Deep-level study of Ga(In)P(NAs) alloys grown on Si substrates

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Abstract. Defect properties of Ga(In)P(NAs) layers with different composition were studied by admittance spectroscopy. For nitrogen content layers the defect level with energy of 0.44-0.47 eV, which related to nitrogen incorporation into GaP, was observed. Its concentration is lower for GaPNAs layers compared to GaPN/InP due to better compensation by arsenic than by indium in lattice of GaP. Other defect level with energy of 0.30 eV was detected in GaPAs and GaPN/InP layers. Likely, the both observed defects in GaPAs and GaPN/InP have the same nature.

1. Introduction

Dilute nitrides III V-N form a new family of perspective materials for optoelectronic devices such as light emitting diodes, lasers and high-efficiency multijunction solar cells, and open the way to novel integrated optoelectronics combining III-V compound semiconductors with silicon [1]. The incorporation of just 0.43 % atomic fraction of nitrogen into the gallium phosphide (GaP) lattice leads to direct band transition while the band gap decreases drastically with small (few percents) N content [2,3]. Furthermore, addition of indium and (or) arsenic atoms allows one to vary the band gap in a wide range of 1.5 to 2.0 eV while remaining lattice-matched to Si substrates. The latter opens a way for the development of high efficiency lattice-matched multijunction solar cells on Si substrates [4]. However, experimental studies demonstrate low minority carriers’ lifetime in active GaPNAs layers grown on GaP and Si substrates by MOCVD [5] and by MBE [6]. This is associated with defect formation and appearance of a significant concentration of non-radiative recombination centers during the growth. Therefore, the study of defects in Ga(In)PN(As) is an important issue for further material development. However the electronic properties of point defects in III-V-N alloys grown on Si are still not enough studied. Most of defect studies were performed for alloys grown on GaP substrates [7-11] which seems necessary as a first step. But there could be a strong difference in defect formation mechanisms for the growth on GaP and Si substrates. For example, formerly it was shown that GaPNAs grown on GaP has a defect level with a characteristic activation energy of 0.18 eV, which is not observed in GaPNAs grown
on Si [12]. Another issue is that a significant part of the experimental study for (Al)Ga(In)PNAs layers was performed using the optically detected magnetic resonance (ODMR) technique [13], which does not allow one to determine the activation energy and capture cross sections of defects that are the most important parameters for recombination mechanisms analysis. To determine these parameters the capacitance techniques like deep-level transient spectroscopy (DLTS) and admittance spectroscopy should be rather used. However the only n-type GaP:N layers were studied by DLTS [7-10]. In addition, according to references [5, 6] the lifetime of minority charge carriers is extremely low in doped GaPNAs layers. Thus p-i-n structures using the i (undoped) layer as the absorber should have the highest interest for optoelectronic applications. Therefore, the properties of undoped III-V-N layers are one of the key issues for optoelectronic devices technology development. To our knowledge no defect studies of undoped Ga(In)PN(As) layers grown on silicon substrates have been reported. Here we use the admittance spectroscopy technique to investigate the defect properties of undoped III-V-N layers grown on Si.

2. Experiment and samples

Three different p-i-n structures with active III-V-N i-layers of different composition were grown on p-type Si substrates (concentration of acceptors $10^{16} \text{cm}^{-3}$) by molecular-beam epitaxy using Veeco GEN III setup with a plasma nitrogen source. The parameters of intrinsic (not intentionally doped) layers are presented in Table 1. The layers were lattice-matched to silicon. Sample #1 based on GaP$_{0.70}$As$_{0.30}$ was grown as a reference and to define the nitrogen role in defect formation. Sample # 2 has the undoped region based on a superlattice consisting of a sequence of 10 nm GaP$_{0.99}$N$_{0.01}$/InP layers separated by monolayers of InP to improve indium incorporation into the alloy. Sample # 3 was grown with 10 atomic percent of As for a better incorporation of nitrogen.

| Sample # | Composition | Width, nm | Lattice mismatch to Si at 300 K, % | Growth temperature, °C |
|----------|-------------|-----------|----------------------------------|------------------------|
| 1        | GaP$_{0.70}$As$_{0.30}$ | 400       | 1.48                             | 610                    |
| 2        | GaP$_{0.99}$N$_{0.01}$/InP | 200 (10.0/0.3)$\times$20 | 0.19                             | 490                    |
| 3        | GaP$_{0.882}$N$_{0.18}$As$_{0.10}$ | 200       | 0.42                             | 530                    |

The admittance spectroscopy technique allows one to determine the activation energy ($E_A$), i.e. the energy location of defects with reference to the majority carrier band, and the corresponding capture cross section ($\sigma_A$) from the analysis of the temperature and frequency dependence of the capacitance $C(T,f)$ and conductance $G(T,f)$ [14]. The measurements were performed using a liquid nitrogen cryostat in the temperature range of 80…380 K and at frequencies from 20 Hz to 1MHz.

