GaInPN/Si HETEROSTRUCTURE GROWTH BY METAL-ORGANIC VAPOUR PHASE EPITAXY

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The growth of InGaPN epitaxial layers on silicon substrates by metal-organic vapour phase epitaxy using dimethylhydrazine, trimethylgallium, trimethylindium and phosphine precursors is reported. In order to reduce interface problems connected with hetero-bonds and antiphase domain formation, a very thin buffer layer of GaP has been grown on the hydrophobic silicon surface. The layers are prepared at temperature of 630°C and have been characterized by high-resolution X-ray diffraction, atomic force microscopy, photoluminescence and Raman scattering. The growth occurs through 3 dimensional processes. Mean surface roughness as high as 20-30 nm is observed and phase separation is evidenced.

1. Introduction

The development of devices based on III-V semiconductors is still hindered by the high cost mainly due to the substrate. Researchers have been working during a period of twenty years or more in order to use silicon as a substrate, but this opportunity has been and is frustrated until now by the presence of lattice mismatch and related extended defects.

Recently, the discovery that III-V alloys containing nitrogen have a strong bowing parameter has given new hope to this research; both families of InGaPN and GaPAsN, having mixing either on both sublattices or only on that of V element group, are able to match precisely Si substrates and in principle they can span an energy gap value ranging approximately from 2.2 to 0 eV, useful for any class of application from solar cells to field effect transistors [1]. Unfortunately, dilute nitrides still have a lot of problems which need to be solved concerning growth process and physical characteristics.

GaInPN alloys can be grown lattice matched to silicon substrate while varying the band-gap by the balanced modulation of the [N]/[In] ratio. GaInPN alloy, with a band-gap of about 1.7 eV, can therefore be lattice matched to Si, and is an excellent candidate for the realization of high efficiency multiple junction solar cells. Y. Fujimoto et.al. [2] have reported for the first time the growth by solid source Molecular Beam Epitaxy of dislocation free InGaPN/GaPN quantum well structure on Si substrate.

The growth of this material by Metal-Organic Vapour Phase Epitaxy (MOVPE) is not an easy task, as it is known that the presence of indium reduces the nitrogen incorporation ratio in this type of alloys [3]. Sanorpim et.al. [4, 5] grew lattice matched InGaPN alloys on GaP substrate by using various ratios of In and N content and characterized the epitaxial layers by various techniques; they showed that the N content decreased from 2.6 % to 1.6% while the In content was increased from 0 to 10.9 %,

Another problem related with heteroepitaxy originates from the different lattice constant and thermal expansion coefficient of the epitaxial layer and of the substrate. It can cause a transition from 2D to 3D growth modes (Stransky-Krastanov mechanism).

A most important effect concerns the composition modulation of the alloy films or even a phase separation. Several variables are responsible for this effect: sizes of the different alloy species, average misfit with respect to the substrate, relative mobilities of the different alloy species, bond energies and of course deposition variables such as deposition rate and alloy composition [6, 7]. For dilute III-V nitrides, in case of phase separation, the lattice mismatch does not only occur with the underlying substrate but also laterally between N-rich and N-poor regions within the film [8]. It has also been shown that the incorporation of indium in III-V alloys facilitate 3D growth and pit formation [9].

The use of non-polar substrates such as silicon substrates for instance adds an extra difficulty: the possible presence of anti-phase domains.

To our knowledge, there is no complete report about MOVPE growth and characterization of InGaPN on Si substrate; in this paper we report on our preliminary results on this subject. Several InGaPN layers with different N content were grown on Si substrate using MOVPE technique and characterized by high-resolution X-ray diffraction (HR-XRD), atomic force microscopy (AFM), photoluminescence (PL) and Raman scattering.

