Photocathodes for near infrared range devices based on InP/InGaAs heterostructures

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Abstract. Results of indium phosphide structures research, showing the possibility of using in the near infrared range photocathodes of InP/InGaAs, are represented. An optimal method of obtaining the atomically clean indium phosphide surface was suggested. The spectral characteristics of InP/InGaAs heterostructure were given. The results of an experimental study of pin-diode, which was used as the receiver of photoelectrons, are presented.

1. Introduction

At present time photodetection devices widely use in various fields of science and technology (night-vision devices, control sensors, fiber optic systems, etc.) [1-4]. One of the most perspective way of development such photodetectors is creation of devices, which work in near infrared range (NIR). [5]. The main element for these devices could be photocathode based on heterostructures of InP/InGaAs. Photosensitive modules for NIR with photocathodes could be used for special purposes, where high processing speed of detection reflected radiation of special laser systems (for example quantum-dot lasers) from the object is needed [6].

The creation of the photocathode, which operates in the NIR, also known as the transferred electron (TE) photocathode, was proposed by Bell [7]. Such photocathodes can move the long-wavelength threshold of photoemission by increasing the internal energy of the photoelectrons (with the help of the metal electrode, which is applied to the effective surface of the photocathode). This structure has been realized on the basis of heteropair indium phosphide – solid solution of indium – gallium arsenide. The InGaAs forbidden band is narrow enough to detect near-infrared range. This narrow–band material (“absorber”) cannot provide by itself the negative electron affinity (NEA) on the surface, which is a determinant factor for obtaining a high quantum efficiency for such structures. However, InGaAs can be perfectly matched to the InP crystal lattice, which is a conductor (emitter) of electrons generated in the absorber, allows to get on its surface the effective state of the NEA.

Schottky barrier is needed for creation of the TE photocathode. It is a thin metallic layer activated by Cs and O which allows to apply a pulling field between two layers of the photocathode structure. This barrier is high enough to have a sufficiently low hole current in case of applying of the locking hole voltage. The bias voltage expands the pulling field to the boundary (absorber - emitter), carrying out the transfer of electrons through a heterojunction (fig. 1). Electrons from the conduction band of the emitter layer due to the pulling field can go over to the upper levels of the conduction band. Electrons from the upper valleys of the conduction band can emit into a vacuum.
Figure 1. Energy band diagram of transferred electron photocathode (a) without applying bias voltage (b) with applied bias voltage, where 1 – conduction band, 2 – Fermi level, 3 – valence band, 4 – substrate, 5 – absorber, 6 – electron emitter, 7 – metallic layer (Schottky barrier), 8 – photoemission direction, 9 – vacuum level.

Semiconductor photocathodes activated to negative electron affinity (NEA) serve as electron beam sources for many applications. InP photocathode is an emitter of InP/InGaAs heterostructure. These heterostructures as compared to other semiconductor materials allows getting greater quantum efficiency in case of detection reflective laser beam in near infrared range. The purposes of the work were to develop the optimal method of obtaining atomic clean photocathode surface, to obtain high quantum efficiency of the InP/InGaAs samples, to estimate the parameters of processing speed and amplification of pin-diode as the photoelectron receiver and to apply the result of the researches for obtaining real photodetector for special purposes, which works in near infrared range.

2. Purifying of InP surface

For effective InP/InGaAs photocathodes, it is necessary to achieve atomic clean surface of structure emitter – InP. The structures based on the indium phosphide are characterized by low thermal resistance and heating over with the temperature of 593 K lead to the degradation of these structures, so that the typical cleaning methods for metals and thermally stable materials cannot be used. Sulfur passivation leads to stable surface termination, but the chemisorbed sulfur atoms cannot be removed completely by thermal annealing at temperatures below the decomposition temperature of InP. Process of obtaining a clean InP surface is rather difficult, especially pre-vacuum chemical cleaning step. The treatment with HCl–C₃H₈O and subsequent vacuum annealing is useful method for obtaining the atomically clean GaAs surfaces, another semiconductor of the A₃B₅ group [8]. However, etching with these chemical compounds is ineffective for InP surfaces. Therefore, we used the efficient three-step method of chemical etching combined with a thermal cleaning in vacuum to obtain the atomic clean surface of InP [9, 10]. Etching time was increased, as compared to [9], and the mode was adjusted to increase in rate of the removing of a thick natural oxide layer by the use of ultrasound in the etching process. Besides that the intermediate etching step was added: a weak solution of sulfuric acid was used. Strong acid solutions with HCl or H₂SO₄, which are used in third step of chemical cleaning, are able to remove the surface oxide and leave the InP surface passivated with elemental P which is, in turn, terminated with H [9]. This yields a hydrophobic surface and allows lower temperatures to be used during annealing. All steps of chemical cleaning are shown in table 1:
Table 1. Optimized three-step method of chemical cleaning

|   | Solution            | Concentration |
|---|---------------------|---------------|
| 1 | H₂SO₄: H₂O₂: H₂O   | 4:1:100       |
| 2 | H₂SO₄: H₂O         | 1:10          |
| 3 | H₂SO₄: H₂O         | 1:1           |

Protective layer formed on InP surface are also allows to carry etched structures from chemical laboratory bench to vacuum installation in atmosphere. This is an important achievement in terms of surface oxidation and uncontrolled contamination of surfaces. We studied the effect of etching on the titanium grid and the possibility of etching agents use without degradation of the grid structure. As a result, we found that etching is equally effective for two different acid solutions HCl and H₂SO₄, however, in case of HCl titanium grid is exposed to chemical degradation. In view of the fact that indium phosphide is emitter of the InP/InGaAs heterostructures, accordingly chemical cleaning of this structures identical to the InP.

