Photoelectric properties of nGa$_2$O$_3$-pGaSe-pInSe cascade heterostructures

V.P. Savchyn, J.M. Stakhira, Ya.M. Fiyala, V.B. Furtak
Ivan Franko National University of Lviv, 50 Dragomanov Str., 79005 Lviv, Ukraine,
e-mail: savchyn@wups.lviv.ua

Abstract. Cascade heterostructure of nGa$_2$O$_3$-pGaSe-pInSe was created, and a corresponding band energy diagram was built. Electrical and photoelectric properties of this structure were investigated. Due to isotype pGaSe-pInSe heterojunction the photosensitivity spectrum of nGa$_2$O$_3$-pGaSe-pInSe heterostructure extends up to 1.2 eV in IR range as referred to the photosensitivity spectrum of anisotype nGa$_2$O$_3$-pGaSe heterojunction.

Keywords: heterostructure, heterojunction, photosensitivity, indium selenide, gallium selenide, gallium oxide.

1. Introduction

As it has been shown [1-3], two materials GaSe and Ga$_2$O$_3$ are suitable for creating of nGa$_2$O$_3$-pGaSe heterostructure (HS). The photosensitivity of such HS covers all visible spectral range (the long-wave edge of spectrum response is limited by the GaSe forbidden gap E_g = 2 eV) and part of UV-range (up to 5.5 eV). Moreover, the spectral response of photosensitivity is defined by the heterojunction (HJ) quality, which depends on the technology conditions of the oxide layer formation. In the case, if the thickness of the oxide layer is comparable with the thickness of the space-charge region, the UV-sensitivity of HJ is not limited by the absorption edge of the oxide layer but is extended to the higher energies than forbidden gap of Ga$_2$O$_3$ [1].

Our purpose was to extend the photosensitivity of nGa$_2$O$_3$-pGaSe to a longer wave range. For that the nGa$_2$O$_3$-pGaSe-pInSe cascade heterostructure (CHS), in which anisotype nGa$_2$O$_3$-pGaSe HJ was modified by an addition of the isotype pInSe-pGaSe one, was created. It is necessary to note, that properties of an isotype pInSe-pGaSe HJ require careful study, because widely were only studied the electrical and photoelectric properties of the anisotype nInSe-pGaSe HJ [4-8]. In particular, it was shown that the effective separation of photo-generated charge curriers in a depletion layer due to an energy band diagram of such HJ took place.

2. Experimental procedures

The preparation of nGa$_2$O$_3$-pGaSe-pInSe CHS was carried out using both thermal oxidation of GaSe and optical contact method. The InSe and GaSe substrates with optically specula surfaces were cleaved from single crystals grown by the Bridgman method. The carrier concentration of undoped pGaSe single crystals at room temperature was p = 2·10^{14} cm^{-3} and pInSe single crystals (p = 1·10^{14} cm^{-3}) were doped by Cd. The GaSe substrates are oxidized at 700°C during 0.25 h. As it was shown in [1], under such treatment the nGa$_2$O$_3$ layer with electron concentration n ≈ 10^{14} cm^{-3} at room temperature was created and the anisotype pGaSe-nGa$_2$O$_3$ HJ was formed. The plate of about 10 μm in thickness was cleaved from an oxidized GaSe sample. Such thickness does not exceed the diffusion length L_{diff} of photo-generated carriers in pGaSe, which according to [9] is equal 14-18 μm. The thickness of pInSe substrates was about 200 μm. For optical contact formation the non-oxidized side of GaSe plate was pressed to the pInSe substrate. The contacts with 2 mm^2 areas were formed by sputtering of semitransparent Ni-film on the oxidized side of GaSe and In-film on the InSe side of CHS.

The spectral response of the photosensitivity and current-voltage (I-U) characteristics of CHS were measured at room temperature.

3. Calculation of energy band diagram

The energy band diagram of CHS was calculated without taking into account interface states and using only the following parameters of main components: pure GaSe $- m_p = 0.57m_0$ [10], $\varepsilon = 6.5$ [11], $\chi = 3.4$ eV [12]; InSe(Cd) $- m_p = 0.73m_0$ [13], $\varepsilon = 8.6$ [11], $\chi = 4.6$ eV [14]. The Ga₂O₃ layer formed by thermally oxidized GaSe - $m_n = 0.55m_0$ [15], $\varepsilon = 10.2$ [16]. The value $\chi = 3.9$ eV for the Ga₂O₃ is calculated using the value of the bend band for HJ created by the optical contact method [3].

