

EPITAXIAL GROWTH OF GaP/In_xGa_{1-x}P ($x_{\text{In}} \geq 0.27$) VIRTUAL SUBSTRATE FOR OPTOELECTRONIC APPLICATIONS

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Compositionally graded epitaxial semiconductor buffer layers are prepared with the aim of using them as a virtual substrate for following growth of heterostructures with the lattice parameter different from that of the substrates available on market (GaAs, GaP, InP or InAs). In this paper we report on the preparation of the step graded In_xGa_{1-x}P buffer layers on the GaP substrate. The final In_xGa_{1-x}P composition x_{In} was chosen to be at least 0.27. At this composition the In_xGa_{1-x}P band-gap structure converts from the indirect to the direct one and the material of such composition is suitable for application in light emitting diode structures. Our task was to design a set of layers with graded composition (graded buffer layer) and to optimize growth parameters with the aim to prepare strain relaxed template of quality suitable for the subsequent epitaxial growth.

Key words: crystal structure, organometallic vapor phase epitaxy (OMVPE), semiconducting III-V materials

1 INTRODUCTION

The excellent properties of blue light emitting diodes (LEDs) based on nitride semiconductor compounds enabled the subsequent developments in solid state lighting. The red side of the visible spectrum is successfully covered with high brightness LED diodes based on (Al_xGa_{1-x})_{0.5}In_{0.5}P material lattice matched to GaAs. The low efficiency of green sources (so called “green or yellow gap”) that are necessary for white and full color applications remains still a problem which has to be solved.

One way how to do it is to use InGaN LEDs emitting blue light which is converted down by suitable color converter- phosphor. Such sources can be used for producing white light but they can also emit nearly monochromatic, high-color-purity light [1].

Green light LED sources can be also realized on a base of (Al_xGa_{1-x})_{0.5}In_{0.5}P material lattice matched to GaAs and joined to the optically transparent GaP substrate by wafer bonding technique [2]. For green emission the content of Al has to be higher than 0.3. Increasing the Al content leads to significant decrease in internal radiative recombination efficiency and causes problems with p-type doping [3].

Another approach is to prepare the light emitting structure in Al free In_xGa_{1-x}P ternary alloy deposited directly on GaP substrate. The In_xGa_{1-x}P alloy exhibits the direct band gap structure (energy gap of 2.24 eV, emission at 554 nm) for the indium content higher than 0.27. The disadvantage of this method is that the lattice parameter of In_{0.27}Ga_{0.73}P is about a 2.1 % higher than that of GaP substrate. It is necessary to insert between the substrate and the active region an intermediate layer

enabling the change of the lattice constant from the substrate to the final active layer. Very important function of this layer is to be able to filter the dislocation propagation to the electroluminescent part of the structure. What is convenient, such graded buffer will be optically transparent for light emitted from LED because of decreasing band-gap with increasing indium content in the growth direction.

Concept of epitaxial graded composition buffers is well known from GaAs/InGaAs [4] and Si/SiGe [5] systems but much less often it is used for GaP/InGaP. As it was shown in [6] the main problem that has to be resolved is to avoid the tendency for material degradation that occurs markedly for $x_{\text{In}} > 0.26$.

In our paper we report on the properties of a set of step-graded GaP/In_xGa_{1-x}P buffers which differ only in the V/III ratio in the reactor applied during the growth. We will show that there exists the boundary value of phosphine (PH₃) molar ratio in the reactor, under which InGaP layers decompose. The influence of the V/III ratio on layer structure will be demonstrated by transmission electron microscopy (cross-sectional micrographs), atomic force microscopy (AFM surface topology), and low temperature photoluminescence measurements (PL).

2 EXPERIMENTAL PROCEDURE

Buffer structures under study were prepared in AIX-TRON AIX 200 IR-heated low-pressure reactor. Phosphine (PH₃), trimethylgallium (TMGa, -10 °C) and trimethylindium (TMIn, 17 °C) were used as precursors. Carrier gas was palladium diffused hydrogen with a total flow of 6.5 slpm.