2. Experimental Procedures

All the InGaPN alloy films were grown by low-pressure (46 torr) MOVPE. Trimethylgallium (TMG), Trimethylindium (TMIn), Dimethylhydrazine (DMHy) and phosphine were used as the source materials for Ga, In, N and P respectively, and hydrogen was used as carrier gas. Before the growth, (100) silicon substrates were degreased and chemically etched using the method described by Ishizaka and Shiraki [10] and then immediately placed in the reactor chamber. Thin (nominally 20 nm) GaP buffer layers were grown on Si substrate at 650°C in order to suppress the generation of threading dislocations, since GaP has a small

lattice mismatch of about 0.4% with Si. [11] After GaP deposition the substrate temperature is decreased to 630°C under DMHy and PH_3 flows and 350 nm thick $Ga_{1-y}In_yP_{1-x}N_x$ epitaxial layers were grown for 15 minutes at this temperature. After the growth the samples are cooled down to room temperature in PH_3 and DMHy atmosphere.

For comparison we have also grown samples on (100) semi insulating GaAs and GaP substrates simultaneously with samples on Si.

Structural characterization has been done by high-resolution X-ray diffraction (HR-XRD) by using an X'pert Philips apparatus.

Surface morphology changes due to incorporation of nitrogen were characterized using a Digital Nanoscope IIIa atomic force microscope.

The photoluminescence was excited by either the 488 nm line of a continuous argon laser or the 337.1 nm line of a Photonics LN 1000 pulsed nitrogen laser. The argon laser excitation power level was below 100 mW for a spot diameter about 1.5 mm. The nitrogen laser pulses had 0.6 ns width and 1.4 mJ energy. The photoluminescence was dispersed using a Horiba Jobin Yvon HR460 monochromator and detected by a multi-channel CCD detector (2000 pixels). Emitted light was collected from the same side as the excitation by an optical fibre placed at about 1 cm from the sample surface. Temperature dependence of the emission was analyzed from 4 to 300K in a temperature controlled Janis Supertran-VP system. The setup has a resolution of 0.3 nm/point for slits narrower than 30 μm.

Raman measurements were performed with a Horiba Jobin Yvon LabRam apparatus, in the Physics Department of the University of Parma, using a He-Ne laser emitting at 632 nm and a $Z(-,-)\bar{Z}$ scattering geometry. The laser spot diameter is about 1 μm and the spectral resolution is estimated about 2 cm^{-1}. The measurements were performed at room temperature between 20 and 1100 cm^{-1}.

3. Results and Discussion

3.1 High-resolution X-ray diffraction

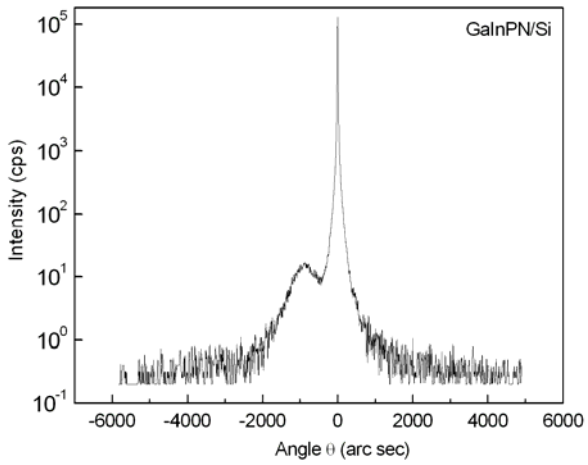

Fig. 1. HR-XRD pattern of a 420 nm thick GaInPN layer on silicon substrate.

Fig. 1 shows part of the X-ray diffraction pattern of a 420μm thick GaInPN film on silicon substrate. The sharp peak is due to the (004) reflection from the silicon substrate while the broader one is the corresponding peak of the layer. Fig. 1 clearly shows that the layer is not lattice matched to the substrate. The lattice mismatch $\Delta a/a$ measured for layers grown on silicon substrate is 0.66 % while it is 3.3 % for layers grown on GaAs substrates.

The full width at half maximum of the GaInPN peak in fig. 1, about 680 arcsec, shows that the layers grown on silicon substrates exhibit a reasonable degree of crystallinity. If islands are present, they are only slightly misaligned.

