Contributed paper

Liquid phase epitaxial III-V technology for photodetectors manufacturing

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The $Al_xGa_{1-x}As/GaAs$ heterostructures represent a potentially useful material for photodetectors with high efficiency in spectral range 0.4 ÷ 0.9 μm. To produce the thermostable detectors with high radiation hardness on the base of liquid phase epitaxy (LPE), the physical and chemical foundation of such epilayers formation was developed. The possibilities of LPE method were developed due to utilization of multicomponent solution-melts with rare-earth additions. As the base of technology, the horizontal sliding-boat step-cooled LPE technique with controlled composition of gaseous medium and additions of Yb in Bi and Ga-Bi-Al solution-melts were used. As a result of our investigation and LPE technology elaboration the quickly responsive photodiodes with improved technical, exploitative and economical parameters have been fabricated.

1. Introduction

For realization of the unique possibilities of the optical fibers, highly reliable and easily controllable AlGaAs/GaAs and InGaAsP/InP photodetectors for near infrared range are necessary. They must meet the following requirements: correspondence to the wave range in which the fiber has minimum loss and small dispersion, long working time (10^5 ÷ 10^6 hours) and high efficiency. Two last factors are also important when application of AlGaAs/GaAs photodetectors as solar cells is discussed.

It is well known that $A^{III}B^{V}$ heterostructures and photodetectors with essentially different photosensitivity for different spectral ranges could be produced by MOCVD (metal organic chemical vapor deposition) and MBE (molecular beam epitaxy) technologies. The liquid phase epitaxy (LPE) method (particularly low-temperature LPE [1]) has happened to be the most useful for 0.4 ÷ 0.9 μm spectral range photodiodes production. Low cost, possibility of the controllable epilayers deposition with thickness from ~100 Å up to about 1 μm and various doping level are the advantages of this method.

The aim of this work is to test and combine achievements of various authors in using of LPE technology for quickly responsive p-i-n photodetectors production. To achieve required spectral range for possible space applications it was necessary to pay attention to the development of thermostable and having good radiation hardness epilayers technology [2]. It was essential for this work to use multicomponent melts (epilayers grown from Bi melts are more thermostable, as Ga inclusions are absent) and to use the rare-earth additions in the melt for i-layer preparation. It has been found that the presence of rare-earth elements during growth from the melt leads to efficient gettering of background impurities [3-7], changing of the stoichiometry and improving quality of epilayers. Our preliminary investiga-

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tions have proved the influence of rare-earth on the increase of the radiation hardness of the diodes [2].

2. Epitaxial layers growth and characterization

As the first stage of our work, for preliminary selection of optimal technology conditions, GaAs and AlGaAs epitaxial layers were grown on semi-insulating (100) GaAs substrates. Then multilayer heterostructures for photodiodes were prepared. GaAs and AlGaAs epilayers with thicknesses in the range 0.1÷12 μm were grown from Ga, Bi, Ga-Bi-Al melts by LPE under the flow of purified hydrogen in a graphite slider boat and quartz reactor. Epilayers were nominally undoped. Various amounts of Yb (up to 1×10^{-2} at.%) were added to the melts. The temperature variations scheme is illustrated in Fig. 1 for epitaxial growth from Ga melt. Saturation temperature for epilayers grown from As-rich melt was T_n = 744°C. At this temperature, solution was homogenized for 1 hour; for Ga-rich layers, solution was homogenized at 760°C for 4 hours. Then, in both cases, the crystal growth temperature T_g ~ 680°C was lowered during $t_3 - t_4$ (v~0.7°C/min) after quick cooling $t_2 - t_3$ (v ~ 2 °C/min). In this way the low level of residual impurities for both Ga and Bi melts was ensured [8]. The supercooling of the melt (ΔT = 20÷60°C) resulted in supersaturation and provided the driving force for epitaxial growth for heterogeneous crystallization with excellent surface morphology and lateral uniformity of interface.

