.33$  eV at 77 K and causes an energy level of  $\text{Si}_2$  molecules in the band gap of the  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}\langle\text{Si}_2\rangle$  SS to occur.

The covalent Si–Si bond in the crystal lattice of the  $(\text{GaAs})_{0.95}(\text{Ge}_2)_{0.05}$  SS under the influence of surrounding atoms of the base material exhibits an increase in bond strength by  $\Delta E = E_{i,\text{Si}_2} - E_{g,\text{Si}} \approx (1.33 - 1.16)$  eV = 0.17 eV at a temperature of 77 K. Since the covalent Si–Si bond is saturated, i.e., since the valencies of atoms composing  $\text{Si}_2$  and GaAs molecules are equal, then, the  $\text{Si}_2$  molecules in the tetrahedral GaAs crystal lattice could exhibit a donor character. The substitution of GaAs molecules by  $\text{Si}_2$  molecules does not lead to any strong deformation of the crystal lattice. The  $\text{Si}_2$  molecules are not recombination-active centers. The studied  $(\text{Si}_2)_{1-x-y}(\text{Ge}_2)_y(\text{GaAs})_z$  solid solution grown on Si substrates can be used as an active material for the development of optoelectronic devices operating in the near infrared range of electromagnetic radiation [20, 21].

The PL spectrum of the  $(\text{Si}_2)_{1-x}(\text{GaP})_x$  ( $0 \leq x \leq 0.98$ ) epitaxial layer has been measured at 5 K (Fig. 2a). The



**Fig. 2.** Photoluminescence spectrum for the epitaxial layer of a  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$  SS at a temperature of 5 K (a), and an energy band diagram for the solid solution with the impurity energy level ( $E_{i, \text{Si}_2}$ ) of the atoms composing  $\text{Si}_2$  molecules (b).

PL was excited by a gallium–cadmium laser (radiation with  $\lambda_{\text{max}} = 325$  nm). The laser radiation is absorbed in the surface region of the epitaxial film, wherein the silicon content is 2 mol %. Consequently, the luminescent radiation is caused by the  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$  SS. As it can be seen from Fig. 2a, the PL spectrum of the  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$  SS exhibits a wide band ranging from 400 to 900 nm with a radiation maximum at 550 nm, which corresponds to a photon energy of 2.26 eV.

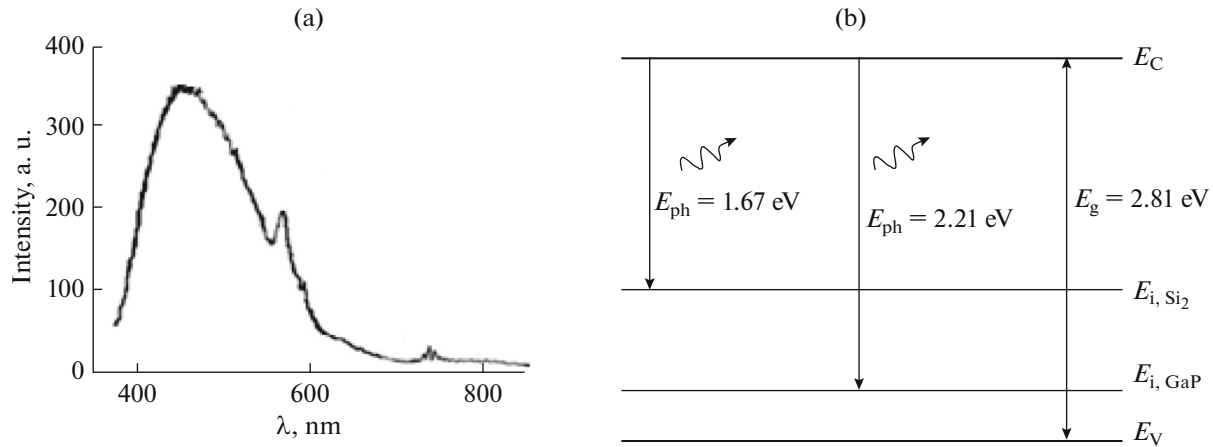
This maximum is caused by a band–band recombination of electron–hole pairs. Consequently, the band gap of the  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$  SS at a temperature of 5 K is  $E_g = 2.26$  eV. It is interesting that one more luminescence response is observed in the long-wavelength region of the spectrum at a wavelength of 840 nm, which corresponds to photon energy  $E_{\text{ph}} = 1.47$  eV. The fact that the mentioned response can be, to all appearance, connected with the formation of the atomic energy level of  $\text{Si}_2$  molecules located at  $E_{i, \text{Si}_2} = 1.47$  eV below the bottom of the conduction band  $(\text{GaP})_{0.98}(\text{Si}_2)_{0.02}$  SS (Fig. 2b). It is known that the silicon band gap at 5 K amounts to 1.2 eV [19]. However, if  $\text{Si}_2$  molecules are located in the GaP crystal lattice, then, the dissociation energy of the Si–Si covalent bond exhibits a decrease by  $\Delta E = E_{i, \text{Si}_2} - E_{g, \text{Si}} \approx (1.47 - 1.20)$  eV = 0.27 eV at a temperature of 5 K under the influence of the surrounding Ga and P atoms. The  $(\text{Si}_2)_{1-x}(\text{GaP})_x$  ( $0 \leq x \leq 0.98$ ) SS ( $0 \leq x \leq 0.98$ ) grown on Si substrates can be used as a substrate material for the further growth of binary III–V compounds, or as active materials for the development of optoelectronic devices operating in the visible and near-infrared regions of the radiation spectrum [22, 23].