3.2 Atomic force microscopy

Figs. 2 (a) and 2 (b) show AFM images of GaInPN samples that are simultaneously grown on Si and GaAs substrates. It can be observed that in both cases the growth occurs through the formation of 3D islands. The surface roughness of the samples grown on Si substrates is about 2-3 times smaller than that of samples grown on GaAs, and in any case it increases when increasing the nitrogen concentration in the gaseous phase.

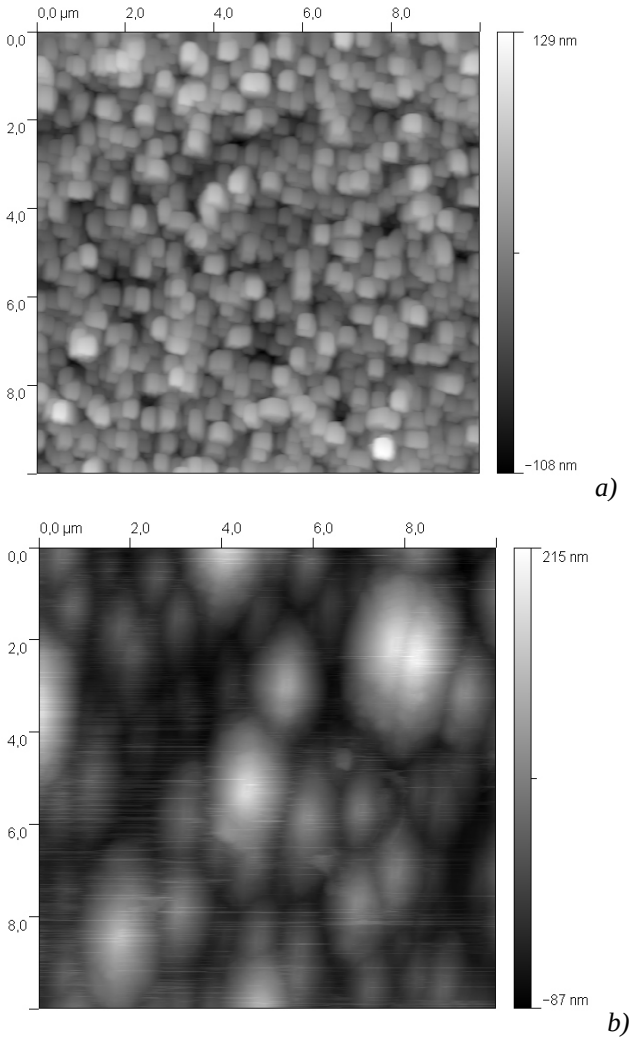

Fig. 2. AFM images of GaInPN layers on (a) silicon substrate, (b) gallium arsenide substrate.

This behaviour can be understood assuming that the lattice mismatch with the substrate plays a prevailing role on heteroepitaxial growth conditions. As regard the role of nitrogen concentration it is possible to suppose that during deposition of the layer at the beginning the adatoms migrate to form N-rich and N-poor regions, driven by spinodal

decomposition. With further deposition, i.e. when the thickness increases, the lateral strains between these neighbouring regions increase substantially increasing the surface roughness [8].

3.3 Photoluminescence

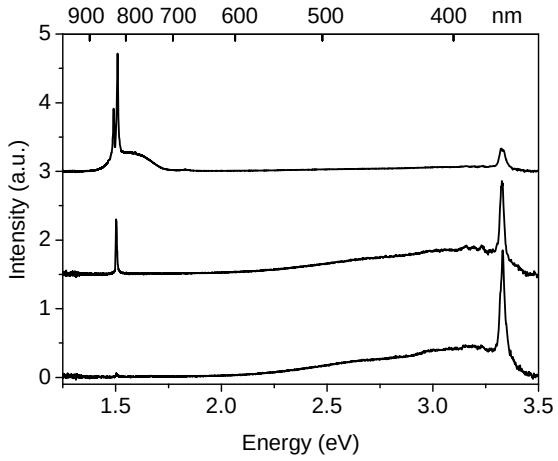

Fig. 3. PL spectra at 5K of GaInPN layers excited by the 337.1nm line of a nitrogen laser. For clarity, the middle and upper spectra have been shifted upwards by 1.5 and 3 a. u. respectively. The upper spectrum concerns a layer grown on GaAs substrate while the two lower ones concern layers grown on silicon substrates.

