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InGaAsP/InP photovoltaic converters for narrowband radiation

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Utilizing performed research, photoelectric converters of narrow-band radiation ($\lambda \approx 1.0-1.3\,\mu$m) based on InGaAsP/InP heterostructures with an epitaxial $p-n$ junction have been developed and created. Technological regimes that apply of for creating high-quality layers of quaternary InGaAsP solid solutions isoperiodic to indium phosphide in a wide range of compositions by liquid-phase epitaxy have been determined.

Keywords: photovoltaic converters, narrowband radiation, InGaAsP, InP, LPE, heterostructures.

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1. Introduction

The main interest in direct-gap quaternary InGaAsP solid solutions is explained by their promising nature for creating receivers and sources of radiation in optical paths [1–3]. These compound have the following advantages: high crystal quality providing almost 100quantum output of the photoconductive response, producibility of effective heterostructures based on these materials using high-productive and relatively simple methods of liquid-phase epitaxy and diffusion out of the gas phase. At the same time, based on the InGaAsP/InP heterostructures, the photovoltaic converters (PVC) can be fabricated for a narrow-band radiation within the spectral range from 0.80 to 1.75 μm. The most interesting wavelengths of the said spectrum range are:

– $\lambda \approx 1.06\,\mu$m, first of all, due to small divergence of the beam and presence within the „large window" of the atmosphere transparency ($0.3-1.3\,\mu$m);

– $\lambda \approx 1.3\,\mu$m or $1.55\,\mu$m, which correspond to the second and third windows of transparency in the optic fiber, where the losses are minimum and equal to 0.4 and 0.2 dB/km.

According to the theoretical estimates, the efficiency of photovoltaic transformation of monochromatic radiation [4] for the „ideal" PVC is up to $\sim 85\%$. The theoretical estimates of the paper [5], for „ideal" photoconverter based on the GaInAs/InP show that the maximum calculated efficiency of this element (when there are not losses on the resistance of the contact reticle and the front layer) exceeded 65%, while practically achievable efficiency is $\sim 55\%$ (at the wavelength of falling laser radiation $\lambda \approx 1.06\,\mu$m).

The present paper is devoted to developing and investigating the InGaAsP/InP heterostructures (the band gap $E_g \approx 1.0-1.15$ eV) and the photovoltaic photoconverters based thereon, which are designed for transforming the narrow-band radiation.

2. Technology description

The studied InGaAsP/InP epitaxial heterostructures were grown by the liquid-phase epitaxy in the hydrogen atmosphere in the slider-type graphite cassette out of the indium melt of purity 5N. The substrate was represented by indium phosphide plates of the *n*-type conductivity with the crystal-lattice orientation of a working surface (100). The melt components were sourced from non-alloyed semiconductor materials InP, InAs and GaAs. The solution melt was pre-homogenized without phosphorous for 1 hour at the temperature of 680°C. Then, a prepared substrate was loaded into the cassette and a phosphorous was added to the melt. The temperature of growth of the quaternary InGaAsP solid solutions varied within the range from 600 to 650°C. An excessive phosphorous vapor pressure was created under the substrate in order to prevent erosion of the indium phosphide surface due to phosphorous evaporation in the epitaxial process. For this, the cassette had been provided with an additional cell with the melt of tin and indium phosphide, which does not contact directly with the substrate during epitaxy, but allows the phosphorous vapor approach its surface.

3. Investigation results

The liquid-phase epitaxy allows etching the surface layer of the substrate just before the epitaxial growth process, thereby excluding contact of an unprotected surface of the substrate with oxygen between the substrate processing and the growth process. The influence of the various methods of pre-epitaxial processing on the quality of the surface layer of the substrate was investigated by undertaking a number of processes using various unsaturated melts-etchants in the conditions, which most closely resemble the conditions of the PVC structure growth. It was compared using the data obtained by the photoluminescence method (Fig. 1). Using for the etchant an unsaturated tin melt (Sn) allows substantially improving the surface quality (increasing the