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Table 1. Structure and properties of buffer systems under investigation. Mole fraction of TMGa in the reactor 5.69×10^{-5} was kept constant. Mole fraction of TMIn was increased from 2.64×10^{-6} for In_{0.03}Ga_{0.97}P to 3.81×10^{-5} for In_{0.27}Ga_{0.73}P. Composition in the gas phase for the final layer expressed as the ratio of partial pressures in the reactor $p_{\text{TMIn}}/(p_{\text{TMIn}} + p_{\text{TMGa}})$ was the same (0.401) for all samples. Sample 7a was prepared in order to examine the influence of reduced grading rate on buffer properties.

Sample No.	1	2	3	4	5	6	7	7a
Number of In _x Ga _{1-x} P layers	8	8	8	8	8	8	8	26
Compositional step Δx_{In} (%)	3	3	3	3	3	3	3	1
Thickness of In _x Ga _{1-x} P layer (nm)	300	300	300	300	300	300	300	200
Grading rate R_{grad} (% $x_{\text{In}}/\mu\text{m}$)	10	10	10	10	10	10	10	5
V/III	80	80-100	80-150	80-200	80-250	80-300	80-350	80-350
PH ₃ mole fraction - initial value	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}	4.62×10^{-3}
PH ₃ mole fraction - final value	6.92×10^{-3}	9.54×10^{-3}	1.43×10^{-2}	1.91×10^{-2}	2.38×10^{-2}	2.85×10^{-2}	3.31×10^{-2}	3.31×10^{-2}
x_{In} (%) (calculated from $\Delta a/a_{\perp}$ measured by X-ray)	31.2	32.8	33.3	33.9	34.0	33.8	33.9	35.5
Bragg peak FWHM (arcsec)	471	218	258	287	257	287	200	179
PL (6 K) peak energy (eV)	Peak1 1.9912 Peak2 2.079 Peak3 2.227	2.201	2.184 1.990	2.173	2.175	2.170	2.183 1.707	2.148 1.684
PL (6 K) peak intensity (a.u.)	Peak1 6.09×10^{-7} Peak2 3.27×10^{-7} Peak3 3.80×10^{-7}	2.01×10^{-4}	1.60×10^{-4} 4.08×10^{-6}	3.04×10^{-4}	2.92×10^{-4}	3.12×10^{-4}	4.28×10^{-4} 3.71×10^{-8}	7.43×10^{-4} 5.01×10^{-8}
PL (6 K) FWHM (meV)	Peak1 199 Peak2 149 Peak3 46	31	26 45	26	27	26	29 31	22 34
R_q (nm) (AFM)	47	19	20	31	26	31	18	52
x_{In} (%) (calculated from PL peak position)	Peak1 0.414 Peak2 0.349 Peak3 0.239	0.258	0.271 0.415	0.279	0.278	0.281	0.272 0.625	0.298 0.642

The substrates were LEC grown sulphur doped GaP wafers (Girmet) with epi-ready finalization. The surface orientation was $(100) \pm 0.25^\circ$.

The reactor pressure of 20 mbar, the growth temperature of 740 °C and the growth rate varying from 0.75 $\mu\text{m}/\text{h}$ for GaP to 1.26 $\mu\text{m}/\text{h}$ for final 1000 nm thick In_xGa_{1-x}P layer were chosen after the optimization procedure described in [7]. Structures consisted of 300 nm thick GaP followed by eight 300 nm thick In_xGa_{1-x}P layers. The composition of adjacent layers was changed in steps, the composition increase in one step was $\Delta x_{\text{In}} = 0.03$. The compositional change was realized by increasing the TMIn flow during the first 4 seconds of deposition of the particular In_xGa_{1-x}P layer, while the TMGa flow was kept constant. The layer composition was set up by changing the composition in the gas phase expressed as a ratio of $p_{\text{TMIn}}/(p_{\text{TMIn}} + p_{\text{TMGa}})$, where p_{TMIn} and p_{TMGa} are partial pressures of TMIn and TMGa in the reactor. As was described in [7], firstly we calibrated the dependence $x_{\text{In}} = f(p_{\text{TMIn}}/(p_{\text{TMIn}} + p_{\text{TMGa}}))$ experimentally, from a set of 1.3 μm thick In_xGa_{1-x}P single layers prepared directly on GaP and GaAs substrates varying the composition in the gas phase. The layer composition x_{In} was determined by the X-ray diffraction and calculated from the perpendicular lattice mismatch $\Delta a/a_{\perp}$ assuming that the layer strain is fully relieved. It was not possible to measure the degree of relaxation with our X-ray diffractometer. Our later experience showed that the in-

