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Study of LPE grown dilute nitride GaInAsN layers with small concentration of Nitrogen by PL and Hall effect measurements

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In this paper electrical and optical properties of GaInAsN layers with small ($< 0.6\%$) nitrogen content have been studied by temperature dependent Hall effect and low-temperature photoluminescent measurements. Dilute nitride layers several microns thick have been grown by low-temperature liquid-phase epitaxy at different epitaxial temperatures. Polycrystalline GaN has been used as a source of nitrogen. The composition of the epitaxial GaInAsN layers has been determined by a combination of X-ray microanalysis and XRD measurements. Temperature dependences in the range 80–300 K of Hall free carrier concentrations and mobility have been analyzed. The effect of nitrogen on the electronic structure of the epitaxial layers have been studied from PL spectral features at 4.5 K.

Key words: dilute nitrides, InGaAsN, PL measurements, Hall effect measurements

INTRODUCTION

Dilute nitride alloys, such as GaInAsN, GaAsSbN, have recently attracted much attention as a potential materials for high-efficiency solar cells fabrication, due to their unique properties [1-3]. The incorporation of a small quantity of nitrogen into GaAs causes a dramatic reduction of the band gap and can be used for solar cells with extended long wavelength edge beyond the GaAs cut-off at 870 nm. Solar cells based on dilute nitride alloys are excellent suited for application in multijunction solar cells [4-6] and recently developed the spectral splitting concentrator photovoltaic system [7].

Unfortunately, the addition of small concentrations of nitrogen to GaAs layers results to a rapid reduction in bandgap energy with increasing of nitrogen concentration, but it also deteriorates the crystalline and optoelectronic properties of the dilute nitride materials, including reduction of the photoluminescence intensity and carrier lifetime, reduction of electron mobility and increase of the background carrier concentration. Near the critical composition the conduction band minimum is an “amalgamated state” form semi-localized and delocalized states of comparable energy and the duality of these states is responsible for many of the anomalous optical and electronic properties of dilute nitride alloys [8]. Technologically, the incorporation probability of nitrogen in GaAs is very small and strongly depends on the growth conditions The growth of dilute nitride alloys is difficult because of the wide immiscibility range, a large difference in the lattice constant value and very small atom radius of N atoms. Despite the progress in application of these materials in many optoelectronic devices based on quantum wells (QWs) structures, such as lasers at 1.3-1.5 μm and long-wavelength photodetectors, it remains difficult to obtain thick epitaxial layers with good crystalline quality [9]. The growth of thick epitaxial layers creates many problems which are absent in QWs structures.

In this paper we examine the electrical behavior of the liquid-phase epitaxy (LPE) grown thick GaInAsN layers with low nitrogen content grown at different technological conditions using Hall effect measurements and study the band gap formation of these dilute nitride layers by low-temperature photoluminescence (PL) measurements.

EXPERIMENT

A series of GaInAsN epitaxial layers have been grown on semi-insulating (100) GaAs substrates. The crystal growth was done in a horizontal quartz tube using a graphite boat designed for 10×15 mm^2 substrate. A flux of Pd-membrane purified hydrogen at atmospheric pressure was used for experiments. No

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special baking of the system was done before epitaxy. Starting materials for the solutions consisted of 6N pure solvent metals Ga, In and of polycrystalline GaAs and GaN with purity of 5N. After the loading the charged boat was heated at 750°C for 1 h in a purified H^2 gas flow in order to dissolve the source materials and decrease the contaminants in the melt. Epitaxial GaInAsN layers 5–8 μm thick were prepared from In-rich solutions from two different initial epitaxy temperatures of 650 and 600°C. The crystallization was carried out from a melts containing 0.1 and 0.5 at.% nitrogen at a cooling rate of 1°C/min for 10 minutes. The composition of the epitaxial $Ga_{1-x}In_xAs_{1-y}N_y$ layers was determined by a combination of X-ray microanalysis and XRD measurements. The In content in the layers measured by X-ray microanalyses was between 2–2.2%. The N content was estimated from HR XRD curves using Vegard's law. The Hall mobility and carrier concentration in the layers were measured by the Van der Paw Hall technique on 5×5 mm^2 samples, with alloyed indium ohmic contacts. The photoluminescence (PL) spectra under excitation of 488 nm Coherent Argon laser were obtained at 4.5 K. They were analyzed with a Jobin-Yvon Spectrometer HR460 and a multichannel CCD detector.