3. Result and discussion

The measured temperature dependences of the capacitance $C(T, f)$ are shown in Figures 1a—1c. The steps in the capacitance (which are accompanied by conductance peaks) observed for the samples #1, #2, #3 are shifted toward higher frequency when the measurement temperature is increased. Such steps are characteristic for the response of gap states and may be caused either by bulk defect levels in the undoped layer or by interface states at the III-V-N/GaP(N) heterojunctions. The measurements of $C(T, f)$ at different bias voltages (not shown here) demonstrate that the step positions are independent of the applied bias voltage indicating that the response originates from bulk defects rather than from the interface.
Figure 1. Capacitance spectrum $C(T, f)$ for a- GaPAs, b- GaPN/InP, c- GaPNAs.

Sample # 1 with an active layer of GaPAs exhibit a pronounced step in the capacitance curves at high temperatures 320-360 K (Figure 1a). The Arrhenius plots of $f/T^2$ ($\omega$ being the turn-on frequency at the capacitance step or maximum of the related conductance peak) are used to derive the activation energy and capture cross section (from the extrapolation to infinite temperature) of the defect responsible for the capacitance step. The Arrhenius plots are shown in Figure 2 for all structures. For GaPAs layer only one defect level with activation energy of 0.30 eV and low capture cross-section $\sigma=3.8 \cdot 10^{-19}$ cm$^2$ was observed. For the sample #2 $C(T, f)$ curve (Figure 1b) is not monotonic meaning overlap of few defect responses for GaPN/InP layer. Detailed analysis of the $C(T, f)$ derivative and $G(T, f)$ curves (not presented) has allowed us to distinguish two capacitance steps (conductance peaks) that correspond to the response from two different defect levels, which are presented in Figure 2. While exact determination of the activation energy and capture cross section is difficult for this structure, the first defect level seems to have the similar parameters to the one observed for GaPAs sample. The second defect level with $E_a=0.44$ eV and $\sigma=1.3 \cdot 10^{-16}$ cm$^2$ has similar parameters to the sample#3 (GaPNAs), which according to Figure 1c exhibits only one defect response with $E_a=0.47$ eV and $\sigma=8.8 \cdot 10^{-17}$ cm$^2$.

The last defect with activation energy of 0.44-0.47 eV was detected only in GaPN/InP and GaPNAs layers, while it was not observed for GaPAs layer. It means that nitrogen plays key role in defect origin. Also, we suppose it is response from the defect B2 which we detected in GaPNAs in our previous work.
According to the literature, the similar defect was described in Ref. [9] and [10] for GaP doped with nitrogen where it was associated with formation of pair N_{P}-N_{P} and V_{Ga}.

The second defect in GaPN/InP (Figure 2b) with lower activation energy was not detected in GaPNAs. Moreover the total defect concentration is higher for GaPN/InP compared to GaPNAs. This fact is in the agreement with the photoluminescence measurements performed in Ref. [15] where indium incorporation into III-V-N was demonstrated to lead to higher non-radiative recombination losses compared to As contain III-V-N alloys. Indium being a III-group element is less efficient to compensate elastic stresses in sub-lattice of V-group compared to arsenic in phosphorus sites (both being V-group elements). We also experimentally demonstrate lower external quantum efficiency for p-i-n structures based on GaPN/InP active layer compared to GaPNAs (Figure 3) indicating lower charge carrier lifetime in GaPN/InP. However we suggest that this defect (0.44-0.47 eV) is not single and has energy distribution due to varying composition of alloy in local area. Thus it is very complicated to obtain its exact parameters values.

**Figure 2.** Arrhenius plot of $f/T^2$ for the defects identified by admittance spectroscopy for the GaPAs, GaPN/InP and GaPNAs structures.

**Figure 3.** External quantum efficiency of p-i-n structures with GaPN/InP and GaPNAs i-layer.
Finally, only one defect level with activation energy of 0.30 eV was detected in GaPAs layers (Figure 1a). The defect concentration of GaPAs layer is higher compared to GaPN/InP and GaPNAs. We suggest, it is the same defect with low activation energy as in GaPN/InP. Further studies will be done applying deep-level transient spectroscopy (DLTS) to get inside in the origin of this defect.

4. Conclusion
Defect properties of Ga(In)P(NAs) layers with different composition were studied by admittance spectroscopy. For nitrogen content layers the defect level with energy of 0.44-0.47 eV, which related to nitrogen incorporation into GaP, was observed. Its concentration is lower for GaPNAs layers compared to GaPN/InP due to better compensation by arsenic than by indium in lattice of GaP. Other defect level with energy of 0.30 eV was detected in GaPAs and GaPN/InP layers. Likely, the both observed defects in GaPAs and GaPN/InP have the same nature. Further studies using DLTS will be carried out.

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