dium content in In_xGa_{1-x}P calculated from $\Delta a/a_{\perp}$ depends on the concrete type of underlayer. The composition x_{In} derived from $\Delta a/a_{\perp}$ for the In_xGa_{1-x}P deposited on step graded buffer is higher than for the layer prepared from the gas phase of the same composition directly on the GaP substrate. There are two possible ways to explain this fact. The first one is that layers on buffer are not fully relaxed. If they are compressed the measured $\Delta a/a_{\perp}$ is higher (and thereby also x_{In}) as it would be in fully relaxed layers. Another explanation is that indium incorporation is higher in layers prepared on graded buffer. We believe that both factors have to be considered. The difference of 5 % x_{In} obtained from X-ray measurement seems to be too high regarding the compositional difference between two last layers in the structure which is only 3 % x_{In} . Composition calculated from the PL peak position is also higher for layers on buffer, but the difference is only 1 % x_{In} . The important growth parameter whose influence on the structure properties was studied is the V/III ratio. The starting value for the V/III ratio should be about 80, as it was shown in [6]. Because the buffer compositional change was realized by increasing the TMIn mole fraction in the reactor with constant TMGa mole fraction, for maintaining constant V/III ratio the PH₃ mole fraction was periodically increased. This is the case of the Sample 1. For Samples 2–7 the V/III ratio was increased during the growth from 80 (for GaP) to the final value. The final value changed from 100 in the Sample 2 to 350 in the Sample 7. During the growth

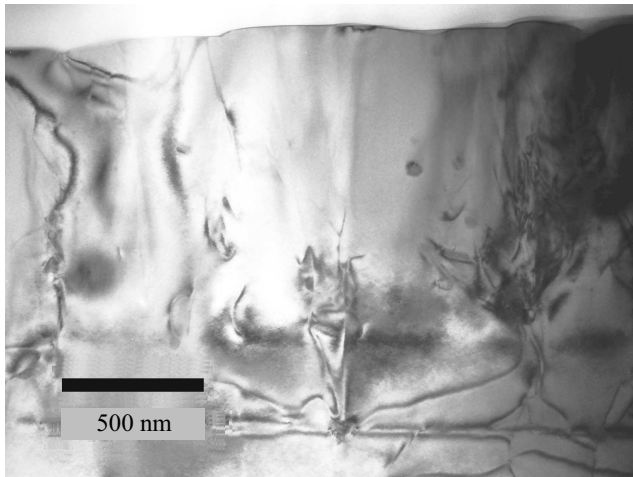


Fig. 1. Cross-sectional TEM micrograph of Sample 1 grown at $V/III=80$. Figure shows the top 1000 nm thick $In_{0.27}Ga_{0.73}P$ layer and the last 300 nm $In_{0.24}Ga_{0.76}P$ layer.

of one structure the V/III ratio was increased in uniform steps from 80 to the final value. The change in the PH_3 flow was realized 100 s before the change of the $TMin$ flow. Sample 7a is different from Sample 7 in half value of grading rate and in dividing the compositional change into 26 steps with $\Delta x_{In} = 1\%$. It is included in the set in order to check the influence of lower grading rate on buffer properties.

The summary of buffer systems under investigation together with the parameters from characterization is presented in the Table 1.