Fig. 3 shows the overall photoluminescence spectra of three samples, one grown on GaAs substrate and the two others grown on silicon substrates, excited by the 337.1 nm line of a nitrogen laser. The spectra are dominated by relatively sharp lines around 3.3eV and 1.5eV. The lines at about 3.3eV are excitonic transitions originating from GaN-like regions of the samples. One could wonder whether these GaN-like regions consist of zincblende or wurtzite type of GaN. In fact the PL line in our samples lies at an energy in between those observed in zincblende and wurtzite type GaN.[12] Most likely, it corresponds to the emission of wurtzite GaN like regions suffering tensile strains. The PL spectrum of the sample grown on GaAs substrate shows two relatively sharp lines around 1.5eV. The highest energy one is due to the emission of the GaAs substrate. The other "sharp" line around 1.5eV is probably due to InP-like regions of the layers. These lines are at higher energy than the excitonic lines in bulk InP; this could be due to the fact that the InP-like islands in our samples suffer compressive strains. In this respect, it is of interest to note that in the layers grown on silicon substrate, this line is at higher energy than in the layer grown on GaAs substrate; this could be due to the fact that InP has a higher lattice mismatch with silicon than with GaAs. The band-gap of InN is still a subject of debate, but it should be noted that one report mentions that the band gap of zincblende InN is about 1.4eV at room temperature.[13] Therefore zincblende InN could be an alternative to InP for explaining the sharp lines around 1.5eV. However, InN should be submitted to tensile strains in our layers that should be larger in the samples grown on GaAs substrates than in the samples grown on silicon substrates; therefore, in the InN islands hypothesis, one would expect the "sharp" line observed around 1.5eV in our samples to be at higher energy in the layers grown on GaAs than in those grown on silicon substrate that contradicts the experimental observation. We therefore favour the InP islands hypothesis.