The AlGaAs films were grown with ΔT = 5°C supercooling. Such ΔT prevented the GaAs from homogeneous crystallization in the melt (AlAs is more refractory than GaAs). Composition of AlGaAs was regulated by

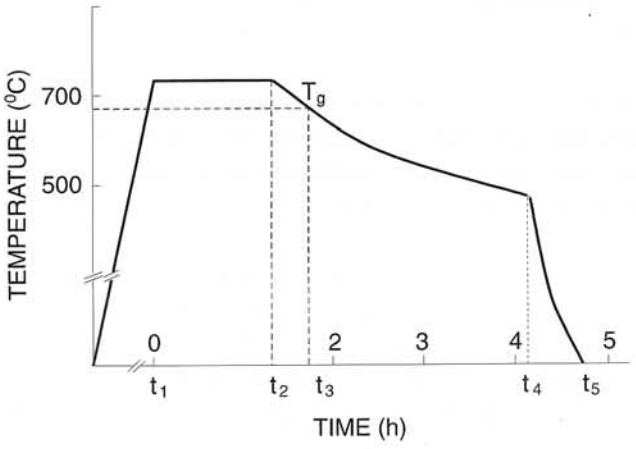

Fig.1. Temperature profile of GaAs LPE growth by controllable cooling (As-rich).

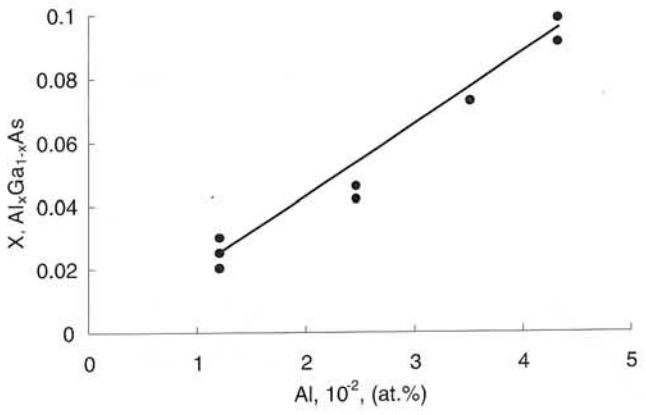

Fig.2. Al content of $Al_xGa_{1-x}As$ epilayers measured by PL as a function of Al content in the melt.

the Al content in the melt and by the value of ΔT [9]. Fig. 2 shows the Al content in AlGaAs epilayers measured by photoluminescence (PL) as a function of Al atomic percent in the melt at our technological conditions.

The as-grown films were characterized by various methods. Carrier concentration, resistivity and mobility were obtained using Hall effect measurements at 300 and 77 K. Near band edge PL spectra excited by Ar^+ or He-Ne laser were recorded at 4.2, 77 and 300 K using KSVU-23 system coupled with FEU-62 or FEU-112 photomultipliers [10]. We used X-ray diffraction measurements on the double-crystal diffractometer with Cu $K_{\alpha 1}$ X-ray source such as (004) reflection rocking curves, measurements of the integrated intensity (R) of X-ray diffraction for Bragg geometry and measurements of R for X-ray (002) quasiforbidden reflections[1] (XFR) to determine the stoichiometry [11]. This method is quite simple but demands proper data processing based on the right predictions and assumptions. The atomic concentration of native defects deduced from the XFR measurements was about 10^{18} cm^{-3} (at R variation ~1%). The as-grown samples were γ-ray irradiated by Co^{60} at room temperature to a fluence of about 8×10^{17} cm^{-2} (~ 5×10^8 rad).

3. Experimental results and discussion: materials and devices

3.1. Materials

This part of the work reports on the results of investigation of technology conditions influence on the stoichiometry and electric properties in LPE GaAs and

[1] (002) and (006) reflections are called quasiforbidden for binary GaAs.

