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EMISSION, OPTICAL AND ELECTRICAL PROPERTIES OF GaInP/GaP NANOFILMS

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Abstract. In order to search for materials with improved semiconductor properties, thin films of GaInP have been fabricated on the GaP surface (the molecular beam epitaxy and ion implantation procedures were used). These films were investigated by the Auger electron spectroscopy, ultraviolet photoelectron and light absorption ones. The energy and angle dependences of the secondary-electron-emission coefficient (SEEC) were obtained as well. An analysis of the experimental data allowed for the first time to determine the main energy-band and emission parameters of the $Ga_{0.6}In_{0.4}P/GaP(111)$ nanofilm. The energy-gap width was found to be 1.85 eV, which was significantly less than that of the substrate GaP, and thus, the maximum value σ_{max} of the SEEC and the quantum yield K of photoelectrons (at $h\nu = 10.8$ eV) values of the $Ga_{0.6}In_{0.4}P/GaP$ system decreased slightly relative to the pure GaP.

Keywords: band gap, photoabsorption, energy-band parameter, nanofilm, heterostructure

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ЭМИССИОННЫЕ, ОПТИЧЕСКИЕ И ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА НАНОПЛЕНОК GaInP/GaP

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Аннотация. С целью поиска материала с улучшенными полупроводниковыми свойствами были изготовлены тонкие пленки GaInP на поверхности GaP (использованы методы молекулярно-лучевой эпитаксии и ионной имплантации). Эти пленки были изучены методами оже-электронной спектроскопии, ультрафиолетовой фотоэлектронной спектроскопии, а также оптической спектроскопии поглощения света. Были также получены энергетические и угловые зависимости коэффициентов вторичной электронной эмиссии. Анализ полученных экспериментальных данных позволил впервые определить основные параметры энергетических зон и эмиссионные параметры нанопленки $Ga_{0,6}In_{0,4}P$/GaP (111). Установлено, что ширина запрещенной зоны пленки равна 1,85 эВ, что существенно меньше, чем таковая у подложки GaP; следовательно, максимальное значение коэффициента вторичной электронной эмиссии σ_{max} и квантовый выход фотоэлектронов K (при $h\nu$ = 10,8 эВ) системы $Ga_{0,6}In_{0,4}P$/GaP немного уменьшаются относительно чистого GaP.

Ключевые слова: ширина запрещенной зоны, фотопоглощение, зонно-энергетические параметры, нанопленка, гетероструктура

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Introduction

$A^{III}B^{V}$ binary semiconductors and multicomponent heterostructures based on them are widely used in the creation of various opto-, micro-, and nanoelectronic devices. In particular, multilayer structures with GaP, GaInP, AlGaInP layers are used and hold promise for the manufacture of laser diodes, solar cells, photovoltaic and optoelectronic devices. Particular interest is the preparation of ternary solid solutions such as $Ga_{1-x}Al_xAs$, $Ga_xIn_{1-x}P$ with an adjustable band gap [1 – 4]. At present, the composition, structure, optical and electronic properties of $Ga_{1-x}Al_xAs$ / GaAs multilayer structures fabricated by various epitaxy methods are well studied, which is associated with their wide use in various micro- and optoelectronic devices [5 – 10].

$Ga_xIn_{1-}xP$ alloys with a large band gap can potentially be used for high junction in tandem solar cells and yellow-green light emitting diodes [5, 6]. Due to the weak luminescence emission, studies of the optical properties of $Ga_xIn_{1-x}P$ alloys near the intersection of straight and indirect bands and in the region of indirect bands are more difficult than those for straight bands [5 – 7]. In addition, the absence of lattice-matched substrates and the ordering of effects complicate the studies. The authors of Ref. [8, 9] provided detailed information on the electronic structure of $Ga_xIn_{1-x}P$ ($0 \leq x \leq 1$).