The analyses of the energy band diagram of CHS shows that under n(Ga₂O₃) ≤ p(GaSe) ≈ p(InSe) condition the band bends supplement each other. It means that the photo-EMFs in both HJs are added up, when the oxide side of CHS is illuminated by the white light.

As shown in [1], the magnitudes of band bending and the widths of depletion regions for anisotype nGa₂O₃-pGaSe HJ depend on the conditions of GaSe-substrate thermal oxidation. The band bending magnitude is approximated as $V_D^{(1)} = 0.5 - 0.8$ eV and the widths of the depletion region in both HJ parts $w_3 \approx w_4$ may be equal to 0.35-0.45 μm. As known, the interface layer of such HJ consists of a composed composition of a few phases (Ga₂O₃-Ga₂Se₃-GaSe) [17-20]. Due to this fact the nGa₂O₃-pGaSe HJ part of the investigated CHS is a smooth junction [1] (as shown in Fig. 1).

The band bending values and the widths of the depletion region for isotype pInSe-pGaSe HJ were calculated using the relative concentrations of major carriers. The magnitudes of these qualities are equal to 0.13 eV and 0.67 μm for GaSe and 0.27 eV and 0.96 μm for InSe accordingly. The energy discontinuities of conduction DE$_c$ and valence DE$_v$ bands for an abrupt isotype HJ are equal to 1.2 eV and 0.4 eV correspondingly.
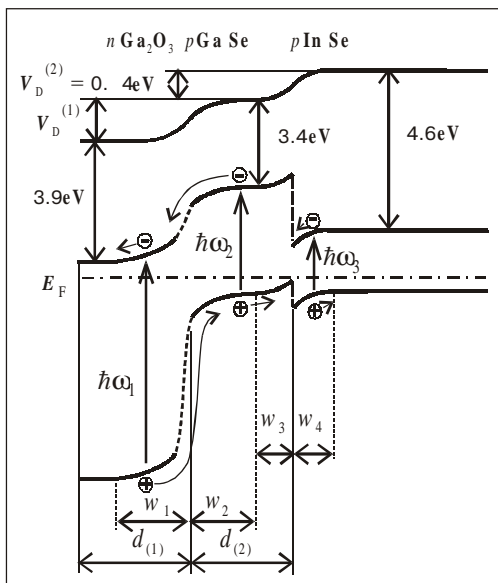

Fig. 1. Energy band diagram of the nGa₂O₃-pGaSe-pInSe CHS.
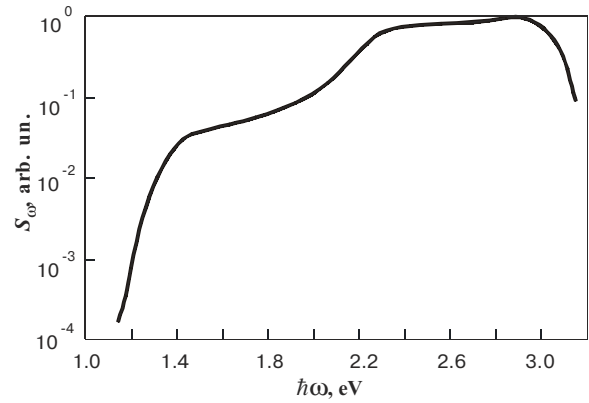

Fig. 2. Photoresponse spectrum of the nGa₂O₃-pGaSe-pInSe CHS.

4. Results and discussion

The photosensitivity spectra of our CHS were measured under illumination within a linear range of the photo-EMF dependence on the illumination intensity. The photosensitivity achieves 10^4 V/W. The positive potential on the InSe side appears under illumination of oxide side of CHS. The photosensitivity spectrum of CHS is calibrated to a constant photon flux and is represented in Fig. 2.

As expected, a photosensitivity spectrum of our CHS at $\hbar\omega > 2$ eV consists of spectrum that is typical to nGa₂O₃-pGaSe HJ prepared by thermal oxidation [1]. This spectrum is extended up to 1.2 eV because a photosensitivity of the isotype pGaSe-pInSe HJ is added. Particularly, a photosensitivity spectrum of CHS in a visible region corresponds to photosensitivity of GaSe.

