EAST EUROPEAN JOURNAL OF PHYSICS. **3.** 314-318 (2025)
DOI:10.26565/2312-4334-2025-3-29 ISSN 2312-4334

THE PHOTOELECTRIC PROPERTIES OF *n*-Si–*p*-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ HETEROSTRUCTURES

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Received March 28, 2025; revised June 28, 2025; accepted July 9, 2025

In this paper, the photovoltaic properties of $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ solid solutions grown on silicon substrates are investigated. It is found that the solid solutions $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ possess selective photosensitivity due to the presence of ZnSe, Ge_2, and $GaAs_{1-\delta}Bi_\delta$ components, as well as the difference in the ionisation energy of their covalent bonds. The photoconductivity mechanisms in n-Si-p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures were analysed based on the E_i values that provided the best fit to the experimental spectrum and Gaussian approximation curves. Photopeaks corresponding to Gaussian curves at the energy levels 1.23 eV, 1.45 eV, 1.64 eV, 1.91 eV, 2.21 eV, and 2.45 eV were observed in the photon energy range: $E_{ph,1}$ - 0.98÷1.75 eV, $E_{ph,2}$ - 1.01÷2.03 eV, $E_{ph,3}$ - 1.15÷2.28 eV, $E_{ph,4}$ - 1.34÷2.52 eV, $E_{ph,5}$ - 1.75÷2.71 eV and $E_{ph,6}$ - 2.1÷2.77 eV. The observation of intermediate states in the photosensitivity spectrum of this solid solution confirmed the presence of nano-objects formed based on ZnSe and Ge_2 molecules, as well as $GaAs_{1-\delta}Bi_\delta$ compounds in these films. It was found that solid solutions $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ have the potential to be used as selective photoactive materials operating in the ranges of infrared and visible radiation.
Keywords: *Silicon; Solid solution; $GaAs_{1-\delta}Bi_\delta$ compound; Covalent bonding; Photosensitivity*
PACS: 78.30.Am

INTRODUCTION

High-performance photovoltaic and optoelectronic devices are largely controlled by the capability of semiconductor materials to react to a wide spectral range effectively. Winding of the photosensitivity range of photoactive elements is one of the major functional parameters of a device. Extending this range not only enhances the efficiency of energy conversion but also widens the use of such devices in various technological applications, including solar energy harvesting, photodetection, and optical communications. Among the most commonly utilized techniques of broadening the spectral response is introducing specific impurities into semiconductor material, especially within the active parts of p-n junctions [1]. This method enables the creation of other energy levels within the bandgap and thus enhances the interaction between incoming photons and charge carriers [2].

There has also recently been a developing interest in adding isovalent impurities into epitaxial semiconductor films. When carefully chosen and controlled, these impurities have been shown to add localized energy levels inside the valence or conduction bands of the host semiconductor material. These newly added levels are of great importance for optical absorption, carrier recombination rates, and transport characteristics, and, in turn, bring about enhancements of photoelectric responses. Such effects need to be investigated for the development of future semiconductor heterostructures optimized for operation under high efficiency in various irradiation conditions [3,4].

This study focuses on a novel class of solid-solution heterostructures based on the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ composition, epitaxially grown on silicon substrates. Such multi-component alloys comprise several semiconductor elements of different bandgaps and ionization strengths that may be engineered to blend together in an array of permutations to yield a required set of electronic and optical properties. Insertion of $GaAs_{1-\delta}Bi_\delta$, for instance, provides deep-level isovalent dopants that serve essentially to redefine the valence band edge along with augmenting infrared absorption. Wide-bandgap response is brought into the matrix with ZnSe and Ge_2 atoms provide long-wavelength sensitivity in virtue of lower bandgap response.

Among the distinctive features of the solid solutions of this kind is the occurrence of nano-objects based on $GaAs_{1-\delta}Bi_\delta$ components incorporated into films, as inferred from the occurrence of intermediate states in the photosensitivity spectrum. Nanoscale structures are responsible for creating localized energy states, which alter the energy band diagram of the heterostructure and develop new channels of photon absorption. These features lead to increased selective photosensitivity, especially in the visible and infrared regions of the spectrum. Such selectivity also arises due to variations in ionization energy of covalent bonds of the element constituting it, producing uneven energy levels as well as specific optical transitions.