Experimental results obtained in Ref. [10] showed that the luminescence efficiency of LEDs based on $Ga_xIn_{1-x}P$ significantly decreases at an emission wavelength shorter than 590 nm (< 2.1 eV). Despite the problems of carrier confinement for $Ga_xIn_{1-x}P$ alloys with a large band gap [11, 12], a simplified approach has been developed to simulate the degradation of luminescence intensity depending on the energy separation between direct and indirect bands [13].

In Ref. [14], $Ga_xIn_{1-x}P$ films were doped with tellurium ions with a concentration from $7\cdot10^{16}$ to $2\cdot10^{18}$ cm^{-2}. The study of the photoluminescence spectra showed that the transition from the indirect band to the direct one occurs at the temperatures between 40 and 100 K, and the direct emission of the band dominates in the photoluminescence (PL) spectra at room temperature.

In recent years, the most common method of fabrication nanofilms on the surfaces of semiconductor and dielectric films has been the low-energy ion implantation in an annealing test [15 – 19]. It has been established in private studies that when high-dose bombarded with argon ions Ar+, the surface is enriched with gallium (Ga) atoms, and when bombarded with metal ions (Me = Ba^{++} and Na^+), Ga and Me atoms are enriched. However, such studies have not yet been practically carried out for the case of gallium phosphide (GaP) implanted with low-energy In^+ ions [20 – 22].

This paper is devoted to investigation of physical properties of GaInP/GaP(111) nanofilms formed by means of implantation of In^+ ions into GaP.

Materials and research methods

GaP(111) single-crystal samples were chosen as target of research. Prior to ion implantation, they were degassed under conditions of ultrahigh vacuum: the pressure $P = 10^{-7}$ Pa at the temperature $T = 900$ K for about 4 hours.

Molecular beam epitaxy (MBE) is the most promising method for growing these structures. In the process of MBE being a vacuum deposition, the film growth is determined mainly by the kinetic interaction of beams with the crystal surface, in contrast to other methods. Prior to MBE, the GaP(111) samples were degassed under conditions of ultrahigh vacuum ($P = 10^{-7}$ Pa).

Ultraviolet photoelectron spectroscopy (UVPS) was used, and the energy and angular dependences of the secondary electron emission (SEE) coefficients were obtained. Ultraviolet photoelectron spectra were recorded at photon energies $h\nu \approx 10.8$ eV. The photon source was a standard hydrogen-discharge lamp.

Results and discussion

The GaInP thin films with a thickness of 30 – 50 Å were formed by implanting In^+ ions into GaP(111) followed by annealing at $T \approx 950$ K. Fig. 1 shows the photoelectron spectra of GaP implanted with In^+ ions with an energy E_0 of 1 keV at a dose of $6 \cdot 10^{16}$ cm^{-2} and annealed at $T = 950$ K for 40 min. In this case, a nanocrystalline film of the $Ga_{0.6}In_{0.4}P$ type with a thickness of $d \approx 30 - 35$ Å was formed. These spectra reflect well the density distributions of electronic state in the valence band. One can see that the pure GaP spectrum exhibits maxima at binding energies $E_b \approx -0.8, -2.2$ and -4.0 eV, probably due to the excitation of electrons from the 4*p* and (4*p* + 4*s*) states of Ga, as well as the hybridization of the 4*s* state of Ga with the 3*s* one of P (see Fig. 1, curve *1*). In the case of the GaInP film, the spectrum (see Fig. 1, curve *2*) contains intense peaks with $E_b = -1.2, -3.3$ and -5.6 eV, apparently associated with the excitation of electrons from the hybridized electronic states of 4*s*(Ga) + 5*p*(In), 4*s*(Ga) + 5*p*(In) + 3*d*(P), and 4*s*(Ga) + 5*s*(In) + 3*d*(P).