As shown earlier [17-20], HJ formed by thermal oxidation of GaSe single crystals is accompanied by inevitable arise of additional Ga₂Se₃ phase on its interface as a result of Se diffusion and Se interaction with GaSe. The CHS photosensitivity at $\hbar\omega > 3$ eV declines sharply due to the light absorption in a relatively wide interface layer of Ga₂O₃-GaSe HJ enriched by Ga₂Se₃ phase. In this interface layer, an intensive recombination of photo-generated carriers prevents their separation by the depletion layer [1]. Only at the 5 eV neighbourhood the UV-band of a photosensitivity is observed (it is not shown in Fig.2). It is caused by photo-generation of charge carriers in the depletion region of the oxide film [1].

The kinetic of a photoresponse was investigated in a short-circuit current state under GaAs-LED pulse irradiation ($\lambda = 0.91$ μm). The determined time of a photocurrent relaxation is approximately 3 ms.

According to the proposed energy band diagram of CHS charge pairs generated in the InSe can be also separated via the recombination between the photoelectrons gathered in a "peak" of a conduction band of InSe and the holes from a valence band of GaSe involving intermediate states in the interface. This is confirmed by the dependence of the photosensitivity at $\lambda = 0.91$ μm on an additional illumination of the structure (Fig. 3). In other words, an additional illumination with a wavelength corresponding to GaSe absorption region causes significant increase of
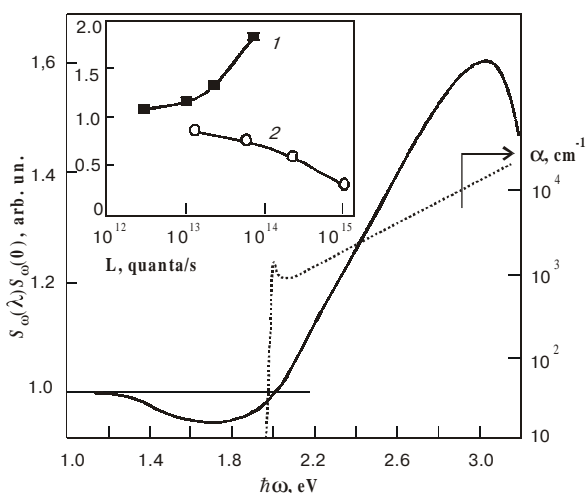
Fig. 3. Relative photoresponse of the nGa$_2$O$_3$-pGaSe-pInSe CHS at 0.91 mm versus a wavelength of an additional continues illumination (S_w(l) and S_w(0) - photoresponses at an additional illumination and without it correspoundly) and absorption spectrum of GaSe single crystal [21]. Insert: relative photoresponse of CHS at 0.91 μm versus intensity of an additional continues illumination at λ = 0.5 (1) and 0.8 μm (2).

the photosensitivity. This increase in the spectrum range from 2.2 to 3.3 eV, where the photosensitivity does not change essentially (Fig. 2), correlates with GaSe absorption spectrum α($\hbar\omega$) [21] (Fig.3). Such behavior of the photosensitivity at λ = 0.91 μm under an additional illumination can be interpreted as follows. At $\hbar\omega$ > 2 eV, where αd > 1, almost all light quanta are absorbed in the GaSe layer. I. e., we can regard that $\alpha L/S$ light quanta are absorbed in a unity time in a unity volume, where L is an amount of light quanta fallen onto the area of CHS in a unity time, S is an area of the irradiated surface. The concentration of photo-generated holes can be determined as $\delta p = v\alpha L\tau/S$ (v - quantum yield, τ - lifetime of photo-generated carriers). Because $d_{(2)} = L_{diff}$, most of the pairs generated in the GaSe layer are separated by the junction field, and therefore the photo-generated holes are accumulated in the "peak" of GaSe valence band near InSe-GaSe interface. Under intensive additional illumination of CHS, for example at $L \approx 10^{14}$ quanta/s (taking into account v~1 and α ~ 3 msec) the concentration of the photo-generated holes in the "peak" of the GaSe valence band is comparable with the concentration of equilibrium holes in GaSe. Consequently the recombination rate of the photoelectrons that gather in the "peak" of InSe conduction band, increases, and thus the charge separation is improved finally.