3. Activation of InP and InP/InGaAs structures

As a result of the etching process the hydrophobic surface of InP and InP/InGaAs structures was obtained [9]. The ultra-high vacuum installation was used to conduct the research in a vacuum, which could reach the level of 1×10⁻⁹ Pa [11]. After heating in a vacuum chamber at a temperature of about 573 K, the net emitter atomic surface was received, that is ready for the activation with Cs and O₂, which allows to form effective state of NEA on photocathode surface. The method of the activation structure called «yo-yo» [12], based on a continuous simultaneous supply of cesium and oxygen was used. The process for obtaining the maximum photoemission current was about 90 minutes.

Research was conducted on InP structures which etched by solutions of C₃H₈O+Br, C₃H₈O+HCl and our new three stage method of chemical cleaning with solutions of H₂SO₄. After graphical analysis, we found that the results of photoemission current using the new method of chemical cleaning increase 6 times as compared to previous experiments.

Measurements were carried out in range of 500 to 950 nm for InP samples. We managed to get quantum efficiency greater than 10% at a wavelength of 630 nm, and more than 1% for 900 nm on Zn-doped InP(111) structures with concentration p=1·10¹⁸ cm⁻³[13]. In [10] the QE at 632 nm was in the range 9-12% and spectral characteristics were not present. The photolithographic grid stamped on of InP, has demonstrated not only the overall photoemission gain increase, but also provided the greater sensitivity at longer wavelengths when a voltage was applied to the grid with the help of the pressure contact.

Results of the investigations of indium phosphide were applied on InP/InGaAS heterostructures, which were grown by MOCVD methods. Heteropair indium phosphide – solid solution of indium – gallium arsenide was realized on substrate InP with thickness 350 mkm. Etching and vacuum annealing were conducted identical to InP structures Spectral characteristics of the InP/InGaAs heterostructure with developed surface grid titanium electrode are shown in the figure 2. The electrode has a grid-lattice structure in form of parallel conductive titanium bands. It is manufactured by photolithographic methods and provides the uniform distribution of bias voltage on the operating surface of the photocathode structure. The thickness of the electrode is about 100 angstroms.

Analyzing obtained dependencies (fig. 2), we found that quantum efficiency of the proposed heterostructure, which operates in reflection mod, reaches 4% at the wavelengths from 900 to 1600 nm. Our studies showed that results of QE obtained on the investigated InP/InGaAs structures are enough to create reliable sensor with such types of photocathodes.
4. Receiver of photoelectrons

In device layout with InP/InGaAs heterostructure the silicon pin-diode was selected as the receiver of the photoelectrons and amplifying element. It is a vertical structure based on pure high-resistance silicon obtained by the zone melting method. To investigate the processing speed, pin-diode was irradiated with a laser light emitting diode with a wavelength of 650 nm and pulse duration of no more than 50 ps (pulse repetition rate 1 kHz). The results of the impulse response are shown in figure 3(a,b). As the supply voltage increased from 190 V to 280 V, the impulse response front decreased from 2.1 ns to 1.1 ns, and the impulse response duration decreased from 5.5 ns to 1.9 ns.

Figure 3. Impulse characteristic of the diode with supply voltage
(a) $U_d=190 V$; (b) $U_d=280 V$

Figure 4. Amplification factor (M) depending on the energy of the photoelectrons $U_p$ (the voltage between the photocathode and the pin-diode).
Amplification is achieved due to the occurrence in the solid-state element (diode structure) of a large number of charge carriers by the influence of high energy (several keV) electrons emitting from the photocathode. Dependence of the amplification factor (M) on the energy of photoelectrons (on the voltage between photocathode and pin-diode) are shown in figure. 4. M is determined by the ratio of output to input current of pin-diode. Value of amplification factor shows the possibility of achieving amplification several hundred times at an accelerating voltage up to 6 kV. It is mainly determined by the electric properties of silicon, it does not depend on the type of conductivity or resistance of the silicon wafer.

5. Conclusion

Photoelectron vacuum devices, where emitter and receiver of photoelectrons are consisted in one vacuum value, have a low level of internal noise as compared to devices with non-vacuum parts. Our results of processing speed and amplification factor, obtained on one pin-diode structure, show the possibility of creation photosensitive devices for near infrared range with line or matrix of pin-diodes. It would help to realize fast, high-sensitive multichannel scanning systems. In addition, amplification factor of photoelectron receiver could be increased up to $10^5$ with the help of avalanche photodiode. Preliminary experiments showed that obtained quantum efficiency on the InP/InGaAs samples is enough for reliable operation of real device because of internal amplification. Our studies showed that increase of QE could be achieved by optimizing thickness and the basic carrier concentration of heterostructure layers. As such parameters influence the minimum energy that is required for generation and emission of photoelectrons.

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