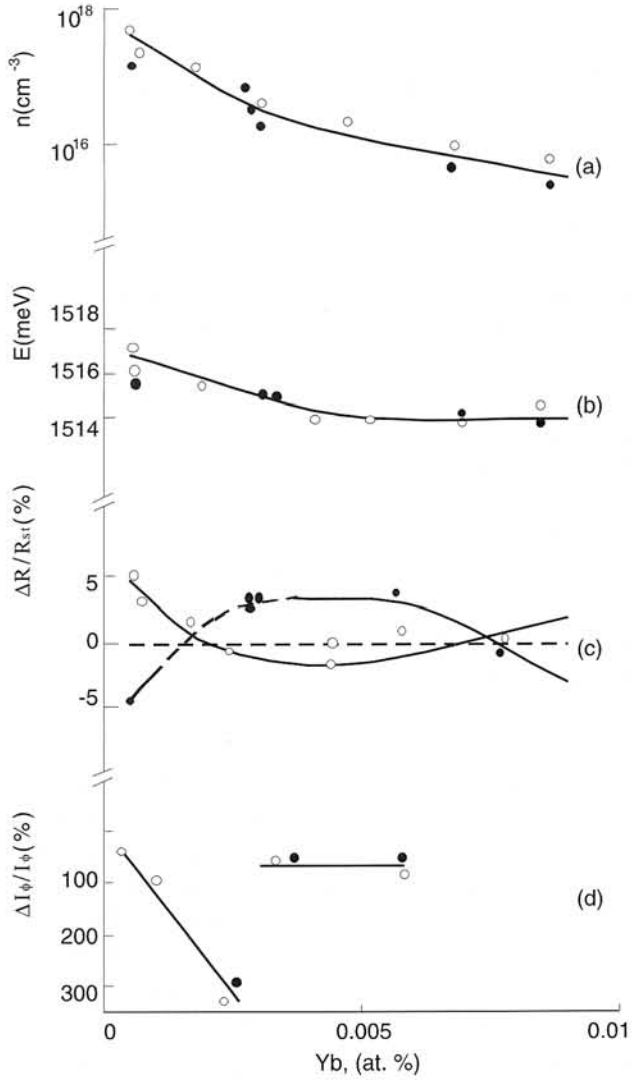

Fig.3. 300 K electron concentration of GaAs layer (a), 4.2 K bound exciton energy (b), R/R_{st} ratio for 002 reflection (c), $\Delta I\phi / I\phi$ ratio as a function of Yb content in Ga melt (d); • – for Ga-rich films, o – for As-rich films.

AlGaAs with increasing amount of Yb (up to 0.01 at.%) added to the Ga or Ga-Bi melts.

Experimental results show that:

a) The electron concentration (see Fig.3) in the layers decreased from about 5×10^{17} cm^{-3} (N^L_{Yb} = 0) (this high value was determined by background contamination in our technology conditions) to $< 1 \times 10^{15}$ cm^{-3} for $N^L_{Yb} \sim 10^{-2}$ at. % without conversion to p-type. Compensation coefficient $K = N_D^+ / N_A^-$ (N_D^+, N_A^- are the densities of ionized donors and acceptors, respectively), and separate values N_D and N_A were calculated from mobility[2] at 77 K [12]. We obtained the increase of K with the increase of N^L_{Yb} and concluded that the gettering properties of the Yb in the melt were restricted by n-type impurities at any growth conditions.

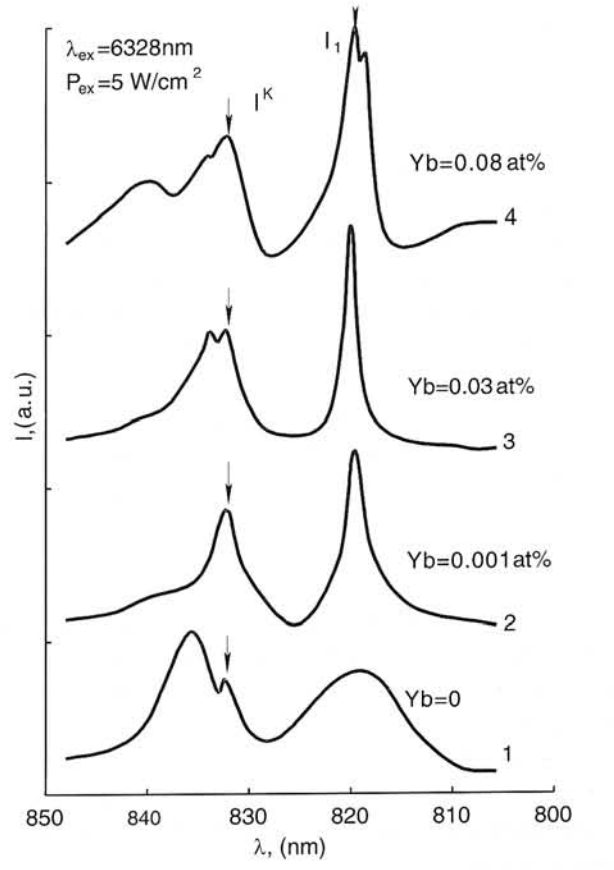

Fig.4. Photoluminescence spectra for GaAs epilayers at the various Yb content in the melt.

b) As shown in Fig. 4, the position of bound exciton line shifted to the lower energy (from 1.518 to 1.514 eV) and the full width at half maximum (FWHM) of its spectra decreased to 2.5 meV with increasing of the Yb addition in the melt for As-rich films. It may be explained by incorporation of Yb into Ga-sublattice as single atoms. The value of the shift corresponded to $\varepsilon \sim 10^{-4}$ which could be attributed to different atomic radii of Ga and Yb ($r_{Ga} << r_{Yb}$). For Ga-rich films the shift of the bound exciton line ($h\nu$ = 1.5144 eV, 4.2 K) was essential.

c) GaAs films grown from Ga-Bi-As solution according to scheme (Fig. 1) were As-rich. With the increasing of Yb content in the melt the $\Delta R / R_{st}$[3] (R_{st} corresponds to quasi-forbidden reflection intensity for

[2] It is known that the mobility which at low temperatures is limited by ionized impurity scattering ($N_A^- + N_D^+$), at room temperature is limited mainly by lattice scattering and is influenced by the crystal quality.