The PL spectrum of the epitaxial  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS layer shown in Fig. 3a has been measured at a temperature of 5 K. The PL

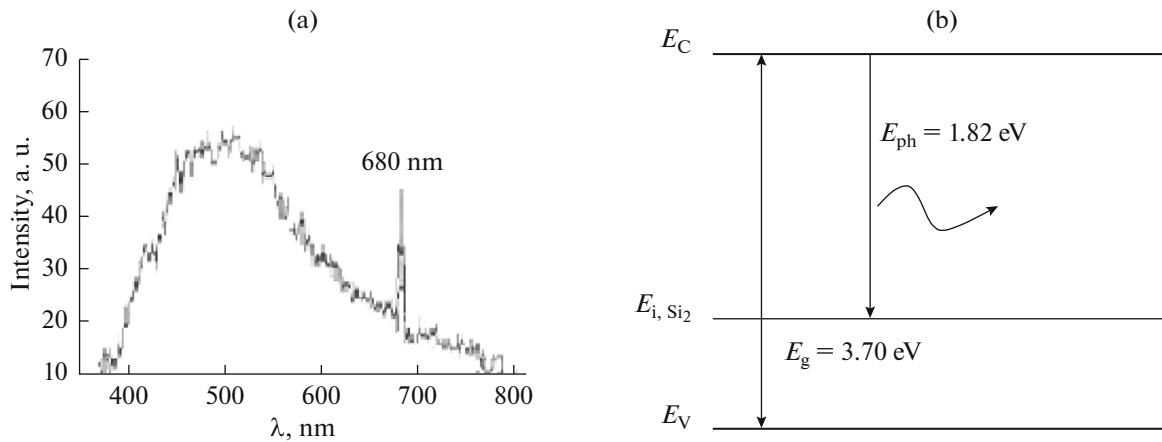
was excited using the radiation of a Ga–Cd laser ( $\lambda_{\text{max}} = 325$  nm). The PL spectrum of the SS covers a wide band in the visible radiation range from 400 to 800 nm. The main broad maximum of radiation at a wavelength of 440 nm is caused by a band–band recombination of electron–hole pairs. The band gap of the investigated SSs at 5 K is  $E_{g, \text{TP SS}} = 2.82$  eV. In the long-wavelength region of the PL spectrum, there are two more peaks at wavelengths of 740 nm ( $E_{\text{ph}} = 1.67$  eV) and 560 nm ( $E_{\text{ph}} = 2.21$  eV). These peaks can be, in all appearance, caused by radiative transitions of electrons from the conduction band to the energy levels of  $\text{Si}_2$  and GaP molecules, respectively.

