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Thermal annealing effect on nitrogen related defects of GaInNAs semiconductors

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Nitrogen related defects of GaInNAs epilayers grown by molecular beam epitaxy were investigated before and after rapid thermal annealing using X-ray photoelectron spectroscopy (XPS). XPS analysis revealed that the N-induced defect configurations are most likely attributed to the N-As spilt interstitials and (N_{As}-As_{Ga}) complex. Comparison of as-grown and annealed samples showed that the nearest N-bonding configuration of GaInNAs changes from Ga_3In_1N to Ga_1In_3N after annealing, which can lead to reduction of the local strain. Annealed sample demonstrated a reduced the defect concentration, which could be due to the transformation of nearest N-bonding configuration after annealing.

Key words: GaInNAs, Thermal annealing, N-induced defect.

Introduction

The III-V-N alloys have attracted a considerable attention for potential applications in lasers for telecommunication as well as in multijunction solar cells. [1-3]. In particular, GaInNAs is a promising material for use in multijuction solar cells, because this material with 1.0 eV bandgap can be latticed to GaAs and Ge substrate by adjusting In and N compositions. Additionally, the conversion efficiency of a four junction InGaP/GaAs/GaInNAs/Ge solar cells is expected to exceed 45% [2]. However, this material still suffers from low minority carrier diffusion length due to both poor carrier lifetime and mobilities. The crystalline qualities of GaInNAs are dramatically deteriorated owing to the nitrogen incorporation into the GaInAs [4, 5]. Low growth temperature is required to avoid separation and to improve compositional homogeneity in GaInNAs [6]. Hence, the as-grown samples of this material contain a high number of defects [7, 8] such as N interstials, As_{Ga} antisites and Ga vacancies, which act as recombiantion and/or scattering centers. The origin of the defect formation has been investigated theoretically [9, 10] and experimentally [7, 11], but still remains unclear. Furthermore, thermal annealing treatments are required in order to reduce the defects and improve the photoresponse [3]. Therefore, detailed understanding of the defect formation mechanisms during the growth and designing strategies to remove defects are essential to the practical device applications.

In this study, using the X-ray photoelectron spectroscopy (XPS) analysis we have investigated the alteration of the atomic configuration related to the defects in GaInNAs thin film after rapid thermal annealing (RTA). The possible defect formation mechanism during growth of the GaInNAs will be discussed.

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Experiments

The samples were grown by gas-source molecular-beam epitaxy on semi-insulating GaAs (001) substrate. Elemental In (7N) and Ga (7N) were used as group III sources, and thermally cracked AsH_3 and ion-removed electron cyclotron resonance (ECR) plasma-assisted N_2 [12] provided the group V sources. 5 nm thick $Ga_{0.70}In_{0.30}N_{0.012}$ $As_{0.998}$ epilayer was grown for XPS measurements, after growth of 300 nm thick GaAs buffer layer on the substrate. The substrate temperature during the growth of the GaInNAs layer was 420 °C and the remaining part of the structure was grown at 560 °C. The growth was monitored with in situ reflection high-energy electron diffraction (RHEED). After growth, to investigate the influence of annealing, rapid thermal annealing (RTA) was carried out under N_2 flow at 700 °C for 1 minute. In order to prevent the evaporation of the constituent atoms from the sample surface during RTA, clean GaAs wafer was placed face to face on the sample surface. XPS measurements were performed using a VG Scientific ESCALAB 220i-XL spectrometer with a monochromatic Al Kα radiation source. Photoelectrons were collected in the surface-normal direction and the electron pass energy in the semi-spherical analyzer was set at 20 eV.

Results and Discussion

Figure 1 shows the N 1s region of XPS spectra for the as-grown and annealed samples. The bonding

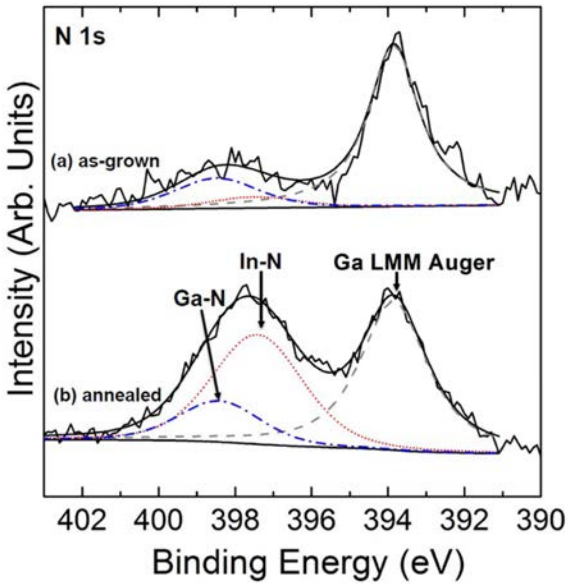

Fig. 1. XPS spectra in the N 1s region for (a) as-grown and (b) annealed GaInNAs samples.