Through detailed experimental analysis, this research demonstrates the potential of $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures as high-performance photoactive materials. Their ability to operate efficiently across a wide spectral range, including both infrared and visible regions, highlights their suitability for next-generation optoelectronic applications [5]. Additionally, the use of silicon substrates ensures compatibility with existing semiconductor processing technologies, further enhancing the practical relevance of the findings.

Cite as: A.Y. Boboev, U.R. Karimberdiev, N.Y. Yunusaliyev, J.S. Madaminov, East Eur. J. Phys. 3, 314 (2025), https://doi.org/10.26565/2312-4334-2025-3-29

We believe that the understanding gained in this work provides new insights to the mechanistics of impurity induced spectral tuning and nanostructure enhanced photoresponse. This work is part of the larger field of semiconductor device engineering, enabling the design of bespoke materials with controlled band structures and localized optoelectronic properties. The findings highlight the potential of such heterostructures in high-performance photovoltaic devices, infrared sensors and phase-locked photonic integrated circuits, where it is crucial to independently control the charge carrier properties and spectral sensitivity.

MATERIALS AND METHODS

Silicon wafers with a radius of 10 mm and an approximate thickness of 350 μm were used as substrates. These wafers had a specific resistivity of 10 Ω·cm, a charge carrier concentration of $4.4\cdot10^{14}$ cm^{-3}, and carrier mobility of 1439 $cm^2/(V\cdot s)$. The possibility of obtaining high-quality solid solutions was established by controlling the thickness of the epitaxial films, the initial and final crystallization temperatures, as well as the cooling rate. Based on preliminary electron microscopic investigations, optimal technological conditions were determined: the initial crystallization temperature of the layers was set at 750°C, the crystallization rate of the epitaxial layers was υ_k = 0.15 μm/min, and the forced cooling rate was 1°C/min.

The initial electrophysical properties of $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ epitaxial films were measured at room temperature using the Van der Pauw method. The type of electrical conductivity was identified using a thermal zone and the Hall constant. It was established that undoped films exhibited predominantly p-type (hole) conductivity. Measurements revealed that at room temperature, the specific resistivity, charge carrier concentration, and mobility of the epitaxially grown films were approximately 10 Ω·cm, $1.8\cdot10^{15}$ cm^{-3}, and 368 $cm^2/V\cdot s$, respectively. Furthermore, based on the preliminary electrophysical parameters, the mobility of minority carriers was estimated to be 4673 $cm^2/V\cdot s$.

Ohmic contacts for the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures were formed using gold (Au) and silver (Ag). The ohmic nature of these contacts was initially confirmed using a characterograph, followed by voltage drop and resistance measurements. Taking into account the p-type conductivity of the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ solid solutions, optimal ohmic contacts with low resistance and linear I–V characteristics were obtained by thermally evaporating Au and Ag onto the epitaxial surface at 150°C under vacuum conditions.

The spectral dependence of the photosensitivity of the resulting n-Si–p $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures was investigated using an optical spectrometer equipped with a CARL ZEISS JENA monochromator and quartz optics. This setup allowed for the study of the samples within the photon energy range of 1 to 3 eV.

RESULTS AND DISCUSSION

Figure 1 presents the photosensitivity spectrum of n-Si–p $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures based on epitaxial layers with a thickness of approximately 10 μm. For comparative analysis, the spectrum of a reference n-Si–p-Si structure is also shown (Figure 1, Spectrum 2). The comparison reveals that the presence of ZnSe and $GaAs_{1-\delta}Bi_\delta$ compounds within the epitaxial layers shifts the sensitivity spectrum toward shorter wavelengths (higher photon energies, $E_{ph} \geq 1.45$ eV), while the incorporation of Ge atoms causes a redshift toward longer wavelengths.