The surface structure was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) using field emission LEO 1550 SEM in secondary electron mode and Topometrics Explorer AFM. AFM data were collected in non-contact mode with scanned area of $50 \times 50 \mu m^2$. Cross-sectional dislocation structure was examined by transmission electron microscopy. TEM investigations were performed using (110) cross-section slides prepared by gluing of two InGaP surfaces together. The samples were thinned by polishing and Ar^+ ion milling. The layer lattice mismatch was evaluated by the standard X-ray diffractometer using CuK_α radiation and the (400) reflection. Low-temperature photoluminescence spectra were measured at $T = 6$ K. Samples were excited with the 488 nm line from an Ar ion laser. The laser beam was focused at normal incidence to a spot with the intensity of $1 W/cm^2$. The luminescent signal was filtered using a quarter-meter monochromator and was detected by a silicon photodiode using a standard lock-in technique. The layer composition was calculated from the PL peak position after [8] using the expression $E_g(x) = 2.549 - 1.347x$.

3 RESULTS AND DISCUSSION

Process of layer degradation is strongly affected by the stability of the growing surface. The reason for ternary

layer decomposition can be the spinodal decomposition or nucleation. Because of the stabilizing influence of the surface energy on the growth interface epitaxially grown layers are decomposed due to the process named in the literature as the surface-directed spinodal decomposition or spinodal-like decomposition. The result is the compositional modulation observed in the $[01\bar{1}]$ direction. Compositionally modulated regions are elongated in the $[100]$ direction with the spacing in the range of 10–100 nm. In InGaP they were observed in [9] and [10]. Compositional modulations generate stresses, which result in the surface roughening. Theoretically, if it would be possible to maintain the layer surface perfectly flat, the spinodal decomposition should be forbidden [11].

More complicated situation occurs during the growth of strained layers. The misfit induced elastic strain acts destabilizing on the growing film surface. The most effective process for relieving misfit strain is the glide of misfit dislocations parallel to the growing surface. If gliding misfit dislocations are immobilized, for example on branch defects, dislocation pileups are formed and the surface roughness is increased [6]. After [12] the compressive strain in alloy thin film is much more destabilizing than the tensile strain. The influence of the strain sign on the growth mode in $In_{0.25}Ga_{0.75}P$ prepared on GaP and GaAs substrates was studied in [13]. It was shown that, contrary to [14], tensile strained $In_{0.25}Ga_{0.75}P$ is much more compositionally modulated than the compressive strained layer. The reason was the higher surface roughness in tensile layer which promotes the effect of In segregation.

The process of layer degradation has to be considered also together with ordering [10]. We assume that in our samples grown at the $740^\circ C$ the effect of ordering is minimized.

From the previous discussion it is clear that for suppressing the material decomposition it is necessary to maintain the growing surface as smooth as possible. The surface smoothness is influenced by the structure design and by the choice of the growth parameters. Details about the structure design were presented in [7]. We have shown that type of structure investigated in this paper is suitable for use as a buffer. Misfit strain is relieved through gliding misfit dislocations and the density of threading dislocations is low. In [7] we have shown that structural properties are influenced not only by structural parameters but also by growth parameters. Two identical buffers prepared using the same growth conditions except of the V/III ratio (80 and 350) exhibited completely different crystallographic structure.

In the next we will discuss properties of buffers as a function of the V/III ratio in the reactor. Samples were deposited at $V/III=80, 100, 150, 200, 250, 300$ and 350.