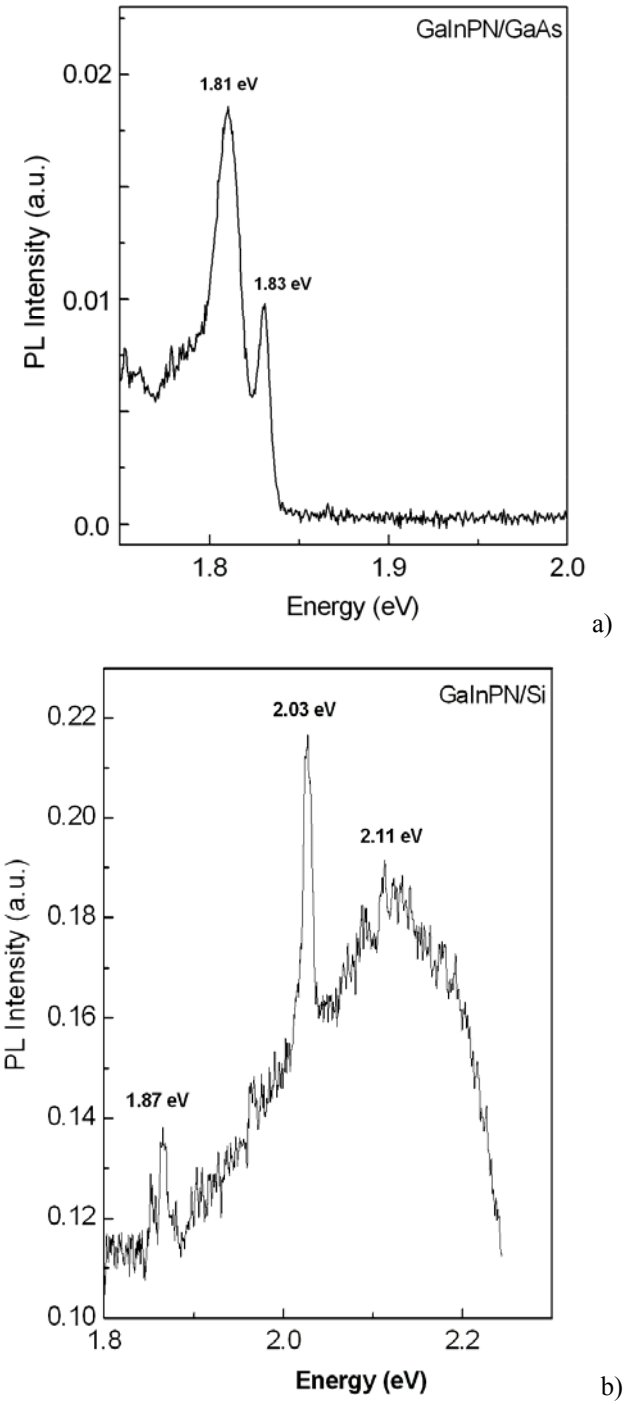

Fig 4. PL spectra at 5K excited by the 488 nm line of an argon laser of GaInPN layers (a) on gallium arsenide substrate, (b) on silicon substrate.

Apart from the relatively sharp lines discussed above, fig.3 evidences broad PL bands in our sample. In the sample grown on GaAs substrate, this band is at the high-energy tail of the 1.5eV lines whereas, in the samples grown on silicon substrates, it is at the low energy tail of the 3.3eV line. This seems to indicate that the PL in the sample grown on GaAs substrate originates from indium rich regions of the samples whereas it comes from gallium rich regions in the samples grown on silicon substrates. These broad PL bands contain some sharp features. Fig 4 (a) shows such features observed

in samples grown on GaAs substrate and fig 4 (b) shows those observed in samples grown on silicon substrates.

One should be careful when analyzing the spectra shown in fig. 3 and in particular the intensities of the various features evidenced in these spectra. PL is not a quantitative technique because it is strongly affected by the non-radiative recombination centres present in the material. The concentration of these non-radiative centres could be much larger in the alloyed regions than in the GaN-like ot InP-like islands. Therefore, the fact that the "sharp" PL lines around 3.3 and 1.5 eV seem to dominate the spectra shown in fig. 3 does not mean at all that the layers consist mainly of GaN-like and InP-like islands. It is also important to notice that PL can evidence mainly direct band-gap material; therefore the composition range corresponding to indirect band-gap material cannot be evidenced from PL spectra.

The photoluminescence measurements clearly evidence that phase separation occur in our layers. The appearance of a GaN-like phase has also been reported for GaInAsN layers grown by molecular beam epitaxy on GaAs substrates [14].

3.4. Raman scattering

Fig. 5 shows the Raman scattering spectra on the one hand of a silicon substrate and on the other hand of GaInPN layers grown on both silicon and GaAs substrates. Apart from the phonon modes due to the substrates, two modes are observed at 364 and 401.8 cm^{-1} that are GaP-like transverse (TO) and longitudinal (LO) optical phonons respectively. Weak overtones at 715 and 779 cm^{-1} are also visible in the spectra of the layers grown on silicon substrates; they are not observed in the layers grown on GaAs substrate because of the strong substrate photoluminescence. There is no evidence of the presence of indium, such as reported by Peternai et al. [15] for instance, in these Raman scattering spectra.