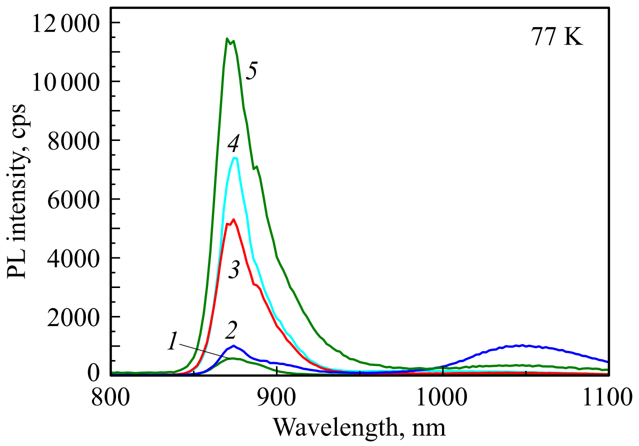

Figure 1. Photoluminescence spectra (PL) of the indium phosphide substrates (InP) without processing (*1*) and with various pre-epitaxial processing: *2* — annealing without etching; *3, 4* — etching with the unsaturated tin melt; *5* — etching with the saturated tin melt.

photoluminescence intensity of the InP substrate by an order when applying etching by the tin melt). Furthermore, tin is a donor impurity and can not affect the conductivity type of the *n*-InP next layer. However, the etching rate in the fully unsaturated tin melt is quite high, the post-treatment surface is somewhat wavy, the etching traces are visible. In order to achieve a planar surface, indium phosphide was added to the etching tin melt to the saturation level $\sim 90\%$. This measure allowed significantly reducing the etching rate and obtaining the mirror surface of the substrate before the epitaxy.

One of the most important characteristics of any heterojunction is compliance of lattice parameters of contacting layers. Despite that the liquid phase composition for the quaternary InGaAsP solid solution is usually calculated based on isoperiodicity to the InP substrate, these calculations are approximate, and the growth parameters are refined experimentally, wherein a degree of crystal quality of the produced samples is evaluated by results of investigation of photoluminescence (PL) and X-ray diffractometry.

The Fig. 2 shows a typical diffraction swinging curve for the photovoltaic structure with the $p-n$-transition, as produced by the liquid-phase epitaxy method, where *2* — is the *p*-InGaAsP layer, alloyed with magnesium (Mn) or zinc (Zn), *3* — the „thick" *n*-InGaAsP basic layer, which is isoperiodic to the InP substrate (the central peak). As it is clear, the obtained values of misalignments between the epitaxial layer and the substrate in the InGaAsP/InP heterostructures, which are measured by the X-ray diffractometry, are $\Delta a/a \leq \pm 0.15\%$, which indicates the satisfactorily compliance of the layers in PVC.

The investigation of the epitaxial interface in the grown heterostructures and control of the layer thickness were carried out by a method of coloring chipped faces in the KOH solution: $K_3Fe(CN)_6 : H_2O$ [6]. Fig. 3 shows a typical image of the colored chipped face, which is obtained in the optical microscope to clearly demonstrate a transition defect layer of the thickness of $\leq 0.5\,\mu$m. Thus, later the thickness of the *n*-InGaAsP basic level in PVC was at least $4\,\mu$m. This allowed producing quite „thick" dislocation-free layers, which should positively affect the operation efficiency of the photovoltaic structures.

A number of test photovoltaic samples was produced based on the InGaAsP/InP heterostructures by the liquid-phase epitaxy method. The thickness of the *n*-InGaAsP : Sn basic layer varied from 4 to $14\,\mu$m, the electron concentration (the measurements were carried out by the Hall method) was $(3-6) \cdot 10^{17}\,\text{cm}^{-3}$. Acceptors for the *p*-layer were represented by magnesium (Mn) and zinc (Zn). The