The covalent Si–Si bond in the tetrahedral crystal lattice of the  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS is strengthened under the influence of strongly bonded atoms of ZnSe molecules to attain the value of  $E_{i, \text{Si}_2} = 1.67$  eV at 5 K instead of the value of  $E_{g, \text{Si}_2} = 1.20$  eV, which is characteristic of pure silicon. In this case, the peak at  $E_{\text{ph}} = 2.21$  eV almost coincides with the band gap of gallium phosphide at 5 K, which indicates that there is an insignificant effect of atoms composing ZnSe molecules exerted on the dissociation energy of the Ga–P covalent bond in the  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS.

The analysis of the PL spectrum shows that Si–Si and Ga–P covalent bonds in the  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS cause deep impurity energy levels at  $E_{i, \text{Si}_2} = 1.67$  eV and  $E_{i, \text{GaP}} = 2.21$  eV below the bottom of the SS conduction band, respectively (Fig. 3b). Thus, the covalent Si–Si bond in the crystal lattice of  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS exhibits an increase by  $\Delta E = E_{i, \text{Si}_2} - E_{g, \text{Si}} \approx (1.67 - 1.2)$  eV = 0.47 eV at a temperature of 5 K under the influence of surrounding atoms inherent in the base material.



**Fig. 3.** Photoluminescence spectrum for the epitaxial layer of  $(\text{ZnSe})_{0.88}(\text{Si}_2)_{0.03}(\text{GaP})_{0.09}$  SS at a temperature of 5 K (a) and an energy band diagram for the solid solution with impurity energy levels of the atoms composing  $\text{Si}_2$  molecules ( $E_{i,\text{Si}_2}$ ) and those atoms composing GaP molecules  $E_{i,\text{GaP}}$  (b).

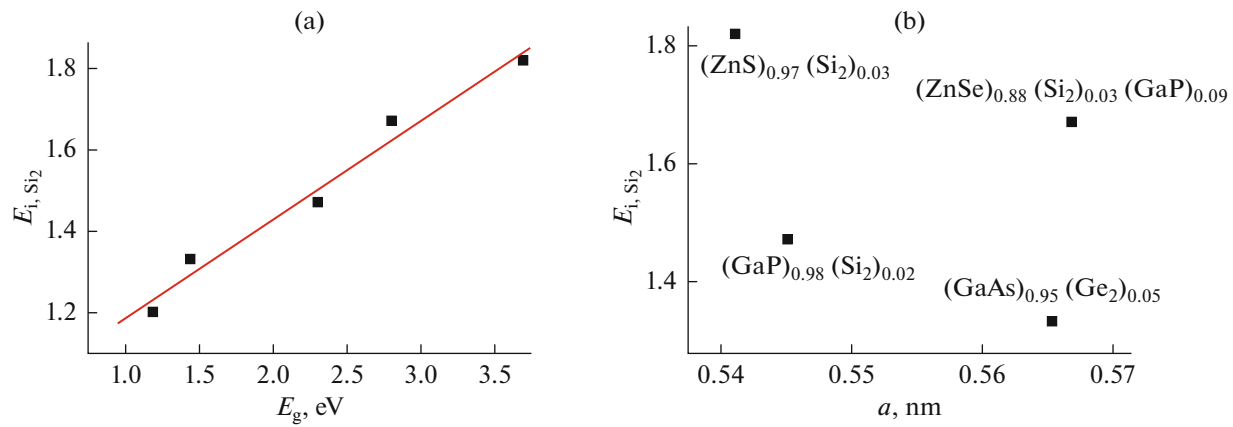


**Fig. 4.** Photoluminescence spectrum for the epitaxial layer of  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$  solid solution at a temperature of 77 K (a) and an energy band diagram for the SS with the impurity energy level ( $E_{i,\text{Si}_2}$ ) of the atoms composing  $\text{Si}_2$  molecules (b).

Figure 4a shows a photoluminescence spectrum of the surface of the  $(\text{ZnS})_{1-x}(\text{Si}_2)_x$  epitaxial film measured at a temperature of 77 K. The laser radiation supplied to the film surface is absorbed in the surface region within a thickness of  $\sim 3 \mu\text{m}$ . In this area, the content of ZnS is 97 mol %. Consequently, the luminescent radiation originates from the sublayer of the  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$  SS.

