GaAs thin films grown by LPE under influence of Yb impurity

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***Abstract* – A comprehensive study of the photoluminescence spectra and the electrophysical parameters have been performed on GaAs epitaxial layers grown by the low temperature liquid phase epitaxy (LPE) method from solution-melts doped with Yb impurity. The characteristic variations of the relative intensity of the components of the PL spectra, electroconductivity, concentration and mobility of the free charge carriers in the grown layers where established as a function of the concentration of the Yb impurity in the initial solution-melts. A possible mechanism of the influence of the Yb impurity on the native defects and background impurities in the epitaxially grown GaAs is proposed.**

I. INTRODUCTION

III-V epitaxial structures, and GaAs in particular, form a basis for a variety of devices of modern electronics, such as laser and power diodes, super high frequency (SHF) transistors, solar cells and so on. Main technological methods used to grow these structures are MBE, MOVPE, VPE, and LPE [1-4]. The problem to obtain the epitaxial structures – with the lowest possible concentrations of the background and structural defects to satisfy device production requirements – is one of the main issues in developing the epitaxial growth techniques. Despite all advantages of the MBE, MOVPE and VPE, LPE technique is the one providing the conceptual possibility to grow epitaxial structures with purification level higher than that of the initial materials. That can be achieved by utilizing the gettering ability of the certain doping impurities during the growth process. In that view doping with the rare-earth elements (REE) is the most effective approach enabling to decrease by 3-4 orders of magnitude the concentration of the background impurities in the active layers of the grown structures, and, at the same time – to increase the mobility of the charge carriers [5-8]. However, the details of the desirable influence of the REE on the quality of the epitaxial structures based on GaAs are not well understood by now. In the present work we have clarified several issues of that problem.

Gallium arsenide is an object of fundamental and applied research for a years. Therefore, energy levels in the GaAs energy band gap originating from a variety of different impurities, native defects, and complexes of those, are well identified and described by now. Relying on that knowledge we chose low-temperature photoluminescence (PL) as a main experimental method to study transformations of the impurity-defect system of the GaAs epilayers grown from the REE doped solution-melts.

II. SAMPLES AND EXPERIMENTS

Epitaxial GaAs layers were grown by the LPE method on semiinsulating GaAs (100) substrates in the horizontally aligned graphite containers. The initial solution-melt prepared using Ga (99.9999) and polycrystalline GaAs ($(2\text{-}3)\times10^{15}$ cm^{-3} free electron concentration) was purified by means of long (8-10 hours) high-temperature annealing (about 850 °C) in the hydrogen atmosphere. Yb concentrations in the solution-melts ranged from 1×10^{-3} to 1.2×10^{-2} at %. The crystallization rate did not exceed 10 nm/c. The thickness of the grown epitaxial layers was about 10 μm.

The impurity-defect structure of the grown epitaxial layers was examined by studying low-temperature photoluminescence (PL) at 10 K as well as electrophysical properties of the layers at room temperature. PL spectra were recorded using a Dilor XY triple spectrometer with liquid nitrogen cooled CCD detector. The spectral resolution of the measurements was 0.25 nm. The 514.5 nm argon ion laser line was used for the excitation.

III. EXPERIMENTAL RESULTS

Typical PL spectra of the GaAs epilayers grown from the undoped and Yb doped solution-melts containing different concentration of the Yb impurity (N_{Yb}) are present in Figs. 1 and 2. An enlarged view of the observed spectral PL lines together with the corresponding line decompositions is presented in the inserts of Fig. 2.

As one can see from the presented spectra, the PL activity of the epilayers undergoes significant changes induced by the Yb impurity. The PL spectra for the layers grown from the undoped solution-melts show one wide relatively weak band with complex shape having its maximum around 1.51 eV (Fig. 1).

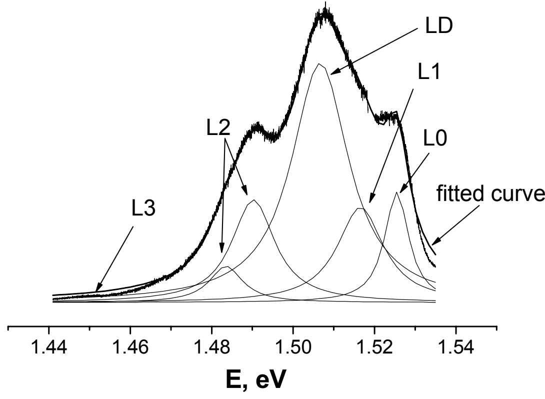

Fig. 1. Typical PL spectra of the GaAs epilayers, grown from undoped solution-melts.
T = 10 K, λ_{ex} = 514.5 nm, P_{ex} = 1 mW/cm^2

Introducing Yb into the solution-melt leads to increasing of the maximum PL intensity, narrowing of the PL band with respect to that for the undoped film and formation of two narrow lines L1 and L2 (Fig. 2). The ratio between intensities of these lines depends on N_{Yb}.