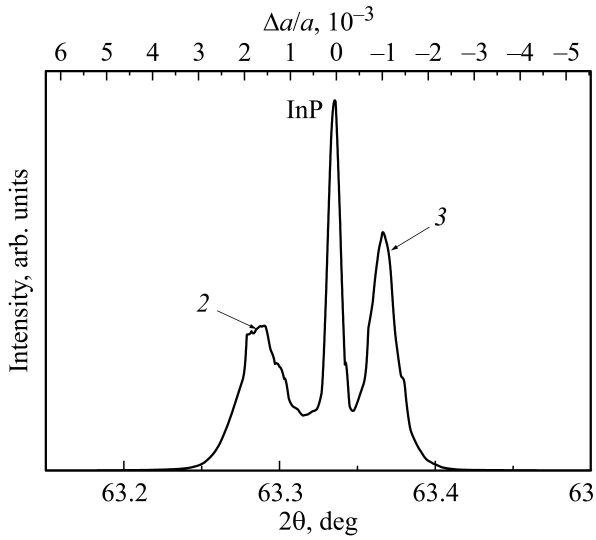

Figure 2. X-ray diffraction swinging curve for the $p-n$-InGaAsP/n-InP structure. *2* — the *p*-InGaAsP layer alloyed with magnesium (Mn) or zinc (Zn); *3* — the „thick" *n*-InGaAsP basic layer; the central peak — the InP substrate.

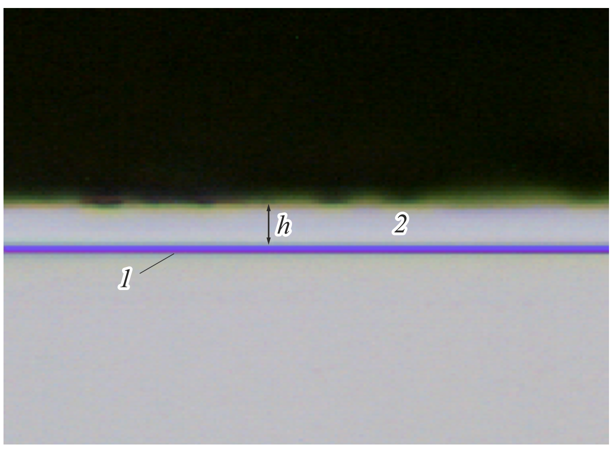

Figure 3. Picture of the chipped face of the InGaAsP/InP heterostructure: *1* — the defect layer on the heterointerface; *2* — the InGaAsP layer of the thickness of $h \approx 4\,\mu$m.

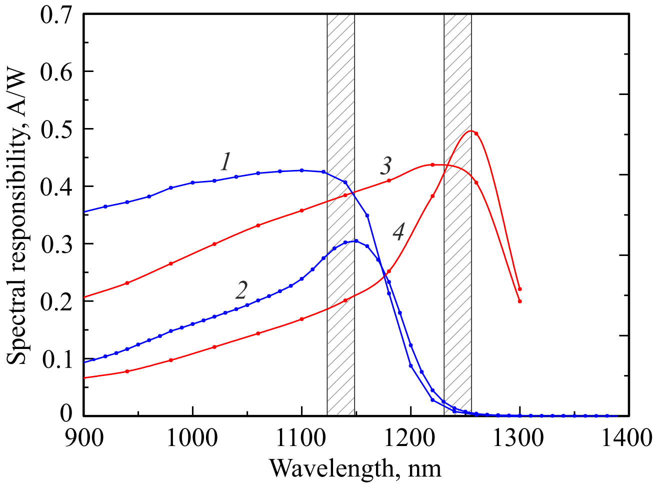

Figure 4. Spectral sensitivity of the photovoltaic converters based on the $p-n$-InGaAsP/n-InP heterostructures, wherein magnesium (*1, 3*) or zinc (*2, 4*) was used an acceptor impurity.