RESULTS AND DISCUSSION

Four series of samples with different nitrogen content have been obtained. The incorporation of nitrogen into InGaAs strongly dependences on the growth temperature and nitrogen content in the growth melts. Samples E93 and E98 prepared from melts with 0.1% nitrogen content at two different temperature ranges of 650–640°C and 600–590°C contain 0.03 and 0.05% nitrogen, respectively. Nitrogen content in the samples E96 and E99 grown at the same temperature ranges from melts containing 0.5% nitrogen is 0.2 and 0.6%, respectively. Obviously the lowering the epitaxy temperatures and increase nitrogen content in the melt enhance the incorporation of nitrogen in the grown layers. Lattice-matched growth conditions have been established for layers containing 0.6% nitrogen. Since In and N have opposing strain effects on the lattice by adjusting the contents of In and N in quaternary InGaNAs alloy lattice-matched to GaAs dilute nitride layers have been grown. The lattice mismatch $\Delta a/a_0$ for sample E99 determined from the XRD spectrum was ~0.07%. The full width at half maximum (FWHM) of X-ray diffraction

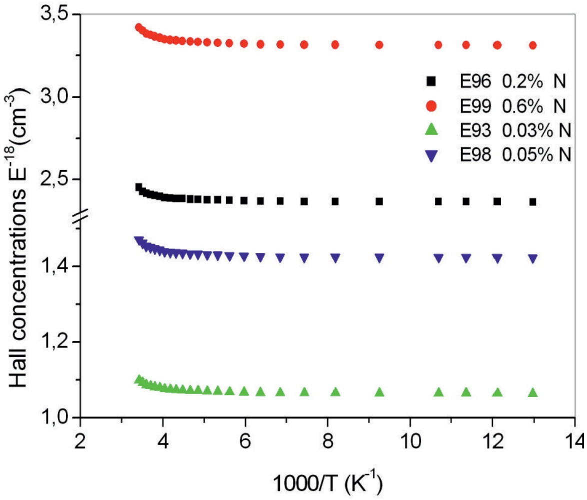

Fig. 1. Hall concentration as a function of inverse temperature for as grown InGaAsN layers with different N content.

(XRD) $\omega/2\theta$ scan was 64 arc seconds for the 5.5 μm thick layer. The measured root mean-square (RMS) surface roughness by AFM method was 0.23 nm. The incorporation of lower N in the other three samples can't compensate the strain effect of In on the epitaxial growth. These samples have been grown metamorphic with rough surface and lower crystalline quality.

In Fig. 1 are plotted the temperature dependences of Hall concentrations nH for the investigated four samples grown at different conditions.

All as grown InGaAsN layers are n-type and exhibit high free carrier concentration in the range (1–3) × 10^{18} cm^{-3}. These measured background doping densities of dilute nitride layers are more than one order of magnitude higher in comparison to GaInAs samples not containing nitrogen grown earlier at the same growth conditions in the growth ambient without nitrogen. It is seen that free carrier concentration increases with increase the nitrogen content in the layers. Two distinct temperature regimes with different temperature dependence of n_H are observed. The saturation of n_H at low temperatures (T < 200 K) is attributed to fully ionized shallow donors. At temperatures higher than 200 K a thermally activated increase in carrier concentration is observed, suggesting the presence of a deep donor level within the InGaAsN bandgap. The deep donors are likely related to the presence of N-related deep-level defects, typically associated with different N-N pair and N-cluster states [10]. The nitrogen pairs and clusters create the localized states near the conduction band edge.

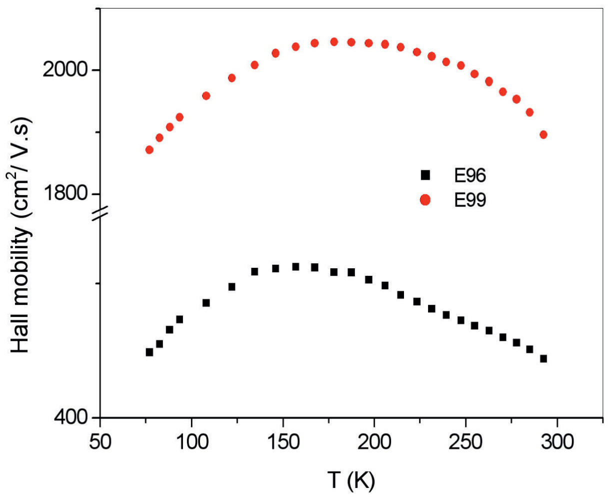

Fig. 2. Hall mobility as a function of temperature for metamorphic (E96) and lattice matched GaInAsN (E99) samples.