[3] The value of $\Delta R/R_{st}=(R-R_{st})/R_{st} \times 100\%$ is determined both by stoichiometry change and by Yb occupation of Ga sites. The intensity decreases if Yb atoms occupy regular Ga sites. This is connected with the structure factor $F \sim 4(f_a - f_b)$ which determines R value, where $f_{a,b}$ are the atomic scattering factors for Ga and As. For Yb atoms on Ga sites $f_{Ga} < f_{Yb}$ [11].

the liquid horizontal Bridgman method grown semi-insulating GaAs wafers as standard reflection) decreased, passed through the minimum at optimal Yb concentration (N^L_{Yb} = 0.0014 at. %) leading to the best electrical properties ($n \leq 1 \times 10^{15}$ cm^{-2}, $\mu \sim 6000$ cm^2/Vs, T = 300 K).

The stoichiometry decreased (increased) with increasing amount of Yb for As-rich (Ga-rich) GaAs films, passed through the minimum (maximum) for the optimal Yb concentration, correspondingly to epilayers stoichiometry. At high concentrations of Yb (up to 0.01 at. %) insignificant deviation from stoichiometry was different for As- and Ga-rich films.

The above deviation from stoichiometry for As-rich films may be explained by incorporation of Yb into Ga sublattice as single atoms as well as its influence on the thermodynamic parameters of the melt as "catalyst" [5]. For Ga-rich films these deviations can be ascribed to Yb atoms incorporated into the films just as impurity on Ga sites which are occupied by host atoms [13].

Nature of residual acceptors (from PL spectra) for films which were grown from Bi melt was not similar, but concepts developed for mechanism of formation of single crystalline films grown by LPE using REEs may still be used interchangeably.

Original AlGaAs epilayers were grown on GaAs substrates with 0.023 at.% of Al content in the Ga melt. Composition of alloy corresponded to x = 0.032. Very high purity $Al_{0.03}Ga_{0.97}As$ epilayers were grown by adding of the optimum amount of the Yb (~ 0.0048 at. %) and have the hole concentration $p \sim 10^{14}$ cm^{-3} and μ= 450 cm^2/Vs, 300 K.

Fig. 3. shows the ratios of the integrated intensities of the near band edge photoluminescence spectra at 77 K of γ-irradiated (I_ϕ) and as-grown samples (I_0). The ratios of the intensities I_0/I_ϕ, where I_ϕ corresponds to a flux of about 5×10^8 P, are plotted as a function of the amount of Yb in Ga or Bi melts. From Fig. 3 one can see that γ-ray irradiation causes the decrease in the PL intensities. Two features are noted. First, for $N^L_{Yb} \leq 0.34 \times 10^{-2}$ at % the decrease in the I_0/I_ϕ is greater than that in the undoped samples. Second, for $N^L_{Yb} > 0.34 \times 10^{-2}$ at. % (optimum concentration) the I_0/I_ϕ ratio does not depend on the rare-earth concentration and is about 30. As shown in Fig. 3, the films purity and the crystal quality become high with the increase of the amount of Yb in the melt ($N^L_{Yb} > 0.34 \times 10^{-2}$ at. %), whereas the radiation resistance does not decrease. The observed effect is independent from the growth conditions (either As-rich or Ga-rich epilayers) but was controlled by the rare-earth concentration and generally could be attributed to the creation of non-radiative centers by γ-ray irradiation. However, the irradiation does not affect PL spectrum of the as-grown samples and the samples with rare-earth additions.

To explain the obtained results we have examined the interaction of radiation-induced native defects with rare-earth atoms (or coagulates). Some of the simple native defects-vacancies and interstitials created by the room temperature irradiation [14] are expected to be mobile and thus may interact (annihilate) with rare-earth complexes or in internal fields around them. A similar situation might also be applicable to AlGaAs epilayers. This rare-earth-impurity defect interaction could play an important role in the increasing of radiation resistance in AlGaAs epilayers.