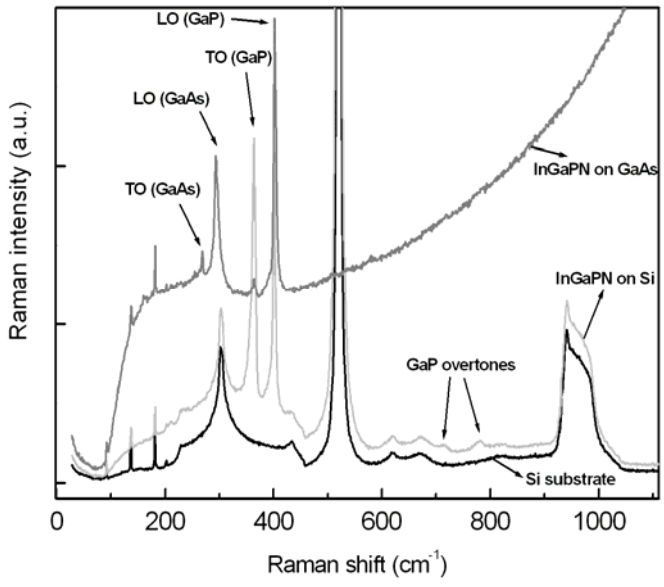

Fig. 5. Raman scattering spectra at room temperature of: a silicon substrate, a GaInPN layer grown on silicon substrate and a GaInPN layer grown on gallium arsenide substrate.

Fig. 6 shows the Raman scattering spectra on the one hand of GaP substrate and on the other hand of a InGaPN layer deposited on this substrate. Indeed, the spectra are dominated by GaP-like phonons as it was already observed in fig. 5. However, smaller features are observed between the GaP phonon modes and their overtones.

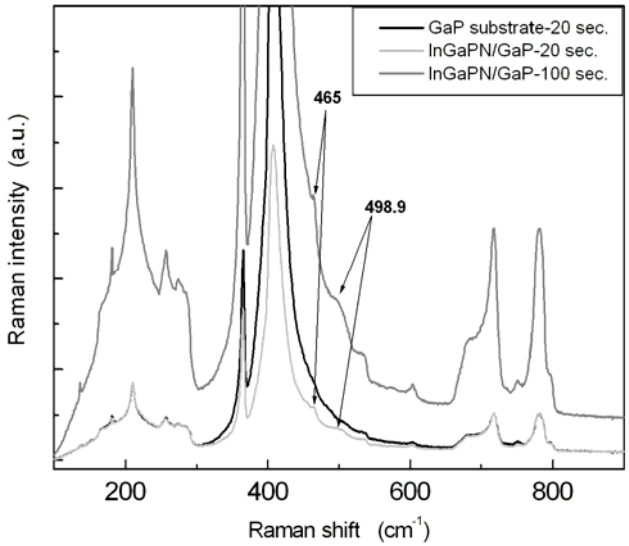

Fig. 6. Raman scattering spectra at room temperature of: a gallium phosphide substrate and a GaInPN layer grown on gallium phosphide substrate. The times indicated in the figure are the acquisition times of the experiments.

Two modes at 498.9 and 465 cm^{-1}, which are not observed in the substrate spectrum, are observed in the layer spectrum. The mode at 498.9 cm^{-1} can be assigned with certainty to the ^{14}N nitrogen isotope in a GaP-like environment. Thomson and Newman [16] identified the ^{14}N local vibrational mode at 496.1 cm^{-1} in GaP by absorption spectroscopy at 77 K. A similar mode has been reported at 497.3 cm^{-1} by Raman spectroscopy at room temperature in $GaP_{0.979}N_{0.021}$ [17]. The observation of this mode in our layers clearly evidences the presence of nitrogen in the GaP-like phase and therefore that it should more appropriate to label it GaPN-like phase.

The mode at 465 cm^{-1} is reminiscent of the mode that had been first observed by Raman scattering at 464.5 cm^{-1} in GaP by Hon et al. [18] These authors originally suggested that oxygen or nitrogen could be responsible for this mode, but it has been clearly demonstrated later on that it was due to ^{28}Si at gallium sites [16]. Therefore, the observation of the mode at 465 cm^{-1} in our samples suggests an unintentional contamination of our layers by silicon [19]. It is not clear what could be the origin of this contamination. As an alternative interpretation of the mode at 465 cm^{-1} in our samples, one could think at a mode due to ^{14}N having not only gallium first neighbours, but for instance a mixing of gallium and indium first neighbours or a nitrogen pair. In such cases, the local symmetry would be lower than T_d and several modes should be observed that is not the case in our observations.