The study of the spectrum of the luminescence excitation for this SS has shown that at an excitation wavelength amounting to 335 nm, a radiation peak is observed in the spectrum corresponding to the band gap inherent in the SS under study ( $E_g = 3.7 \text{ eV}$ ). The long-wavelength edge of the PL spectrum is extended to the right, and there is a peak corresponding to a photon energy amounting to 1.82 eV ( $\lambda = 680 \text{ nm}$ ). The occurrence of this peak could be caused by a

luminescent radiation under electron transition from the conduction band to the impurity levels originated from the atoms composing  $\text{Si}_2$  molecules (Fig. 4b). Just as it was in previous cases, under the influence of more strongly bonded atoms of ZnS molecules, the dissociation energy of a Si–Si covalent bond in the  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$  SS exhibits a gain in value to 1.82 eV instead of 1.16 eV, which is typical for pure silicon at 77 K. Thus, the covalent Si–Si bond in the crystal lattice of a  $(\text{ZnS})_{0.97}(\text{Si}_2)_{0.03}$  SS exhibits an increase of  $\Delta E = E_{i,\text{Si}_2} - E_{g,\text{Si}} \approx (1.82 - 1.16) \text{ eV} = 0.66 \text{ eV}$  at a temperature of 77 K. The  $(\text{ZnS})_{1-x}(\text{Si}_2)_x$  SSs grown on Si substrates could be used either as a substrate material for the further growth of binary II–VI compounds, or as an active material for the development of optoelectronic devices operating in the visible and infrared regions of the radiation spectrum [24, 25].



**Fig. 5.** Covalent bond dissociation energy for  $Si_2$  impurity molecules (a) depending on the band gap and (b) depending on the crystal lattice parameter of  $(GaAs)_{0.95}(Ge_2)_{0.05}(Si_2)$ ,  $(GaP)_{0.98}(Si_2)_{0.02}$ ,  $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$ , and  $(ZnS)_{0.97}(Si_2)_{0.03}$  solid solutions.

## DISCUSSION

The analysis of PL for the studied  $(GaAs)_{0.95}(Ge_2)_{0.05}(Si_2)$ ,  $(GaP)_{0.98}(Si_2)_{0.02}$ ,  $(ZnSe)_{0.88}(Si_2)_{0.03}(GaP)_{0.09}$ , and  $(ZnS)_{0.97}(Si_2)_{0.03}$  SSs shows that in all cases the atoms composing  $Si_2$  molecules form deep impurity energy levels located in the band gap of the SSs. Since the  $Si_2$  molecules are isovalent with respect to the molecules of the SS components, the Si–Si covalent bond can act as a donor. Based on the experimental data of the PL spectrum, we have analyzed the covalent bond dissociation energy of  $Si_2$  impurity molecules ( $E_{i, Si_2}$ ) depending on the band gap ( $E_g$ ) and on the crystal lattice parameter of the base material (Fig. 5). From Fig. 5a one can see that, with increasing  $E_g$  an increase in the value of  $E_{i, Si-Si}$  is observed. At the same time, the value of  $E_{i, Si_2}$  depending on  $E_g$  can be approximated by a linear functional relationship expressed in the following form:

$$E_{i, Si_2} \text{ (eV)} = 0.94 \text{ (eV)} + 0.24E_g \text{ (eV)}.$$

The increase in  $E_{i, Si_2}$  with increasing  $E_g$  inherent in the base semiconductor could be caused by the hybridization of the electron shells of the atoms of  $Si_2$  molecules with the electron shells of atoms of the base material molecules. The stronger the covalent bond between the atoms of the base material molecules, the greater the energy of the breaking of the covalent bond between the atoms of impurity  $Si_2$  molecules.

The analysis of  $E_{i, Si_2}$  depending on the crystal lattice parameter (Fig. 5b) of the base material shows that the value of  $E_{i, Si_2}$  depends on the crystal lattice parameter too. The dependence on the crystal lattice parameter is more complicated. It is different for different III–V and II–VI binary compounds. At close crystal lattice parameters of the base material,  $E_{i, Si_2}$  has a

higher value in SSs based on II–VI binary compounds than in SSs based on III–V compounds, which could be caused by the influence of the fraction of the ionic component in the chemical bonding of the atoms in the base material molecules.