In contrast, the additional illumination with a wavelength, corresponding to InSe absorption region, leads to decrease of CHS photosensitivity at λ = 0.91 μm (Fig. 3). It is because the photoelectrons additionally are accumulated in a "peak" of the conduction band of InSe and therefore the recombination of those electrons generated by λ = 0.91 μm pulse irradiation becomes more difficult.

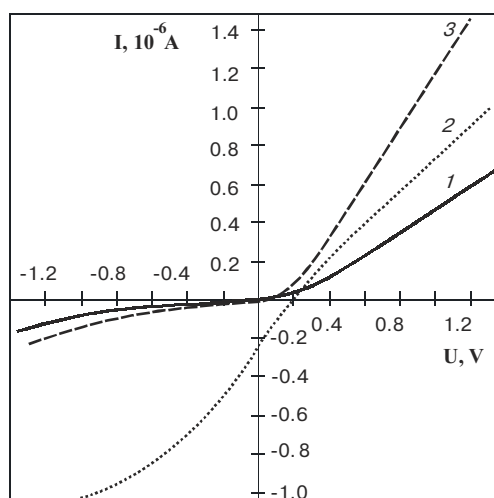**Fig. 4.** I-U characteristics of nGa$_2$O$_3$-pGaSe-pInSe CHS: 1 – in dark; 2 and 3 – under illumination at λ = 0.5 μm (10^{13} quantum/sec) and λ = 0.8 μm ($L = 10^{14}$ quantum/sec) accordingly.

The current-voltage (I-U) characteristics of CHS are shown in Fig. 4. The polarity of voltage corresponds to the polarity mark on InSe-side of CHS. Evidently, the dark I-U characteristic of CHS illustrates a rectifying property. The differential dark resistance of CHS approaches to the resistance of InSe substrate as a forward bias voltage is increased. The appreciable increase of forward current under illumination at λ = 0.8 μm (Fig. 4, curve 3) can be related to a photoconductive effect in InSe substrate. The pinch-off voltage of forward I-U characteristic is about 0.25 V and well corresponds to a band bending in InSe part of pGaSe-pInSe HJ. Because this band bending is a potential barrier for the holes (Fig.1), the holes are current carriers through the isotype junction. On the other hand, a forward current through the anisotype nGa$_2$O$_3$-pGaSe HJ occurs due to the interface recombination [1]. When illuminating light is absorbed mainly in this HJ, a significant increase of the reverse current is observed (Fig. 4, curve 2). It means that the reverse branch of I-U characteristic of the investigated CHS is formed due to the processes in nGa$_2$O$_3$-pGaSe HJ and, as it is shown in [1], the main mechanism of reverse current flowing is the heat generation in the depletion region.

5. Conclusions

Thus, the obtained results show the possibility of the practical use of nGa$_2$O$_3$-pGaSe-pInSe CHS due to the wide spectral range of photosensitivity (from 1.2 to 5.0 eV). It should be noted that nGa$_2$O$_3$-pGaSe-pInSe structure can be formed using, for example, the Van-der-Waals epitaxy method that as is well known [22, 23], provides high quality and stoichiometry of the epitaxial films of InSe (GaSe) in spite of high lattice mismatch.

