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Narrow gap III–V materials for infrared photodiodes and thermophotovoltaic cells

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ABSTRACT

The paper describes liquid phase epitaxial growth and characterization of the GaSb- and InAs-related materials for the photodiodes and thermophotovoltaic applications. It was shown that doping of the melt with holmium results in obtaining the high purity GaInAsSb and InAs layers. The passivation with the 1 M Na_2S aqueous solution makes it possible to prepare flat growth surfaces of GaSb(1 0 0) and InAs(1 0 0) substrates after annealing. A reproducible technique has been developed for fabrication of the high-efficiency GaInAsSb/GaAlAsSb and InAs/InAsSbP photodiodes with the long-wavelength photosensitivity edge of 2.4 and 3.8 μm, respectively. Room temperature detectivity in the spectral peak reaches $D^* = (0.8–1.0) \times 10^{11}$ W^{-1} cm $Hz^{1/2}$ for the GaInAsSb/GaAlAsSb photodiodes and $D^* = (3.0–5.0) \times 10^9$ W^{-1} cm $Hz^{1/2}$ for the InAs/InAsSbP devices. We have adapted the technology for thermophotovoltaic cells operating at an emitter temperature of 1000–1700 °C.

1. Introduction

Narrow gap III–V semiconductors are of interest from both the fundamental physics viewpoint and from viewpoint of infrared (IR) optoelectronics. In recent years this class of materials has become the subject of extensive investigations because of the progress in developing infrared lasers, light emitting diodes, photodiodes, solar cells and thermophotovoltaic (TPV) devices for mid-infrared spectral range [1–4].

High-efficiency IR photodiodes based on GaSb- and InAs-related materials are extremely important now for optical fiber communication, eye-safe laser rangefinding systems. The strong absorption bands of such natural and industrial substances as H_2O, CO_2, CO, CH_4, H_2S, NH_3, CH_3Cl, HCl, HBr, NO_2, SO_2, glucose and many others lie in the spectral range of 1.6–5.0 μm. Thus, the photodiodes operating at these wavelengths attract the considerable interest for spectroscopic studies, ecological monitoring and medicine [5,6].

The systems for converting IR radiation from a heated source to electricity have been intensively discussed in terms of applying III–V materials [7,8]. GaSb, InAs and related compounds have turned out to be promising materials for TPV applications. At present, high-performance GaSb-based, single-junction as well as tandem TPV cells are used for TPV generators [9]. The GaInAsSb TPV devices for the temperature range of 1200–1700 °C can operate as cheap, portable and ecological converters of energy from the heaters using gas fuels, carbon, wood and biomass burning. New generation InAs/InAsSbP TPV cells with band gaps in the 0.3–0.5 eV range [9,10] allows to extend the range of spectral sensitivity to longer wavelengths and to convert efficiently thermal energy from sources with the temperature as low as 1000–1200 °C.

In this paper we present our results, including the growth of the GaSb- and InAs-related materials and device investigation aspects. Our research activities focus on GaInAsSb/GaAlAsSb and InAs/InAsSbP photodiodes for mid-IR spectral range, as well as TPV cells operating at an emitter temperature of 1000–1700 °C. The optical and electrical characteristics of the devices are given.

2. Technologies and materials

Several epitaxial techniques for growth high-quality GaSb- and InAs-based materials have been developed in Ioffe Physical-Technical Institute RAS [liquid phase epitaxy (LPE), metal organic vapor phase epitaxy (MOCVD), and molecular beam epitaxy (MBE)]. The main drawback of a near-equilibrium technique such as LPE is the existence of a wide range of solid composition which can not be obtained because of fundamental thermodynamic limitations. But it should be noted that this method makes it possible to grow the high-quality bulk layers with composition near the miscibility gap boundary. Such advantages of LPE as its simplicity, relatively low cost, the absence of toxic precursors or by-products are of current importance.