N_{Yb}, 10^{-3} at %	1	1.8	6.4	12.0
N, cm^{-3}	$1.3{\cdot}10^{17}$	$1.3{\cdot}10^{17}$	$7.0{\cdot}10^{16}$	$2.4{\cdot}10^{16}$
I_{L2}	1.33	0.88	1.34	9.7
I_{L3}	0.020	0.0096	0.023	0.18

Table 1. Free carrier concentrations N and the total intensities of the luminescence lines L2 and L3 with respect to L1 normalized to unity. (See Fig. 2 for details)

Apart from the lines L1 and L2, another much weaker line L3 shifted to the longer wavelength region (near 1.45 eV) also appears as a result of the Yb doping. Normalizing the averaged intensity of the high-energy spectral line L1 to unity, the calculated relative intensities of the others lines depending also on the N_{Yb} are presented in Table 1.

PL lines L1, L2 as well as L3 are also complex. Essential parameters of the Voigt shaped components revealed by fitting for each of these lines are listed in the Tabl. 2.

IV. Discussion

The technologically most important result of the performed studies is the demonstration that the Yb impurity introduced into the initial solution-melt improves significantly the structural perfection of the epitaxially grown GaAs layers. That was clearly shown by the observed increasing of the PL intensity of the layers and the narrowing and structuring of the PL bands under influence of the Yb impurity.

The analysis of the shape of the experimental PL lines revealed the following: the PL spectra of the undoped structures can be decomposed into (i) the high-energy line L0 (1.525 ± 0.001 eV) and the most intense component of the spectrum LD with energy 1.506 ± 0.001 eV, which were never observed in the PL spectra of the layers grown from the Yb doped solution-melt; (ii) two lines with the energy being close to that for the lines L1 and L2 of the doped epilayers. The spectral line L1 is well represented by two component lines with transition energies of 1.515 and 1.512 eV for all samples grown from the Yb doped solution-melts. The component with the energy 1.512 eV was not revealed in the PL spectra of the undoped samples probably because of the very intensive LD component (1.506 eV) introducing masking effect. The relative contribution from the low-energy component (1.512 eV) in the total intensity of the L1 line for the Yb doped samples shows a decreasing tendency when N_{Yb}

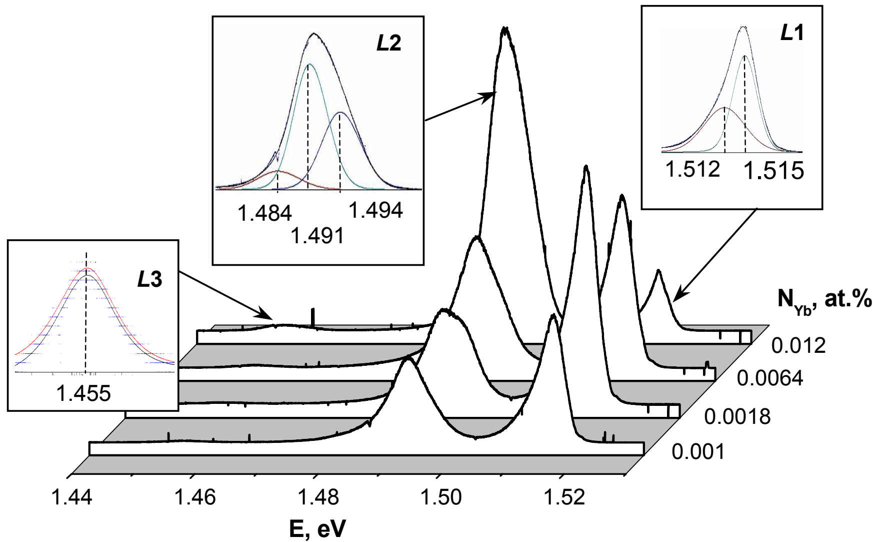

Fig. 2. Typical PL spectra of the GaAs epilayers, grown from the Yb doped solution-melts.
T = 10 K, λ_{ex} = 514.5 nm, P_{ex} = 1 mW/cm^2

N_{Yb} 10^{-3} at. %	Relative intensity of the spectral components *					
	L1		L2			L3
	1.515	1.512	1.494	1.491	1.484	1.455
1	0.51±0.05	0.49±0.05	0.02±0.01	0.98±0.01	0	1
1.8	0.47±0.05	0.53±0.05	0.24±0.02	0.76±0.02	0	1
6.4	0.50±0.03	0.50±0.03	0.21±0.03	0.55±0.03	0.24±0.03	1
12.0	0.60±0.03	0.40±0.03	0.09±0.01	0.52±0.02	0.39±0.02	1
Origin of the lines	free exciton	exciton on acceptor	e – A A = C_{As}	e – A A = Si_{As}	D – A D = C_{Ga} A = Si_{As}	D – A D = not established A = Si_{As}