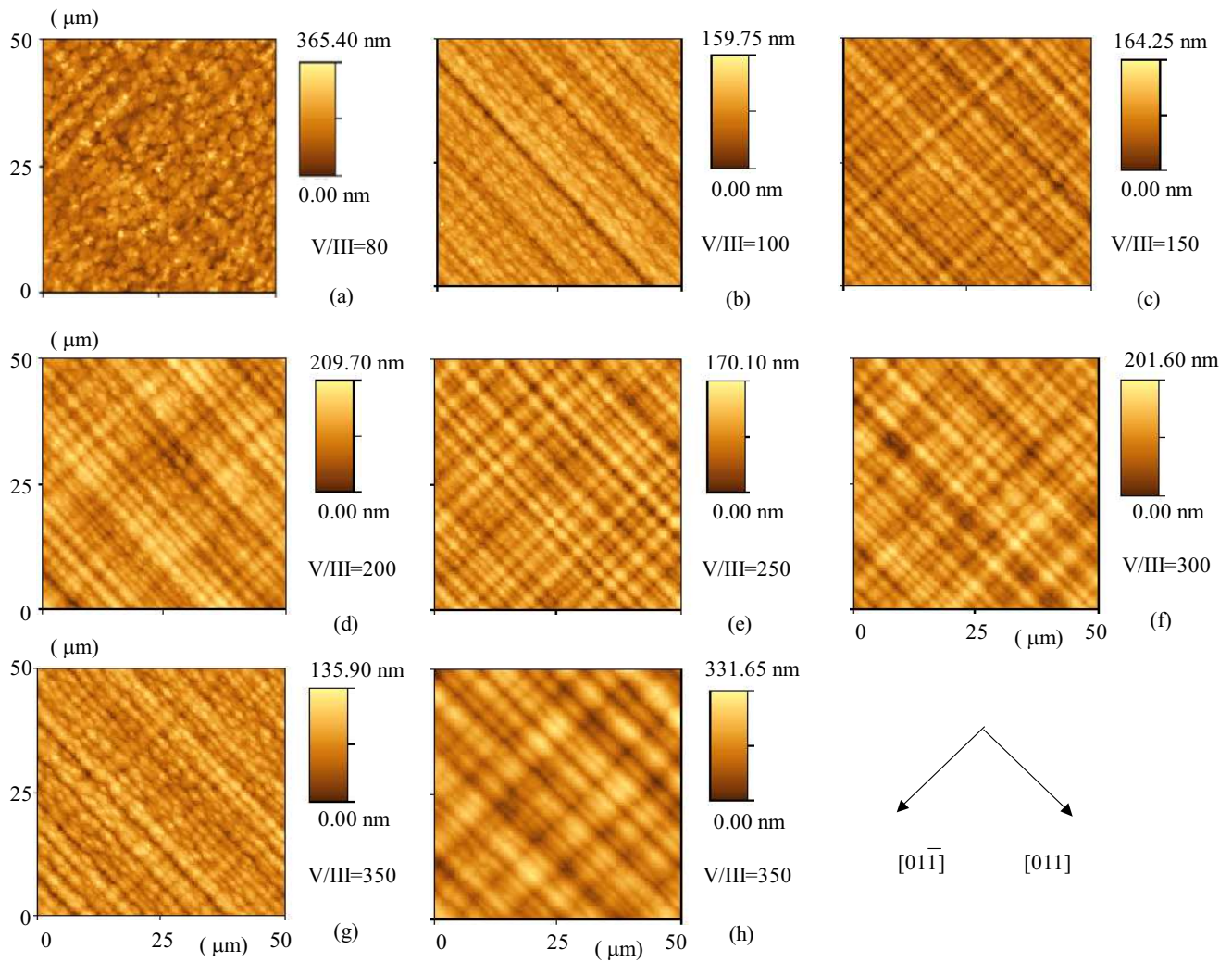


Fig. 2. AFM topographic images of buffer systems under investigation. Figure a) belongs to Sample 1, b) to Sample 2, c) to Sample 3, d) to Sample 4, e) to Sample 5, f) to Sample 6, g) to Sample 7 and h) to Sample 7a.