With an increase in the crystal lattice parameter, both for III–V binary compounds and for II–VI ones, a decrease in the value of  $E_{i, Si_2}$  is observed (see Fig. 5b). This is caused by a change in the length of the Si–Si covalent bond under the influence of atoms belonging to the molecules of the base material. The  $Si_2$  impurity molecules introduced into the crystal lattice are tuned with respect to the crystal lattice under the action of nodal atoms of the base material and the length of the Si–Si covalent bond ( $L_{Si}$ ) exhibits either an increase or a decrease depending on the type and number of surrounding atoms. With decreasing  $L_{Si}$ , the interaction forces between the atoms of  $Si_2$  molecules increase and, accordingly, the interaction energy increases.

It should be noted that a similar dependence of changes in the covalent bond dissociation energy inherent in impurity molecules depending on the band gap and the crystal lattice parameter of semiconductor materials has been observed earlier by the authors of this paper for GaAs impurity molecules in semiconductor materials based on Si, Sn, GaAs, GaSb, and  $nSb$  [9].

One urgent problems in semiconductor materials science consists in the integration of silicon technology with the technology of  $A^{III}B^V$  and  $A^{II}B^{VI}$  binary compounds in order to reduce the cost of production.

The  $(Si_2)_{1-x}(GaP)_x$  SS is a photoactive material in the photon energy range from 1.2 to 3.1 eV, whereas the  $(Si_2)_{1-x}(ZnS)_x$  solid solution is photoactive from 1.25 to 3.2 eV. The crystal lattice constants of Si ( $a = 0.54307$  nm), GaP ( $a = 0.5451$  nm) and ZnS ( $a =$



0.54109 nm) have close values, the difference between them is less than 0.37%. This is very important for obtaining high-quality epitaxial films of such SSs on Si substrates with a low density of dislocation defects. Therefore, these solid solutions are promising materials for the development of silicon photocells with an extended range of photosensitivity in the short-wavelength region of the solar radiation spectrum.

## CONCLUSIONS

Silicon molecules that replace two atoms of the base semiconductor form deep impurity energy levels lying in the band gap of SSs obtained based on Ge, GaAs, GaP, ZnSe, and ZnS. Since the difference between the sums of the covalent radii of the atoms forming the molecules of the considered compounds and Si<sub>2</sub> molecules does not exceed 10% and the sums of the valences of the atoms forming these molecules are equal, the Si<sub>2</sub> molecules do not represent active recombination centers. They can promote radiative electronic transitions of nonequilibrium carriers at high levels of charge carrier injection into the semiconductor. The spectral region of (Si<sub>2</sub>)<sub>1-x</sub>(GaP)<sub>x</sub> and (Si<sub>2</sub>)<sub>1-x</sub>(ZnS)<sub>x</sub> SS photosensitivity covers a wavelength range from ~400 to ~900 nm, therefore, these SSs can be used as a photoactive material for the development of photocells and photosensors operating in the visible and near-infrared region of the radiation spectrum.

## ACKNOWLEDGMENTS

The authors express gratitude to their colleagues at the Physicotechnical Institute of the Academy of Sciences of the Republic of Uzbekistan for their permanent support.

## FUNDING

This study was financially supported by internal grant FA-F2-003 RUz: Photoelectric, Thermoelectric and Emission Effects in Novel Multicomponent Solid Solutions with Nanocrystals Based on Molecules of Elemental Semiconductors and Semiconductor Compounds.