∗ error in the line positions ±0.001 eV

Table 2. Composition and possible origin of the luminescence lines L1, L2 and L3 of the PL spectra shown in Fig.2 and their components revealed by fitting

increases. At low Yb concentrations, $N_{Yb} < 2\times10^{-3}$ at. %, the experimental PL line L2 is well represented by two components at 1.491 and 1.494 eV (see Table 2). Increasing N_{Yb} above 6×10^{-3} at. % yields an additional component of weak intensity with energy 1.484-1.485 eV appearing in the L2 line, which is also present in the PL spectra of the undoped samples. The intensity of that component increases with increasing N_{Yb}. The low-energy line L3 can be represented satisfactorily by one component with transition energy 1.456 eV.

Detailed investigations of the observed variations in relative intensities of the different lines composing the PL spectra, the comparison of that with corresponding changes of the electrophysical parameters of the layers and also available literature data on the possible nature of various luminescence centers in GaAs [9], enabled us to propose an interpretation of the luminescence transitions observed experimentally in our samples (see Table 2). We associate line L0 with the radiative band-to-band transition. Apparently, that line can only be observed in the undoped samples because of the lowest overall quality among all samples studied suppressing the excitonic luminescence and the highest free electron concentration (about 7.5×10^{17} cm^{-3} at room temperature). In case of GaAs the line with the energy 1.506±0.001, marked as LD line in the Fig. 1, is usually ascribed to the photoluminescence on the dislocations [9]. The absence of that line in the samples grown from the Yb doped solution-melts is an indication therefore of the significantly lower dislocation density in the doped layers than that in the undoped ones. It is important to note, that irrespective of whether or not the Yb impurity is introduced into the initial solution-melts in the optimal concentration from the point of view of the electro-physical parameters of the grown layers, it reduces effectively creation of the dislocations in the layers.

The observed Yb induced variations of concentration of the background impurities in the LPE grown GaAs layers participating in the formation of the PL spectra are interpreted as follows. At low Yb concentrations in the solution-melts, Yb binds the background impurities in the melt and prevents them from entering the growing epitaxial layers, in particular Si (which is responsible for the 1.491 eV component) and C impurity. (The Si impurity source is first of all remaining impurities in the initial polycrystal, but also the quartz reactor used to grow the epilayers). Experimentally, it correlates with significant increasing of the intensity of the free exciton luminescence line (1.515 eV), corresponding decreasing the relative intensity of the line associated with "c-band – acceptor (Si_{As})" transition (1.491 eV), increasing of the mobility of the free charge carriers in the layers. These are indications for an increased overall quality and purification level of the layers. Upon increase of N_{Yb} in the melt, the Yb atoms apparently start to enter the lattice in significant amounts, introducing with them also the bound impurity atoms, such as C and Si. The latter can at low temperatures be incorporated in As sites and act as acceptor [10]. This results in pronounced increase of the intensity of the impurity-related line (1.491 eV) ascribed to the "c-band – acceptor (Si_{As})" transition, decomposition of the free excitons with corresponding decrease of the intensity of their luminescence line (1.515 eV). Compensation of the donors responsible for the electronic conductivity of the layers occurs, leading to a decrease of the concentration and mobility of the free electrons. Because of the covalent radius of Yb is larger than that of Ga, Yb mechanically stresses and distorts the GaAs lattice when entering it. These mechanical stresses could be partially compensated by redistribution of the C atoms having covalent radius smaller than that for Ga between the As and Ga sublattices. Such a redistributing process will be accompanied by the transition of a certain amount of C atoms from the acceptor into the donor state resulting in the appearance of the additional component line with transition energy 1.485 eV in the PL spectra of the GaAs epilayers grown from the Yb-rich solution-melts, and can also be responsible for the decreasing tendency of the relative contribution to the L1 line from the excitons bound to the acceptors.

V. Conclusion

The performed investigations showed that introducing Yb impurity into the initial solution-melts for LPE growth of GaAs epitaxial layers leads to the structuring of the near-edge photoluminescence and characteristic redistribution of the relative intensities between the exitonic and impurity related spectral lines. The ratio of the intensities nonmonotonically depends on the Yb impurity concentration in the initial solution-melt, and for the Yb concentration range studied shows its optimum at $N_{Yb} = 1.8 \cdot 10^{-3}$ at. %. The observed PL behaviour is interpreted as the result of: (i) an increase of the structural perfection and purity of the grown GaAs epilayers caused by the gettering action of the Yb impurity in the initial solution-melt; (ii) changes of the concentrations and redistribution of the main background impurities Si and C between Ga and As sublattices during crystallisation of the epilayers from the doped solution-melts.

Acknowledgments

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