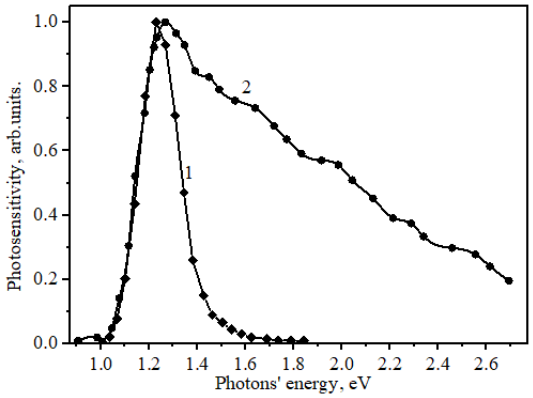

Figure 1. Photosensitivity spectra of the n-Si–p-$((Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ (1) and n-Si-p-Si (2) structures

The maximum photosensitivity peak is observed at a photon energy of 1.26 eV (Figure 1, Spectrum 1), which suggests that the heterostructure includes a thin Ge buffer layer on the silicon surface. Subsequent formation of the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ epitaxial layers involve partial atomic substitution between ZnSe molecules and Ge_2 atom pairs, resulting in a solid solution with a bandgap of approximately 1.26 eV. This bandgap value was experimentally determined using the following equation [6]:

$$E_{g,s.s.}=(1-x-y)E_{g,Ge}+(x)E_{g,ZnSe}+(y)E_{g,GaAs/Bi}-\xi_1(x)(1-x-y)-\xi_2(y)(1-x-y). \quad (1)$$

Here, x=0.31 and y=0.12 are the molar fractions of ZnSe and $GaAs_{1-\delta}Bi_\delta$, determined from X-ray microanalysis. The micmatch parameters between the lattice constants of Ge, ZnSe, and $GaAs_{1-\delta}Bi_\delta$ are given by

$\xi_1 = 2|a_{Ge}-a_{GaAs}| / (a_{Ge} + a_{ZnSe}) = 0.0017$ and $\xi_2 = 2|a_{Ge}-a_{GaAs/Bi}| / (a_{Ge}+a_{GaAs/Bi}) = 0.037$. For the given composition, the calculated bandgap of the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ epitaxial layers is 1.248 eV, which is in excellent agreement with the experimentally observed values.

In addition, the photosensitivity spectrum of the n-Si–p$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures exhibited several weak sensitivity peaks at photon energies of 1.45, 1.64, 1.91, 2.21, and 2.45 eV. During the spectral analysis, significant overlapping of multiple photoresponse peaks of varying intensities was observed, which is likely associated with the close proximity of the absorption energies of the film constituents.

To further explore the photoconductivity mechanicms in the n-Si–p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures, the photosensitivity spectrum was reanalyzed using the Gaussian approximation method implemented in Wolfram Mathematica 7. The resulting spectrum was deconvoluted into Gaussian components. The initial energy values (E_e) of each individual photopeak were selected based on the experimentally observed maximum sensitivity points on the original curve. As a result, the photosensitivity spectrum was successfully modeled using six Gaussian components with optimal fitting to the experimental and total Gaussian curves. The deviations between the calculated peak energies and the tabulated values did not exceed 0.01 eV, confirming high accuracy.

All six photopeaks corresponding to the Gaussian fits were observed in the following photon energy ranges: $E_{ph,1}$ – 0,98-1,75 eV, $E_{ph,2}$ – 1,01-2,03 eV, $E_{ph,3}$ – 1,15-2,28 eV, $E_{ph,4}$ – 1,34-2,52 eV, $E_{ph,5}$ – 1.75-2.71 and $E_{ph,6}$ – 2.1-2,77 eV

The corresponding maximum sensitivity peaks were identified at 1.23, 1.45, 1.64, 1.91, 2.21, and 2.45 eV, respectively (Figure 2).