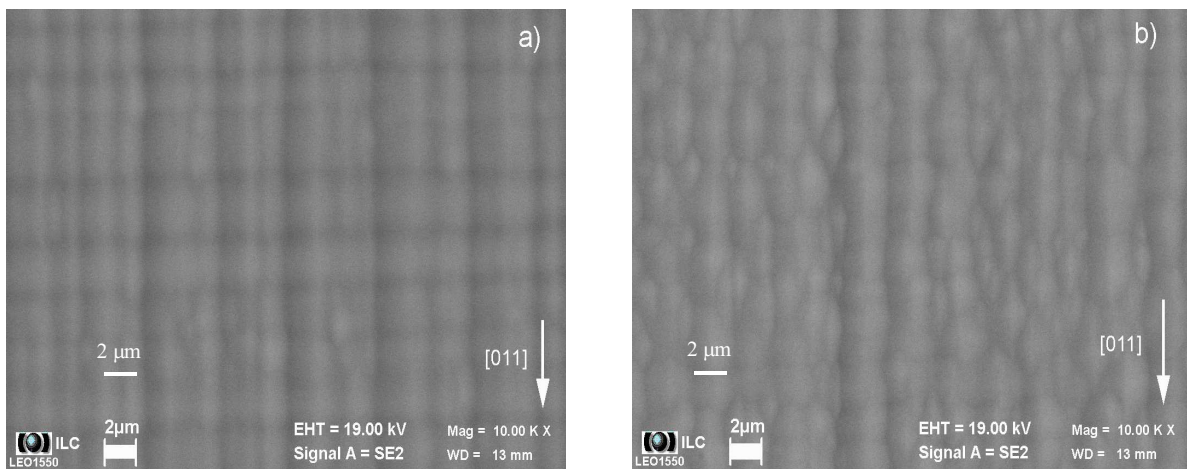


Fig. 3. Two kinds of surface structure observed in SEM for samples with $V/\text{III} \geq 100$: (a) – is a top view SEM micrograph of Sample 5 (similar is for Sample 6); (b) – belongs to Sample 3 (similar surface have samples 2, 4, 7, 7a).

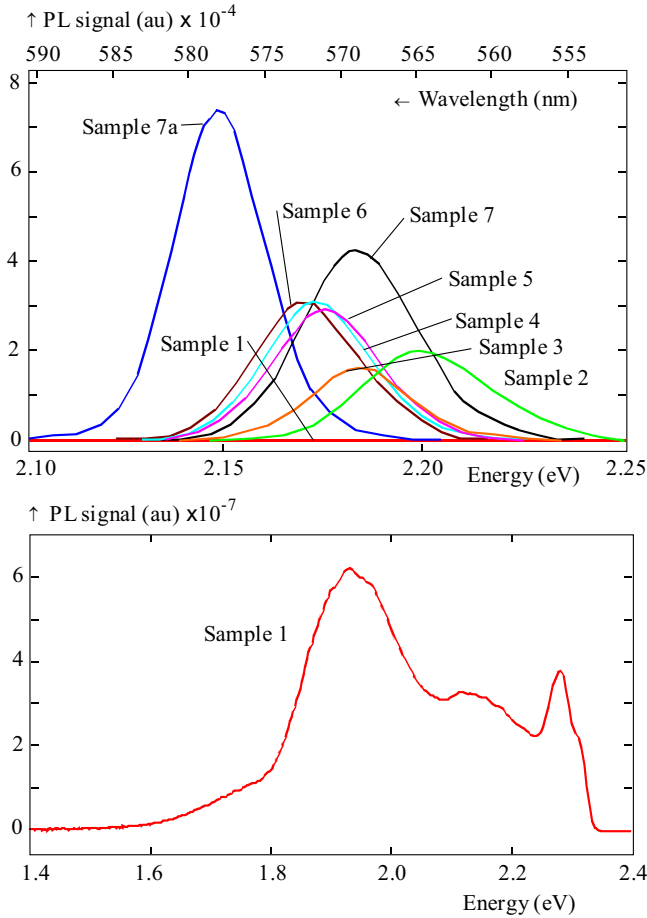


Fig. 4. The comparison of 6K PL spectra for all samples under investigation. The peak position, occurrence of additional peaks and peak FWHM are presented in the Table 1

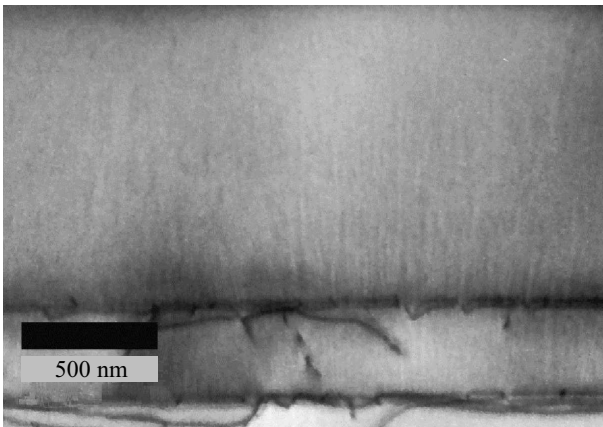


Fig. 5. Cross-sectional TEM micrograph of Sample 5 grown at $V/III=250$ with typical spinodal-like contrast observed in the last two layers