In our study, to grow the GaSb, InAs, GaInAsSb, GaAlAsSb, InAsSb, and InAsSbP materials standard LPE system with the

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horizontal quarts reactor was used. After loading the source materials, a graphite boat was annealed in H_2 flow at 720 °C for 4 h in the case of the GaSb-related semiconductors or at 950 °C for 6 h in the case of the InAs-related semiconductors. Then the system was cooled to room temperature, and the substrate was placed in the boat. The temperature was raised to 640 °C and held for 15 min. The system was then cooled down to the growth temperature. Just prior to growth, the substrates were prepared according to the conventional technique for LPE. After cleaning by immersion in boiling and cold acetone, the GaSb(1 0 0) substrates were etched with CrO_3/HF/H_2O, and then treated with HCl:2H_2O. Preparing the InAs(1 0 0) substrates included cleaning with acetone and etching in CrO_3/HCl/H_2O. Finally, the substrates were washed in deionized water and blown dry with nitrogen. The growth parameters of the materials obtained by LPE for photodiode applications are presented in Table 1.

The chemical composition of the solid solutions was determined by X-ray spectral microanalysis. The crystalline quality of the grown layers, the surface morphology and heterostructure interface abruptness have been studied with photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM), atomic-force microscopy (AFM), transmission electron microscopy (TEM), and X-ray diffraction methods. Transport properties were determined through low-field (<0.5 T) Hall effect measurements in the temperature range 77–300 K. Spectral characteristics were recorded using SPM-2 (Carl Zeiss) monochromator with a globar as IR source. Quantum efficiency was evaluated by comparison with sensitivity of the calibrated Carl Zeiss thermopile with a flat response.

The operating wavelength region of the IR photodiodes is strongly connected with the band gap energy of the active absorbing layer. The GaSb- and InAs-related materials are suitable for IR detection in the 0.9–2.5 μm and the 1.5–4.4 μm spectral ranges, respectively. In this study, GaInAsSb solid solutions and InAs epitaxial layers obtained by LPE were chosen as active areas for the GaSb- and InAs-based photodiodes. High-quality $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ solid solutions with composition near the miscibility gap boundary were grown at $T = 600$ °C on tellurium-doped GaSb(1 0 0) ($n = (1–3) \times 10^{17}$ cm^{-3}, $\mu = 5720$ cm^2/V s at $T = 80$ K) substrates. The width of the $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ band gap determined from PL data and transmission spectrum was 0.58 eV at $T = 80$ K. These experimental results are in good agreement with our calculations of the band gap energy as a function of the solid phase composition according to the interpolation formulae [11]. The n-InAs layers were obtained at $T = 597$ °C on sulfur-doped InAs(1 0 0) ($n = 6.0 \times 10^{16}$ cm^{-3}, $\mu = 24{,}000$ cm^2/V s at $T = 80$ K). The 80 K PL spectra exhibit a dominant line with a maximum at 0.41 eV, which is associated with the InAs band gap width at the measurement temperature and the direct interband transitions.

The spectral photosensitivity distribution at room temperature in Fig. 1 (curve 1) shows that for the GaSb-based heterostructures the half maximum wavelength ($\lambda_{50\%}$) of sensitivity determined by energy gap of the $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ active layer ($E_g = 0.53$ eV at $T = 300$ K) is 2.32 μm, the long-wavelength edge (λ_{th}) lies at 2.4 μm. At the same time, for the InAs-based heterostructures with n-InAs active layer ($E_g = 0.38$ eV at $T = 300$ K) the half maximum wavelength ($\lambda_{50\%}$) of sensitivity is 3.5 μm, the long-wavelength edge (λ_{th}) is 3.8 μm (Fig. 1, curve 3). The photosensitivity edge can be shifted to longer wavelengths. Thus, when the active region is $Ga_{0.76}In_{0.24}As_{0.18}Sb_{0.82}$ material ($E_g = 0.51$ eV at $T = 300$ K), the long-wavelength threshold of the heterostructure spectral sensitivity is red shifted to 2.55 μm (Fig. 1, curve 2). In the case of the InAs-based heterostructure, the use of $InAs_{0.91}Sb_{0.09}$ active layer ($E_g = 0.3$ eV at $T = 300$ K) makes it possible to achieve $\lambda_{th} = 4.4$ μm (Fig. 1, curve 4).