## REFERENCES

1. Taboada, A.G., Meduna, M., Salvalaglio, M., et al., GaAs/Ge crystals grown on Si substrates patterned down to the micron scale, *J. Appl. Phys.*, 2016, vol. 119, no. 5, ID 055301. <https://doi.org/10.1063/1.4940379>
2. Sharma, P., Milakovich, T., Bulsara, M.T., and Fitzgerald, E.A., Controlling epitaxial GaAs<sub>x</sub>P<sub>1-x</sub>/Si<sub>1-y</sub>Ge<sub>y</sub> heterovalent interfaces, *ECS Trans.*, 2013, vol. 50, no. 9, pp. 333–337. <https://doi.org/10.1149/05009.0333ecst>
3. Olsen, V.S., Bazioti, C., Azarov, A., et al., Bandgap bowing in crystalline (ZnO)<sub>1-x</sub>(GaN)<sub>x</sub> thin films; influence of composition and structural properties, *Semi-*

*cond. Sci. Technol.*, 2019, vol. 34, ID 015001. <https://doi.org/10.1088/1361-6641/aace4a>

4. Bolkhovityanov, Yu.B. and Pchelyakov, O.P., III–V compounds-on-Si: heterostructure fabrication, application and prospects, *Open Nanosci. J.*, 2009, vol. 3, pp. 20–33. <https://doi.org/10.2174/1874140100903010020>
5. Khludkov, S.S., Tolbanov, O.P., Vilisova, M.D., and Prudaev, I.A., *Poluprovodnikovye pribory na osnove arsenida galliya s glubokimi primesnymi tsentrami (Gallium Arsenide Semiconductor Devices with Deep Impurity Centers)*, Tolbanov, O.P., Ed., Tomsk: Izd. Dom Tomsk Gos. Univ., 2016.
6. Mironov, A.G. and Serov, A.S., Electron energies and states at the deep impurity level in a semiconductor, *Moscow Univ. Phys. Bull.*, 2011, vol. 66, no. 3, pp. 272–277. <https://doi.org/10.3103/S0027134911030143>
7. Khelifi, S, Burgelman, M., Verschraegen, J., and Belghachi, A., Impurity photovoltaic effect in GaAs solar cell with two deep impurity levels, *Sol. Energy Mater. Sol. Cells*, 2008, vol. 92, no. 12, pp. 1559–1565. <https://doi.org/10.1016/j.solmat.2008.07.003>
8. Deenapanray, P.N.K., Petravic, M., Jagadish, C., et al., Electrical characterization of pGaAs epilayers disordered by doped spin-on-glass, 2005, *J. Appl. Phys.*, vol. 97, no. 3, pp. 033524.1–033524.7. <https://doi.org/10.1063/1.1846140>
9. Usmonov, Sh.N., Influence of GaAs molecules on the photosensitivity of p-Si–n-(GaSb)<sub>1-x</sub>(Si<sub>2</sub>)<sub>x</sub> and n-GaAs–p-(InSb)<sub>1-x</sub>(Sn<sub>2</sub>)<sub>x</sub> heterostructures, *Appl. Sol. Energy*, 2016, vol. 52, no. 3, pp. 211–214. <https://doi.org/10.3103/S0003701X16030178>
10. Saidov, A.S., Usmonov, Sh.N., and Asatova, U.P., Growth of Ge<sub>1-x</sub>Sn<sub>x</sub> solid solution films and study of their structural properties and some of their photoelectric properties, *Semiconductors*, 2012, vol. 46, no. 8, pp. 1088–1095. <https://doi.org/10.1134/S1063782612080180>
11. Saidov, A.S., Usmonov, Sh.N., and Saparov, D.V., Structural studies of the epitaxial layer of a substitutional solid solution (GaAs)<sub>1-x</sub>(ZnSe)<sub>x</sub> with nanocrystals, *Adv. Mater. Sci. Eng.*, 2019, vol. 10, ID 3932195. <https://doi.org/10.1155/2019/3932195>
12. Andreev, V.M., Dolginov, L.M., and Tret'yakov, D.N., *Zhidkostnaya epitaksiya v tekhnologii poluprovodnikovykh priborov* (Liquid epitaxy in semiconductor technology), Moscow: Sov. Radio, 1975.
13. Saparov, D.V., Saidov, M.S., and Saidov, A.S., Expansion of the spectral sensitivity range of the silicon photocells by growing a solid (Si<sub>2</sub>)<sub>1-x</sub>(GaP)<sub>x</sub> (0 ≤ x ≤ 1) solution, *Appl. Sol. Energy*, 2016, vol. 52, no. 3, pp. 236–237. <https://doi.org/10.3103/S0003701X16030154>
14. Saidov, A.S., Saidov, M.S., Usmonov, Sh.N., and Rakhmonov, U.Kh., Photothermovoltaic effect in a pSi–n(Si<sub>2</sub>)<sub>1-x-y</sub>(ZnSe)<sub>x</sub>(GaP)<sub>y</sub> (0 ≤ x ≤ 0.88, 0 ≤ y ≤ 0.09) structure, *Appl. Sol. Energy*, 2013, vol. 49, no. 4, pp. 241–243. <https://doi.org/10.3103/S0003701X13040154>
15. Nakarmi, M.L., Nepal, N., Lin, J.Y., and Jiang, H.X., Photoluminescence studies of impurity transitions in