An interesting feature is the mode at 605.6 cm^{-1} that is due to unintentional carbon impurities at phosphorus sites in GaP [16]. This mode is observed in the substrate; as a matter of fact, it is known that GaP substrates grown by liquid encapsulation Czochralski technique contain unintentional carbon impurities and that this local mode is commonly observed in them [20]. The important issue is that the

intensity of this mode is not larger in the layer spectrum than in the substrate one. This means that, even though organo-metallic precursors used for the growth of the epitaxial layer contain carbon, they do not induce a noticeable carbon contamination of the layer.

Therefore, Raman scattering experiments have evidenced the presence of GaP and/or GaPN phases in our layers. No evidence of the presence of indium or GaN-like phase in the layers comes out from them; this contrasts with the photoluminescence experiments. It has to be recalled that the Raman scattering experiments have been performed using an helium-neon laser; the energy of the photons emitted by this laser, about 2 eV, is close to the low energy tail of the GaP or GaPN absorption edge. Therefore the use of this laser favours the observation of GaP and GaPN-like phases in the layers. GaN is too transparent at 2 eV for the helium-neon laser beam interacting efficiently with this material and InP, which has a direct band-gap, is too absorbing at 2 eV for allowing to evidence InP Raman modes.

4. Conclusion

We have grown InGaPN alloys by MOVPE on GaAs, GaP and silicon substrates and analyzed the layers by complementary techniques : HR-XRD, AFM, PL and Raman scattering. The layers grown on silicon substrate are slightly lattice mismatched (0.66 %). It appears that the growth occurs through 3D processes and that the layers consist of relatively well oriented islands. The islands are larger for layers grown on GaAs substrates than for layers grown on silicon substrates. Composition modulation and phase separation occur; GaN, InP and GaPN –like phases are evidenced. No carbon contamination due to the use of organo-metallic precursors has been detected, but the observation of a local vibrational mode at 465 cm^{-1} suggest the contamination of the layers by silicon.

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METAL-ORQANİK QAZ FAZA EPİTAKSİYA METODU İLƏ YETİŞDİRİLMİŞ GaInPN/Si HETEROSTRUKTURU

Metal-orqanik gaz faza epitaksial (MOGFE) üsulu ilə silisium altlığı üzərində InGaPN epitaksial təbəqəsi yetişdirilmişdir, bu zaman element mənbəyi kimi Dimetilhidrazin, Trimetilgallium, Trimetilindium və fosfin istifadə olunmuşdur. Heterorabitələrin və antifaza sahələrinin yaranması ilə bağlı olan interfeys problemini azaltmaq məqsədilə hidrofob silisium altlığı üzərində çox nazik GaP bufer təbəqəsi yetişdirilmişdir.

Təbəqələr 630°C –də hazırlanmış və yüksək həssas rentgendiffraktometr, atom –güc mikroskopu, fotolüminessent və Raman metodu ilə xarakterizə olunmuşdur.

Yetişdirmə 3 ölçülü qaydada getmişdir. Müşahidə olunmuşdur ki, səth kələ-kötürlüyü 2-30 nm –dən çoxdur və materialın faza ayrılması baş verir.

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ГЕТЕРОСТРУКТУРА GaInPN/Si, ВЫРАЩЕННОГО МЕТОДОМ МЕТАЛЛОРГАНИЧЕСКОГО ХИМИЧЕСКОГО ГАЗОВОГО ОСАЖДЕНИЯ

Выращены эпитаксиальные слои InGaPN на кремниевой подложке методом металлорганического химического газового осаждения, используя источники диметилгидразина, триметил галлиум, триметилиндиум и фосфин.

Для того, чтобы уменьшить проблемы интерфейса, связанные с образованием гетеросвязей и противофазных областей, на поверхности гидрофобной подложки кремния выращен очень тонкий буферный слой GaP.

Слои приготовлены при температуре 630°C и исследованы с помощью рентгенодиффрактометра с высоким разрешением, атомно-силового микроскопа, фотолюминесценции и Рамановского метода.

Выращивание происходило в трехмерном порядке. Наблюдалась шероховатость поверхности больше 20-30 нм. Обнаружено фазовое отделение материала.

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