The activation energy of these states is much greater than the activation energy of the hydrogen-like shallow donor levels, suggesting the presence of a second deep donor level. The deep donors act as carrier trapping centers. Their activation energy decreases with increasing N composition which could be explained by the downward shift of the conduction band edge with increasing nitrogen content, while the N-related defect level remains unchanged.

Fig. 2 presents the temperature dependencies of the Hall-mobility for two of the samples. It is seen a well expressed low-temperature mobility decrease which suggests that the mobility is being limited by some kind of defect scattering and trapping. The mobility of the metamorphic GaInAsN sample E96 is low, down to 500 cm^2/V.s, since it possibly contains threading dislocations of high density and the latter causes relatively poor material quality. High values about 2000 cm^2/V.s for Hall mobility exhibits the lattice matched to GaAs substrate InGaAsN E99 sample. These values are about the theoretical limit predicted by Fahy and O'Reilly [11].

Low-temperature PL spectra of the investigated samples grown at different conditions are plotted in the Fig. 3. PL spectra recorded on samples E93 and E96 grown from an initial epitaxy temperature of 650°C from different melts are presented in the Fig. 3a. PL spectrum of E93, containing nitrogen at doping level of 0.03% dominates by sharp free exciton line at 1.484 eV. The peak at 1.45 eV is most probably due to an excitonic recombination on carbon acceptors; the carbon contamination probably comes from the graphite boat used in the LPE growth. A weaker structured emission band with two peaks around 1.370 and 1.405 eV localized far from band-gap edge is also observed. It is a nitrogen related band, associated with In-rich N-nanoclusters and different N-N pair. The similarly nitrogen related peaks we have observed for GaAs layers simultaneously doped with In and N, but they are absent for GaAs layer doped only with In [12]. In our previous work it was found a preferential formation of In-N bonds and the dominant local environment for N atoms was In-rich clusters [13]. The PL spectrum of sample E96 exhibits lower intensity and different shape compare

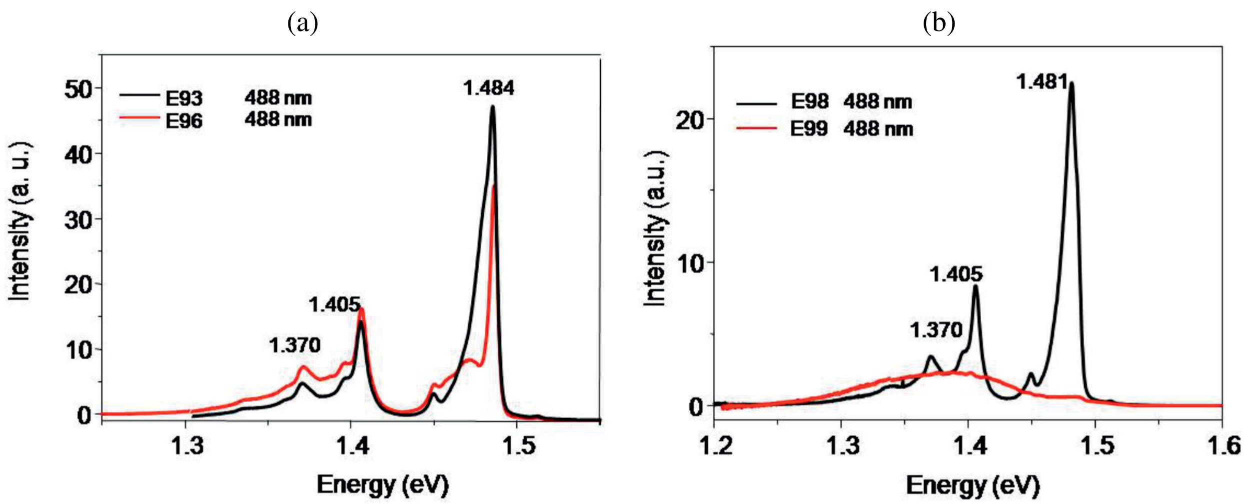

Fig. 3. PL spectra at 4.5K for samples grown from two different initial epitaxy temperatures of: a) 650°C; b) 600°C.

to PL spectrum of E93 sample. The effect of nitrogen in this layer containing 0.2% nitrogen in the solid is registered also additional wide peak at the low energy side of the free exciton line.