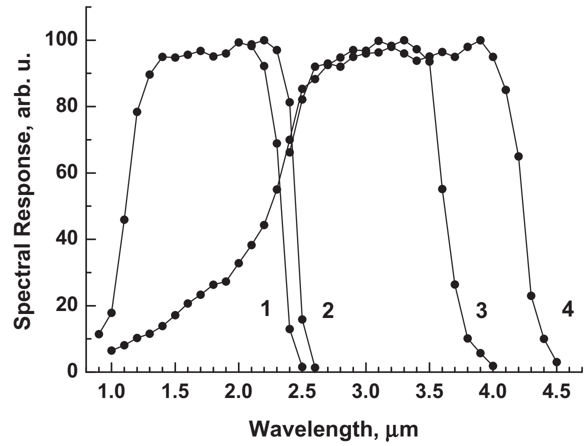

Fig. 1. Spectral distribution of photosensitivity for the GaSb-based and the InAs-based heterostructure at 300 K: (1) $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ active layer ($E_g = 0.53$ eV), $\lambda_{th} = 2.4$ μm; (2) $Ga_{0.76}In_{0.24}As_{0.18}Sb_{0.82}$ active layer ($E_g = 0.51$ eV), $\lambda_{th} = 2.55$ μm; (3) InAs active layer ($E_g = 0.36$ eV), $\lambda_{th} = 3.8$ μm; (4) – $InAs_{0.91}Sb_{0.09}$ active layer ($E_g = 0.3$ eV), $\lambda_{th} = 4.4$ μm.

One of main requirements for the photodiode heterostructures are a low carrier density in the active area. Undoped $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ solid solutions grown on Te-doped n-GaSb(1 0 0) substrate without the buffer layer demonstrate the hole density as high as $p = (1–3) \times 10^{17}$ cm^{-3} and mobility of $\mu = 300–400$ cm^2/V s at $T = 80$ K. Epitaxial InAs material has the electron density of $n = 1 \times 10^{17}$ cm^{-3} and mobility of $\mu = 32{,}000$ cm^2/V s at $T = 80$ K. It was shown in a number of studies [12–14] that rare-earth elements can be successfully used for growth of high purity III–V materials by LPE. Especially the group-six elements acting as shallow-level impurities in these semiconductors are effectively gettered due to the enhanced chemical affinity of rare-earth elements towards them [15]. In this study, holmium of 3 N purity was introduced into the melt with preliminarily homogenized source materials. Before loading into the graphite boat Ho was cleaned mechanically and weighed. We have found that the hole density in the $Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$ material and the electron density in the InAs layers fall by about two orders of magnitude (to $(2–4) \times 10^{15}$ cm^{-3} at $T = 80$ K) with increasing the Ho content in the melt up to 0.01at.%. At that, the concentration of shallow

Table 1
Growth parameters of the materials obtained by LPE for photodiode applications.

Composition	Substrate	Growth temperature (°C)	Cooling rate (°C/min)	Time of growth (s)	Thickness (μm)
$Ga_{0.78}In_{0.22}As_{0.18}Sb_{0.82}$	GaSb	600	0.6	100	2.0–2.5
$Ga_{0.76}In_{0.24}As_{0.21}Sb_{0.79}$	GaSb	597	0.6	90	2.0–2.5
$Ga_{0.66}Al_{0.34}As_{0.025}Sb_{0.97}$	GaSb	599	0.6	100	1.5–2.0
$Ga_{0.50}Al_{0.50}As_{0.04}Sb_{0.96}$	GaSb	599	0.6	100	1.5–2.0
GaSb	GaSb	599	0.6	5	2.0–2.5
InAs	InAs	597	0.3	10	2.0–2.5
$InAs_{0.91}Sb_{0.09}$	InAs	547	0.3	60	2.0–2.5
$InAs_{0.53}Sb_{0.16}P_{0.31}$	InAs	594	0.3	540	2.0–2.5