References

1. V. Vasyltsiv, V. Kytsai, V. Savchyn, Ya. Fiyala. Electric and photoelectric properties of heterostructures based on gallium monoselenide // *Ukr. Phys. J.* **44**(11). pp1380-1386 (1999).
2. V. P. Savchyn, V. B. Kytsai. Photoelectric properties of heterostructures based on thermo-oxidated GaSe and InSe crystals // *Thin solid films* **361-362** pp.123-125 (2000).
3. J. Stakhira, V.Savchyn, V. Kytsay. Electric and photoelectric properties of GaSe-Ga₂O₃ heterostructures // *Molecular Physics Reports* **23** pp.184-186 (1999).
4. V. L. Bakumenko, Z. D. Kovalyuk, L. I. Kurbatov, V. G. Tagaev, V. F. Chishko. Investigation of InSe-GaSe heterojunctions prepared by optical contact // *Physics and Technics of Semiconductors.* **14**(6). pp.1115-1119 (1980).
5. T. V. Averyanova, V. L. Bakumenko, L. I. Kurbatov, V. F. Chishko. Investigation of InSe-GaSe heterojunctions prepared by optical contact // *Physics and Technics of Semiconductors.* **14**(8). pp.1573-1576 (1980).
6. V. L. Bakumenko, L. I. Kurbatov, V. G. Tagaev. Investigation of InSe-GaSe heterojunctions prepared by optical contact // *Physics and Technics of Semiconductors* **16**(7). pp.1145-1148 (1982).
7. A. G. Kjazym-zade, R. N. Mekhtieva, A. A. Akhmedov. Sandvich-photoresistors based on InSe-GaSe heterojunctions // *Physics and Technics of Semiconductors.* **25**(8). pp.1393-1396 (1991).
8. V. N. Katerinchuk, Z. D. Kovalyuk, V. M. Kaminskii. P-GaSe-n-recrystallized InSe heterojunctions // *Letters in J. Techn. Phys.* **26**(2) pp.19-22 (2000).
9. V. Capozzi, M. Di Giulio, S. Galassini, C. Manfredotti. Lifetime and diffusion length of electrons in p-GaSe by photovoltaic effect measurements at room temperature // *Physica* **BC105**(1-3) pp.50-53 (1981).
10. C. Manfredotti, R. Murri, A. Rizzo, S. Galassini, L. Ruggiero. Deep hole in p-type GaSe single crystals // *Phys. Rev.* **B10**(8) pp.3387-3393 (1974).
11. V. V. Sobolev. Bands and Excitons of Gallium, Indium and Thallium Selenides. Shtiintsa. Kishinev 1982.
12. A. G. Kjazym-zade, D. Kh. Drzafarov, V. V. Tagirov. N-Si-p-GaSe heterojunctions // *Physics and Technics of Semiconductors* **13**(11) pp.2237-2239 (1979).
13. Ch. Ferrer-Roca, A.Segura, M.V. Andres, J. Pellicer, V. Munoz. Investigation of nitrogen-related acceptor centers in indium selenide by means of photoluminescence: Determination of the hole effective mass // *Phys. Rev.* **B55** (11) pp.6981-6987 (1997).
14. V. L. Bakumenko, Z. D. Kovalyuk, V. G. Tagaev, V. F. Chishko, V. P. Fedorov. Same characteristics of heterojunctions between InSe and narrow -band InSb, PbTe, Pb₀.₈₂Sn₀.₁₈Te and Cd₀.₂Hg₀.₈Te semiconductors // *Physics and Technics of Semiconductors* **16**(7) pp.1149-1151 (1982).
15. N. Ueda, H. Hosono, R. Waseda, H. Kawazoe. Synthesis and control of conductivity of ultraviolet transmitting b-Ga₂O₃ single crystals // *Appl. Phys. Lett.* **70**(26). pp.3561-3563 (1997).
16. B. Hoeneisen, C.A. Meed, M.A. Nicolet. // *Solid State Electronics* **14**(10) pp.1057-1059 (1971).
17. V. Savchyn, J. Stakhira. Cathodoluminescence studies of thermally oxidized cleaved surfaces of gallium selenide layered crystals // *Physica Status Solidi* **A156** pp.113-118 (1996).
18. N. N. Berchenko, O. A. Balitskii, R. V. Lutsiv, V. P. Savchyn, V. I. Vasyltsiv. Characteristics of phase formation during GaSe oxidation // *Materials Chemistry and Physics* **51** pp.125-129 (1997).
19. O. A. Balitskii, N. N. Berchenko, V. P. Savchyn. Partial pressure diagrams of the In-Se-O and Ga-Se-O systems // *J. Physical Studies* **4**(4) pp.431-436(2000).
20. O. A. Balitskii, V. P. Savchyn, J. M. Stakhira, V. O. Yuchymchuk. Raman study of gallium selenide single crystal oxidation // *Ukrainian Journal of Physical Optics* **2**(2) pp.81-83 (2001).
21. R. Toullec, N. Piccioli, M. Mejatty, M. Balkanski. Optical constants of GaSe // *Nuovo Cimento* **38B**(2) pp.159-167 (1977).
22. K. Saiki, K. Ueno, T. Shimada, A. Koma. Application of Van der Waals epitaxy to highly heterogeneous systems // *J. Cryst. Growth* **95**(1-4) pp.183 (1989).
23. S. Ercoc, K. Allahverdi, Z. Ibrahim. Electronic staste of InSe/GaSe superlattice // *Sol. St. Commun.* **90**(9) pp.553-556 (1994).