Low V/III ratio

The surface of Sample 1 grown at constant $V/III=80$ was grey and opaque. The SEM and AFM surface analysis show the granular surface completely different from

the surface of Samples 2–7. The luminescence signal is of low intensity and consists of separated peaks localized in the energy interval 1.6–2.3 eV. This indicates the compositional inhomogeneity or existence of phases with various compositions. The cross-sectional TEM micrograph in Fig. 1 reveals vertical features of strong contrast modulation in the last two layers directed toward the surface and confirms the crystalline non-uniformity.

Higher ratio $V/III \geq 100$

All samples grown with $V/III \geq 100$ are of specular surface with visible smooth cross-hatch pattern. AFM topographic images in Fig. 2 show the dependence of the cross-hatch dislocation pattern shape on the V/III ratio. With increasing V/III ratio corrugated dislocation segments straighten, but for $V/III=350$ they are again corrugated. Fig. 3a shows the surface morphology with straight dislocation segments observed in SEM for samples 5 and 6. Figure 3b is typical for samples 2, 3, 4, and 7.

PL spectra depicted in Fig. 4 confirm the trend seen from the evolution of surface morphology in the meaning that PL spectra for Samples 4, 5 and 6 prepared with V/III from interval 200–300 indicate the best structural quality. PL spectra of these samples are composed of only one peak which intensity and energy does not depend on the V/III ratio. PL spectrum of Samples 3, 7, and 7a contain additional PL peak at lower energies. Cross-sectional TEM micrographs of these samples show homogeneous structure with spinodal-like contrast similar to that presented in [10]. This contrast is seen in the last 1000 nm thick layer and eventually also in the few 300 nm thick underlying layers. The difference between samples is in the number of layers in which this contrast can be seen. Figure 5 shows the cross-sectional TEM micrograph of Sample 5 with the spinodal-like contrast occurred in the last two layers. In Sample 6 this contrast is clear in the last layer; in Sample 7 it is evident in the last four layers.

The parameters of Sample 7a did not confirm the expected improvement in the buffer quality due to the lowered grading rate to $5\%x_{In}/\mu m$. The strain relaxation is probably not as effective as in the buffer with 8 step-graded layers what leads to the higher surface roughness.

4 CONCLUSION

Strained InGaP epitaxial layers incline to degradation. During the growth it is very important to maintain the growing surface smooth. It can be achieved by the appropriate structure design and by the choice of optimal growth parameters. The stability of the InGaP (100) growing surface is strongly dependent on the surface coverage with $[01\bar{1}]$ P dimers. The surface concentration of the $[01\bar{1}]$ P dimers is dependent on the PH_3 partial pressure in the reactor or on the V/III ratio respectively. The

relatively small decrease in the V/III ratio from 100 to 80 leads to essential change in the growth mechanism. We suppose that for $V/\text{III} < 100$ (PH_3 partial pressure in the reactor p_{PH_3} was 0.191 mbar for $V/\text{III} = 100$) the surface is not fully covered with $[01\bar{1}]$ P dimers and it is unstable. Increasing the PH_3 partial pressure stabilizes the surface, improves the layer smoothness, and suppresses the tendency to degradation. There exist the optimal range of the V/III between 200 ($p_{\text{PH}_3} = 0.382$ mbar) and 300 ($p_{\text{PH}_3} = 0.569$ mbar). Further increase of the V/III ratio leads to the less stable growing surface probably due to the formation of the second excess phosphorus phase [14].

Acknowledgements

This contribution/publication is the result of the project implementation: Centre of Excellence for New Technologies in Electrical Engineering, ITMS code 26240120011 and Effective Management of Production and Consumption of Energy from Renewable Sources (ENERGOZ), ITMS code 26240220028, supported by the Research & Development Operational Programme funded by the ERDF.

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Received 27 October 2010

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Alexander Šatka, biography not supplied.