- Mg-doped AlGaIn alloys, *Appl. Phys. Lett.*, 2009, vol. 94, ID 091903, p. 3.  
<https://doi.org/10.1063/1.3094754>
16. Gfroerer, T.H., Photoluminescence in analysis of surfaces and interfaces, in *Encyclopedia of Analytical Chemistry*, Meyers, R.A., Ed., New York: Wiley, 2000, pp. 9209–9231.  
<https://doi.org/10.1002/9780470027318.a2510>
  17. Johnston, K., Henry, M.O., McCabe, D., et al., Identification of donor-related impurities in ZnO using photoluminescence and radiotracer techniques, *Phys. Rev. B*, 2006, vol. 73, ID 165212.  
<https://doi.org/10.1103/PhysRevB.73.165212>
  18. Saidov, M.S., Approximate estimate of the ionization energy of impurities causing a photovoltaic effect in silicon and gallium arsenide, in *Materialy konferentsii "Fotoelektricheskie yavleniya v poluprovodnikakh"* (Proc. Conf. on Photoelectric Phenomena in Semiconductors, Tashkent, Apr. 20–21, 2004), pp. 19–21.
  19. Sze, S., *Physics of Semiconductor Devices*, New York: Wiley-Interscience, 1981, Vol. 1.
  20. Roelkens, G., Van Campenhout, J., Brouckaert, J., et al., III–V/Si photonics by die-to-wafer bonding, *Mater. Today Adv.*, 2007, vol. 10, no. 7–8, pp. 36–43.  
[https://doi.org/10.1016/S1369-7021\(07\)70178-5](https://doi.org/10.1016/S1369-7021(07)70178-5)
  21. Heyns, M., Alian, A., Caymax, M., et al., Advancing CMOS beyond the Si roadmap with Ge and III/V devices, in *International Electron Devices Meeting, Washington, DC, USA, Dec. 5–7, 2011*, Washington, 2011.  
<https://doi.org/10.1109/IEDM.2011.6131543>
  22. Grassman, T.J., Carlin, J.A., Galiana, B., et al., MOCVD-grown GaP/Si subcells for integrated III–V/Si multijunction photovoltaics, *IEEE J. Photovoltaics*, 2014, vol. 4, no. 3, pp. 972–980.  
<https://doi.org/10.1109/JPHOTOV.2014.2308727>
  23. Volz, K., Beyer, A., Witte, W., et al., GaP-nucleation on exact Si (001) substrates for III/V device integration, *J. Crystal Growth*, 2011, vol. 315, no. 1, pp. 37–47.  
<https://doi.org/10.1016/j.jcrysgro.2010.10.036>
  24. Fang, X., Zhai, T., Gautam, U.K., et al., ZnS nanostructures: From synthesis to applications, *Prog. Mater. Sci.*, 2011, vol. 56, pp. 175–287. .  
<https://doi.org/10.1016/j.pmatsci.2010.10.001>
  25. Kaplan, H.K., Sarsıcı, S., Akay, S.K., and Ahmetoglu, M., The characteristics of ZnS/Si heterojunction diode fabricated by thermionic vacuum arc, *J. Alloys Compd.*, 2017, vol. 724, no. 15, pp. 543–548.  
<https://doi.org/10.1016/j.jallcom.2017.07.053>

Translated by O. Polyakov