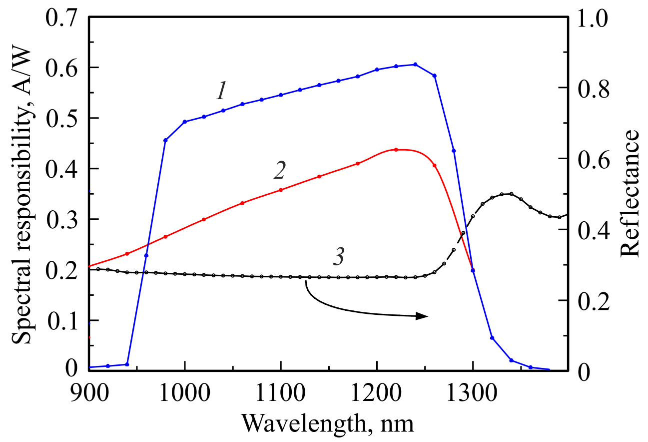

Figure 5. Spectral sensitivity (*1, 2*) and surface reflection (*3*) of the photovoltaic samples based on the p-InGaAsP : Mg/n-InGaAsP : Sn/n-InP heterostructure without the anti-reflecting coating.

thickness of the p-InGaAsP emission layer varied within the range from 0.5 to $3\,\mu$m, its hole concentration was $\geq 10^{19}\,\text{cm}^{-3}$. Fig. 4 shows a number of the spectral characteristics of the test structures with the $p-n$-transition without an anti-reflecting coating.

The PVC spectral characteristics were investigated to show that using of zinc (Zn) as an acceptor for creating the epitaxial $p-n$-transition results in significant reduction of the sensitivity in the short-wave part of the spectrum (Fig. 4). No such effect was observed in the similar samples based on the p-InGaAsP : Mg/n-InGaAsP : Sn/InP heterostructure. At the same time, the maximum of the spectral sensitivity for the samples with zinc (Zn) in relation to the samples with magnesium (Mg) was shifted by 30 nm to the long-wave region at the same band gap of the InGaAsP quaternary compound.

The paper [7] includes results of modeling of the spectral characteristics of the photosensitive structures based on the $p-n$-transitions at various rates of surface recombination. These results show that with increase in the absorption coefficient to $100\,\text{cm}^{-1}$ the quantum output is quickly increasing and this increase is almost unaffected by the change of the changing rate of surface recombination. At the same time, with increase in the absorption coefficient to the values $\alpha = 105\,\text{cm}^{-1}$, the increase in the rate of surface recombination results in reduction of the quantum output by two orders, wherein the sensitivity in the maximum of the spectral characteristic decreases by at most 20%.

Thus, it can be assumed that when using zinc as the alloying impurity the epitaxial $p-n$- InGaAsP/InP structures have significant increase in the rate of surface recombination due to evaporation of phosphorous atoms at the epitaxial temperature (similar to a mechanism of diffusion of Zn to InP) and formation of neutral complexes including the zinc atoms and phosphorous vacancies [8]. At the same time, it is not exhibited in the photovoltaic converters with magnesium as the alloying impurity. It is probably due to significantly less magnesium pressure in comparison with zinc at the epitaxial temperatures.

Fig. 5 shows the investigations of the photovoltaic samples base on the p-InGaAsP : Mg/n-InGaAsP : Sn/n-InP structure with the wide-band window and without it. The inverse structure (the InP is used as the wide-band window), the spectral sensitivity was 0.6 A/W without the anti-reflecting coating. At the same time, with no wide-band window (a direct structure) the spectral sensitivity was noticeably lower and was 0.44 A/W. With increase in the PVC photosensitivity, when applying the anti-reflecting coatings, the maximum spectral sensitivity should be > 0.8 A/W for the range of the wavelengths $\lambda = 1.1-1.25\,\mu$m. This value is comparable with limit values of the spectral sensitivity, which is 0.89−1.01 A/W for the wavelengths $\lambda = 1.1-1.25\,\mu$m.

4. Conclusion

Thus, the paper shows that using substrate etching with the unsaturated solution-melt just before the epitaxy process substantially improves the quality of the grown InGaAsP/InP-structures, while the liquid-phase epitaxy growing of quite „thick" quaternary InGaAsP ($> 5\,\mu$m) solid solutions as basic and buffer layers allows producing the photovoltaic converters, which provide for high spectral sensitivity (> 0.8 A/W) for monochromatic radiation with the wavelengths from 1.1 to $1.25\,\mu$m.

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Conflict of interest

The authors declare that they have no conflict of interest.

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