As seen in Figure 2, the primary Gaussian curve's (dashed line 1) onset at 0.98 eV suggests a shallow level, which can be explained by covalent bonding resulting from a partial substitution of ZnSe molecules and Ge_2 atomic pairs during the early stage of the Ge buffer layer crystallization and the latter epitaxy portion [7]. Also, research works [8] has pointed out that atoms of Zn, in particular, which are constituent of the germanium layer, as well as the other Zinc along with Molecule of Selenium, are able to act as recombination centers bearing acceptor type features, which corresponds with a very large increase of sensitivity to the spectrum starting at approximately 1.0 eV. Also, in another study [9], it was noted that minor atomic substitution between the molecules of ZnSe and pairs of Ge_2 causes the spontaneous formation at nanocrystals with variable dimension and shape positioned in regions of the crystal lattice with a high density of defects. Related study [10] reported an energy level in the 1.23 eV region in the bandwidth of absence of $(GaAs)_{1-x-y}(ZnSe)_x$ structures. This energy matches with what has been identified as the first maximum of the first Gaussian component in our work. In addition, other literature [11] has also indicated that nanocrystals of ZnSe implanted in monocrystals of germanium produce levels of energy which are similar to acceptor.

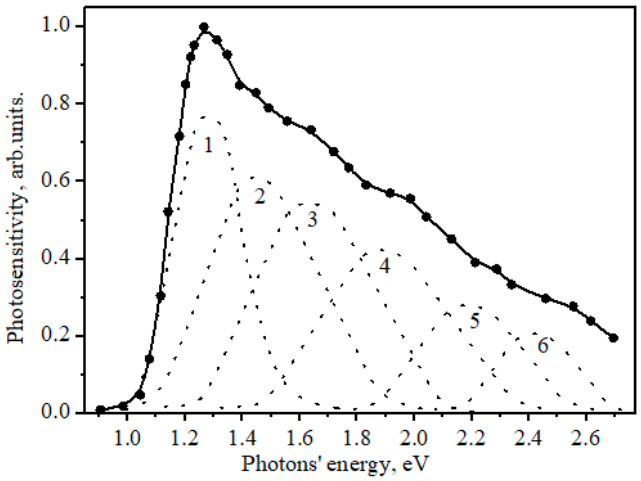

Figure 2. Photosensitivity spectrum of n-Si–p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures in Gaussian approximation; - experimental points – solid line – general Gaussian approximation line; continuous (dotted) lines – general Gaussian approximation line organizers

The maximum of the second Gaussian component (Figure 5.4.2, dashed line 2) was observed at a photon energy of 1.53 eV. This corresponds to the known photoluminescence range of p-GaAs crystals, typically within 1.35–1.65 eV, and confirms their spectral contribution to the heterostructure's response [12]

The third Gaussian component showed its peak sensitivity at 1.64 eV (Figure 2, dashed line 3), which can be attributed to the formation of isovalent Ge–Se valence-band-related impurity states in the GaAs layers. The study [13] reported three distinct photoresponse peaks in GeSe-doped GaAs layers at 1.43, 1.63, and 2.25 eV, all of which were also observed in the current study. Among these, the first peak in our sample shifted toward longer wavelengths, while the second peak matched the third Gaussian component at 1.64 eV.

Two additional Gaussian components were identified in the photosensitivity spectrum of the n-Si-p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructure within the 1.34–3.71 eV photon energy range, showing maximum

photoresponse at 1.91 eV and 2.21 eV (Figure 2, dashed lines 4 and 5). According to [14] the photoluminescence spectrum of $(GaAs)_{1-x}(ZnSe)_x$ solid solutions grown by liquid-phase epitaxy spans almost the entire visible spectrum (400–760 nm). Moreover, [15] identified deep energy levels associated with GaSe ($h\nu_{max}$ = 1.88 eV), ZnAs ($h\nu_{max}$ = 2.15 eV), and ZnSe ($h\nu_{max}$ = 2.69 eV). In the present study, three photoresponse peaks were detected at 1.91 eV and 2.21 eV, suggesting that atomic-scale modifications of GaSe and ZnAs within the crystal lattice may be responsible for the observed spectral shifts toward shorter wavelengths.