Fig. 2 presents optical absorption spectra (graphs of the relative intensity *I* of the light passing through the sample versus the photon energy $h\nu$) for GaP(111) and GaP(111) with a $Ga_{0.6}In_{0.4}P$ film with a thickness of $d \approx 50$ Å.

As Fig. 2 suggests, at first the *I* value does not change practically with an increase in $h\nu$, and then sharply decreases approaching zero. For the GaP(111) and GaInP/GaP nanofilms, a decrease in the *I* value is observed from $h\nu \approx 2.2$ eV and $h\nu \approx 1.7$ eV, respectively. Extrapolation of the sharply decreasing parts of the curves to the $h\nu$ axis gives the value of the band gap E_g of

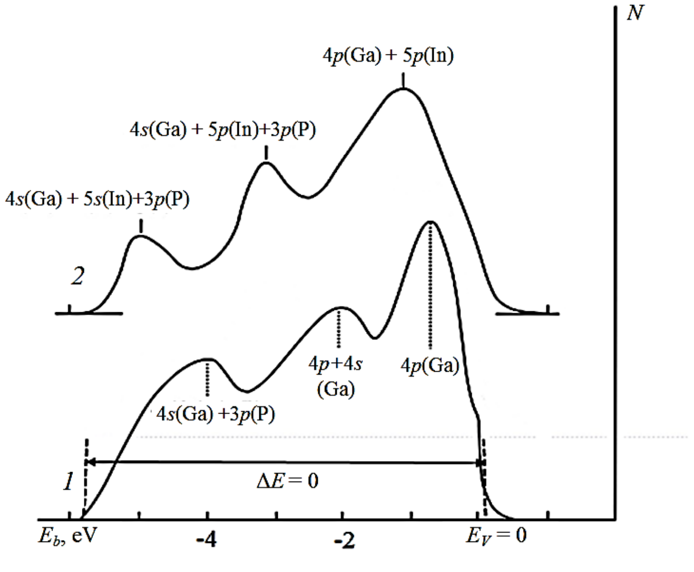

Fig. 1. Photoelectron spectra of the samples under study:
GaP(111) (curve *1*); GaP(111) with the $Ga_{0.6}In_{0.4}P$ film about 50 Å thick (curve *2*)
Identification of peaks is given

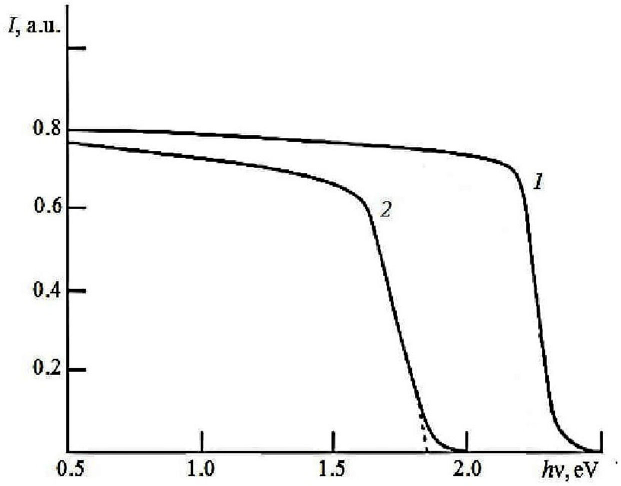

Fig. 2. Optical absorption spectra of GaP(111) (*1*) and GaP(111) with the $Ga_{0.6}In_{0.4}P$ nanofilm about 50 Å thick (*2*)

the material. As can be seen from Fig. 2, the E_g value for GaP(111) is approximately equal to 2.36 eV, and for the $Ga_{0.6}In_{0.4}P$ film it is about 1.85 eV.