3.2. AlGaAs/GaAs heterostructure photodiodes

The epitaxial layers for p-i-n photodiodes were grown by LPE on (100) oriented n$^+$ GaAs:Sn ($n = 2 \times 10^{17} \div 2 \times 10^{18}$ cm^{-3}) substrates. The cross-section of the integrated structure is shown in the inset to Fig.5. The structure consists of the following parts: about 7 µm thick n-$Al_xGa_{1-x}As$ (x = 0.2÷0.35, $n \leq 1 \times 10^{18}$ cm^{-3}) base layer; 1÷ 3 µm thick i(ν)-$Al_xGa_{1-x}As$ (x = 0.0÷0.1, $n \leq 1 \times 10^{15}$ cm^{-3}); 0.25 ÷ 1.5 µm thick p-$Al_xGa_{1-x}As$ (x = 0.3 ÷ 0.8, $p \approx 5 \times 10^{17} \div 1 \times 10^{18}$ cm^{-3}) window

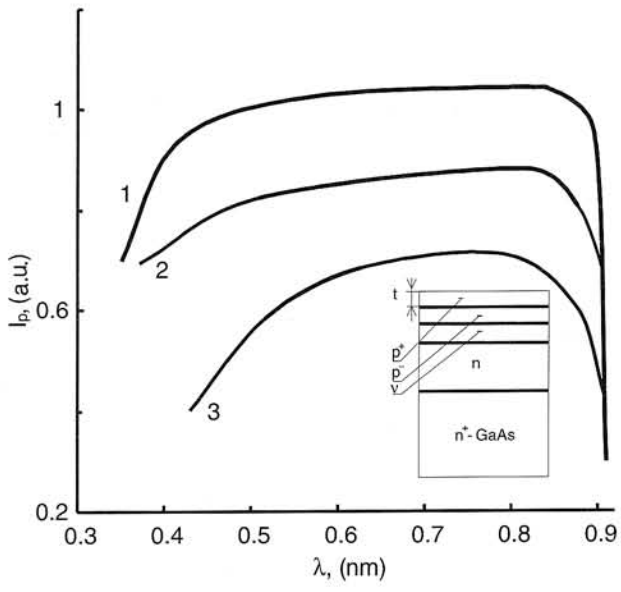

Fig.5. Photoresponse spectra of AlGaAs photodiodes with different thickness of wide-gap window: 1-300 Å, 2-700 Å and 3-1 µm. Basic photodiode structure is shown in the insert.

layer and a 0.5 μm-thick p-$Al_xGa_{1-x}As$ ($p \geq 10^{18}$ cm^{-3}) cap layer.

Both the optimal growth conditions, predetermined by composition of the Ga-Bi-Al solution-melt, and the rare-earth concentration in the melt ($N^L_{Yb} \approx 0.05$ at. %) for obtaining *i*-layer (ν-layer, actually) were preliminary found. The room-temperature spectra of the photoresponse in the 0.4 ÷ 0.9 μm region of the samples grown by LPE method with rare-earth addition are shown in Fig. 5. The difference between 1, 2 and 3 spectral curves is due to the difference in the wideband window layer thickness *t*. The intensity of the photoresponce is correlated with the value of thickness *t*. As shown clearly in Fig. 5, the photoresponse intensity increases and spectral sensitivity enlarges more at the short wavelength limit than at the long wavelength limit with the window layer thickness decrease.

The following characteristics were achieved for low-cost photodetectors grown by the high productive LPE technology with rare-earth addition in the Ga-Bi-Al melts:

– spectral sensitivity range	$\Delta\lambda = 0.4\text{-}0.9$ μm;
– responsivity on the peak of spectral response wavelength	$S_{0.63} = 0.4$ A/W;
– rise and decay time of the transfer characteristics	$\tau = 1 \times 10^{-9}$ s
– operation voltage	$U = 5 \times 10$ V
– dark current	$I_d = 1 \times 10^{-6}$ A
– effective area of the responsive element	$A_{eff} = 1 \div 50$ mm^2
– capacitance	$C = 5 \div 10$ pF

The thermostability and radiation hardness of these detectors were higher than those of photodiodes grown from Ga-melts without rare-earth additions.

4. Conclusion

AlGaAs/GaAs based heterostructures for photodiodes application were grown by the specially developed LPE method. The optimal growth conditions, solution melt composition and rare-earth concentration in the melt for obtaining thermostable heteroepilayers with high radiation hardness were found.

5. Acknowledgements

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