Furthermore, a sixth Gaussian peak was observed at 2.45 eV. Although the bandgap energy of pure ZnSe is $E_{g,ZnSe}$ = 2.70 eV, in these solid solutions, covalent bonds within ZnSe molecules are weakened due to interaction with Ge_2 and $GaAs_{1-\delta}Bi_\delta$ components. This interpretation is consistent with findings by Zainabidinov et al. [16], who reported that in such solid solutions, tetrahedral ZnSe crystal structures undergo partial substitution with GaAs or Ge_2, thereby weakening Zn–Se bonds due to interactions with Ga, As, and Ge atoms. Additional support comes from Saidov et al. [17], who observed that continuous substitution in $(GaAs)_{1-x}(ZnSe)_x(Ge_2)_y$ leads to the emergence of impurity states below the valence band edge ($\Delta E_i = E_{ph} - Eg_{,t\cdot r}$) of ZnSe. Given ZnSe's direct bandgap nature and its molar concentration in the present material (~10^{20} cm^{-3}), these structures exhibit photosensitivity at photon energies above 2.4 eV.

CONCLUSIONS

The n-Si–p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ heterostructures showed results of spectral photosensitivity analyses which suggest that the $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ solid solutions have selective photosensitivity because of integrated ZnSe and Ge constituents and the ionic bond covalent energies' differences in their ionization. The energy band diagram reveals the presence of impurity-related states that indicate the existence of nano-objects based on on $GaAs_{1-\delta}Bi_\delta$ compounds within the films. In conclusion, these results prove that the obtained solid solutions are likely barrier-layer structures and can also be utilized as selective photoactive materials for hyper/MW and visible optoelectronic devices in the infrared radiation spectrum.

Conflict of Interests

The authors declare that they have no conflict of interests.

Funding

The present research work was financed under the project FZ-292154210 granted by the Ministry of Innovative Development of the Republic of Uzbekistan.

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ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ГЕТЕРОСТРУКТУР *n*-Si–*p*-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$

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У цій статті досліджуються фотоелектричні властивості твердих розчинів $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$, вирощених на кремнієвих підкладках. Встановлено, що тверді розчини $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ мають селективну фоточутливість завдяки наявності компонентів ZnSe, Ge_2 та $GaAs_{1-\delta}Bi_\delta$, а також різниці в енергії іонізації їх ковалентних зв'язків. Механізми фотопровідності в гетероструктурах n-Si-p-$(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ були проаналізовані на основі значень Ei, які забезпечили найкраще наближення до експериментального спектру та кривих гауссового наближення. Фотопіки, що відповідають гауссовим кривим на рівнях енергії 1,23 еВ, 1,45 еВ, 1,64 еВ, 1,91 еВ, 2,21 еВ та 2,45 еВ, спостерігалися в діапазоні енергій фотонів: $E_{ph,1}$ - 0,98÷1,75 еВ, $E_{ph,2}$ - 1,01÷2,03 еВ, $E_{ph,3}$ - 1,15÷2,28 еВ, $E_{ph,4}$ - 1,34÷2,52 еВ, $E_{ph,5}$ - 1,75÷2,71 еВ та $E_{ph,6}$ - 2,1÷2,77 еВ. Спостереження проміжних станів у спектрі фоточутливості цього твердого розчину підтвердило наявність нанооб'єктів, сформованих на основі молекул ZnSe та Ge_2, а також сполук $GaAs_{1-\delta}Bi_\delta$ у цих плівках. Було виявлено, що тверді розчини $(Ge_2)_{1-x-y}(ZnSe)_x(GaAs_{1-\delta}Bi_\delta)_y$ мають потенціал для використання як селективні фотоактивні матеріали, що працюють у діапазонах інфрачервоного та видимого випромінювання.

Ключові слова: *кремній; твердий розчин; сполука $GaAs_{1-\delta}Bi_\delta$; ковалентний зв'язок; фоточутливість*