Table presents the obtained values of main energy band parameters and emission characteristics of the samples under study. The photoelectric work function and electron affinity are determined by the formulas:

$$\Phi = h\nu - \Delta E,$$

where ΔE is the width of the photoelectron spectra, and

$$\varkappa = \Phi - Eg.$$

In heterostructural systems, the degree of crystallinity and epitaxiality of a nanofilm is of particular interest. For the film thickness $d < \lambda$ (λ is the photon wavelength), the degree of epitaxiality can be estimated from the angular dependences of the secondary electron emission (SEE) coefficients. Fig. 3 shows the dependences $\sigma_{800}(\varphi)$ for pure GaP(111) and for GaP with a GaInP film 50 E thick formed by ion implantation in combination with annealing and MBE. Here σ_{800} is the value of σ at electron energy E_p = 800 eV. The angle φ was determined with respect to the normal of the sample.

Table

The obtained values of main energy-band parameters and emission characteristics of the samples under study

Parameter	Notation	Unit	Parameter value	
			GaP(111)	$Ga_{0.6}In_{0.4}P$
Photoelectric work function	Φ	eV	5.3	5.5
Band gap	E_g		2.36	1.85
Electron affinity	$\varkappa$		2.94	3.65
Coefficient of secondary electron emission (max)	σ_{max}	–	1.95	1.70
Quantum yield of photoelectrons (at $h\nu$=10.8 eV)	*K*		$6\cdot10^{-3}$	$4\cdot10^{-3}$

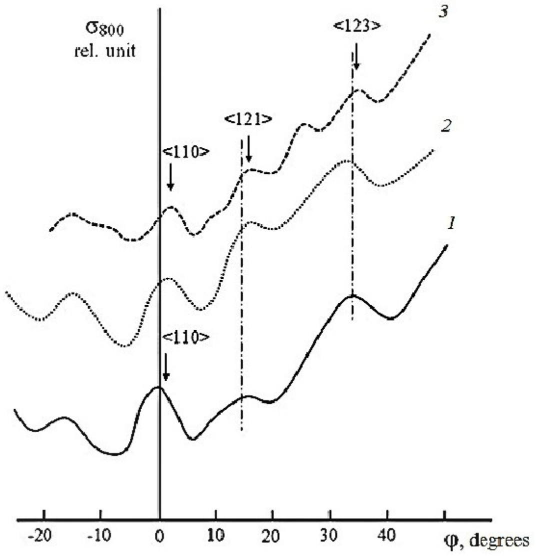

Fig. 3. The angular dependences of the secondary electron emission coefficient for pure GaAs (*1*), for GaP with the $Ga_{0.5}Al_{0.5}As$ film (50 Å thick) formed by ion implantation (*2*) and MBE (*3*). Crystallographic directions are shown

As evident from Fig. 3, a nonmonotonic increase in the value of σ_{800} with increasing φ occurs in all cases. Maxima and minima are observed on the $\sigma_{800}(\varphi)$ curves, and their positions are related by certain crystallographic directions.

The angular positions of the peaks for GaP and the GaInP nanofilms formed by ion implementation are in well arrangement with each other. From this observation, we can conclude that a strict epitaxial growth of the $Ga_{0.6}In_{0.4}P$ film takes place in this case. As for the MBE case (see Fig. 3, curve 3), The peak intensity on the $\sigma_{800}(\varphi)$ curve significantly decreases as compared to the corresponding GaP one, and new peaks appear near these peaks. The processing of the σ(φ) dependences taken at different Ep values made it possible to establish that the exit depth was about 50 Å at $E_p \approx 200$ eV. In this case, the GaP peaks completely disappeared on the σ(*d*) curve, while the intensity of the GaInP peaks increased significantly.

Conclusions

The information about the state density of valence electrons and the energy bands parameters of $Ga_{0.6}In_{0.4}P$ nanofilms has been presented. The nanofilms were fabricated by In^+ implantation in GaP with subsequent annealing; in this case, a strict epitaxial growth of the film took place. The crystallographic orientations of GaInP and GaP were established to coincide completely at the interface. Moreover, the energy gap of the GaInP nanofilm was found to be 1.85 eV.

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