Sample E98 grown at the lower temperatures with 0.05% nitrogen content exhibits similar spectrum as those of E93 as it is seen from the Fig. 3b. A dramatic reduction in the PL intensity is observed for PL spectrum of the sample E99 containing 0.6% nitrogen in the layer presented at the same figure. It is dominated by wide emission band covering the peaks from nitrogen related clusters. This could be explained by pseudopotential theory of Kent et al [14]. According this theory the conduction band edge is formed from the delocalized and some localized cluster states. At the critical composition of N the deepest cluster states is overtaken by delocalized ones, since they are moving rapidly to the lower energies with increasing of N content in the alloy.

CONCLUSIONS

Four series of samples have been grown from melts with nitrogen content of 0.1 and 0.5 at.% from two different initial epitaxy temperatures. Nitrogen incorporation in the layers grown from melts with low nitrogen content of 0.1 at.% is in the range 0.03–0.05% and it acts as an isoelectronic impurity. The PL spectra consist of several peaks: sharp free exciton line; peak related to recombination on carbon acceptors and low energy peaks relating to the excitons bound to the N isoelectronic traps. Additional nitrogen related band appears at the law energy side of the sharp free exciton line of the alloy for sample E96 with 0.2% nitrogen content grown from 650°C. PL spectrum of sample E99 grown at lower temperatures containing 0.6% nitrogen in the solid exhibit wide emission band with low intensity due to the transition from nitrogen doping to alloy formation.

Hall effect measurements reveal sharp increase in the free background carrier concentrations up to $(2–3) \times 10^{18}$ cm^{-3} for all as grown GaInAsN samples which is about one order of magnitude higher in comparison with not containing nitrogen layers. The Hall electron mobility values about 2000 cm^2/V.s are measured for lattice matched to GaAs dilute nitride layers.

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НОВИ МАТЕРИАЛИ ЗА ПРИЛОЖЕНИЕ В МНОГОПРЕХОДНИ СЛЪНЧЕВИ ЕЛЕМЕНТИ НА ОСНОВАТА НА A^3B^5 ХЕТЕРОСТРУКТУРИ

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(Резюме)

Създаването на нова генерация многопреходни слънчеви елементи (СЕ), които използват целия слънчев спектър, води до значително повишаване ефективността на СЕ. Изборът на подходяща комбинация от материали за изготвяне на многопреходните СЕ е определящ за увеличаване ефективността на преобразуване на слънчевата радиация над 40%. Рекордната стойност от 41% за ефективността на преобразуване на концентрирано слънчево излъчване в трипреходни СЕ, разработени от Spectrolab, САЩ, дава надежда за практическа реализация на значително по-висока ефективност при увеличаване броя на СЕ в каскадата. Тези очаквания могат да се реализират, ако бъдат намерени нови материали, подходящи за използването им в многопреходните СЕ.

Твърдите разтвори от разредени нитриди са ключов нов материал за приложение в многопреходните СЕ и дават възможност за „инженеринг" на забранените зони и константите на решетката на материалите.

В настоящата работа е демонстрирана възможността за израстване на разредени нитриди GaAsN, InGaAsN върху подложки от GaAs от течна фаза. Израснатите структури са с добро кристалографско качество. Нелегираните слоеве са с n-тип проводимост. Установена е аномална промяна на концентрацията на свободните токови носители в сравнение с конвенционалните III-V съединения. Измерените стойности на подвижността на Хол в слоевете е ~ 2000 cm^2/V.s.

Изследван е механизмът на включване на азотните атоми в кристалните решетки на твърди разтвори от разредени нитриди GaAsN, InGaAsN при кристализация от течна фаза. Посредством методите на Раманова и ИЧ спектроскопия е определена локалната микроструктура на получените съединения от разредени нитриди. Получаването на изорешетъчни ненапрегнати дебели слоеве InGaAsN с високо кристалографско качество върху подложки от GaAs е свързано с преференциално формиране на In-N връзки в кристалната решетка на тези съединения.