energies ~ 393.8 eV, ~ 397.5 eV and ~ 398.3 eV can be assigned to the Ga LMM Auger line, In-N bond and Ga-N bond, respectively [13, 14]. During epitaxial growth of GaInNAs quaternary alloys, the development of nearest neighbor configuration is more driven by maximizing the cohesive bond energy than minimizing the local strain in the surface [15]. The cohesive energies of the respective binary compounds follow the sequence GaN > InN > GaAs > InAs (2.24, 1.93, 1.63, and 1.55 eV per bond, respectively) [16], so Ga-N and In-As configuration is preferred during the growth [15]. Comparison of the N 1s spectra of the as-grown and annealed GaInNAs samples revealed that the intensity ratio between the Ga-N and In-N bond peaks is increased from 2.7 : 1 to 1 : 2.8 after annealing. This indicates that the preferred configurations during the growth are Ga-N and In-As bonds in this material system. This result is in good agreement with the theoretical prediction of Kim *et al.* [15]. This atomic configuration causes higher local strain compared to the Ga-As and In-N bonds owing to the difference in the bonding lengths (being 2.61, 2.45, 2.15, and 1.94 Å, for InAs, GaAs, InN, and GaN, respectively) [16], which is reduced by the change of configuration from Ga-N and In-As bonds to In-N and Ga-As bonds during annealing. This change in bond configuration is related to the point defects as reported by Karirinne *et al.* [17]. The theoretical investigations [9] have predicted that the formation of isolated interstitial nitrogen in (In)GaAsN is unlikely because of their high formation energy in the lattice. Instead, N complexes such as N-N and N-As split interstitials (bonding lengths: 1.39 and 1.85 Å, respectively) and (N_{As}-As_{Ga}) nearest neighbor pairs, which minimizes the total strain energy associated with the defects, are energetically favored to form. It is considered that the defect formation in this material system is driven by minimizing the local strain under our growth condition. Hence, the N-As split interstitials and/or (N_{As}-As_{Ga}) nearest neighbor pairs are the most likely candidates.

In order to verify our expectation concerning the defect configuration, we carried out the XPS measurement in the As 3d region. Fig. 2 shows the XPS spectra in the As 3d region for the as-grown and annealed GaInNAs layers. There are two peaks in the As 3d spectrum for as-grown sample. The main peak located around 42 eV is well fitted with two spin-orbit doublets, which energy separation reflects the $d_{3/2}$-$d_{5/2}$

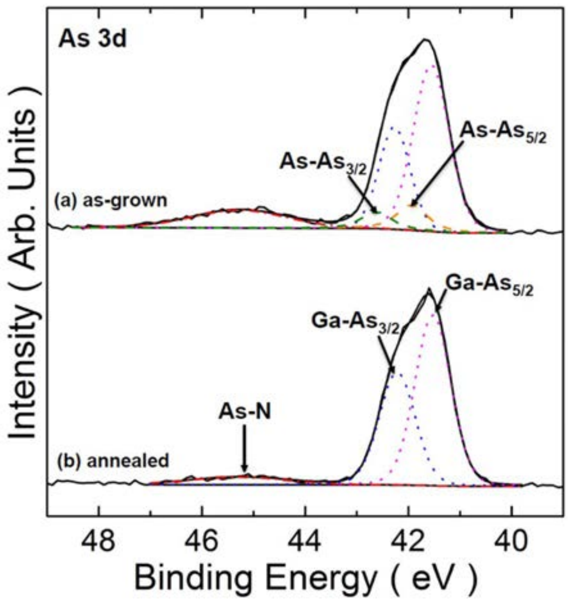

Fig. 2. XPS spectra of As 3d photoelectron for (a) as-grown and (b) annealed GaInNAs samples.

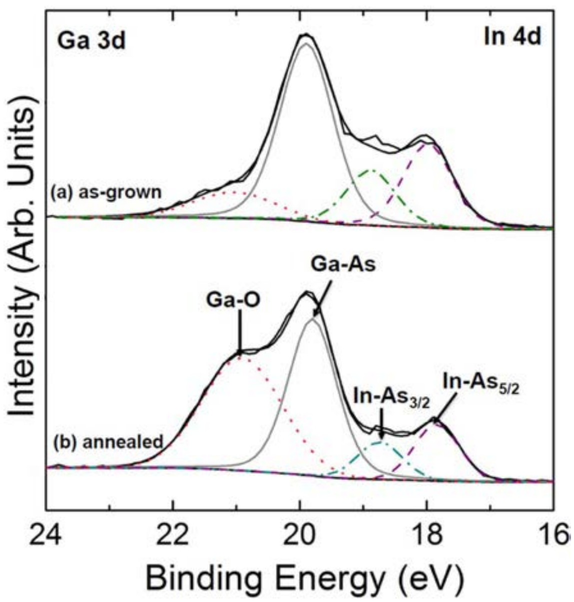

Fig. 3. XPS Ga3d/In4d spectrum for (a) as-grown and (b) annealed GaInNAs samples.

spin orbital splitting. The doublet peaks at 42.2 and 41.5 eV are assigned to Ga-As bond, and the smaller doublet peaks at 42.6 and 41.9 eV can be attributed to As-As bond [18, 19]. The measured value of spin-orbit splitting for arsenic (0.7 eV) is good accordance with previous reports [18, 20]. The N and As atoms in the formation of (N_{As}-As_{Ga}) nearest neighbor pairs are threefold coordinated with Ga and As, respectively [9]. Therefore, the As-As bond can presumably be attributed to the N_{As}-As_{Ga} complex. The sub-peak at 44.9 eV can be assigned to the N-As or As-O bond [21]. Fig. 3 shows the Ga3d/In4d region of the XPS spectra before and after the annealing. The peaks at 17.8 eV, 18.7 eV, 19.8 eV and 20.9 eV correspond to In-As5/2, In-As3/2, Ga-As and Ga-oxides, respectively [22]. It is clear that the intensity of the Ga-O bond for the annealed sample increases as compared with that of the as-grown sample. This indicates that the oxygen bond increased after annealing. This oxygen feature is related to the surface oxidation during the annealing, caused by native oxide of GaAs wafer used as cap or residual oxygen in the furnace. From this result, the peak at 44.9 eV in Fig. 2 corresponds to the N-As bond, since the intensity of the sub-peak was decreased due to annealing. Hence, N-As split interstitials and (N_{As}-As_{Ga}) complex are the N-induced defects formed in this material system. Furthermore, the intensity of the N-As bond and As-As bond peaks reduced with annealing. This indicates that the thermal annealing leads to the decreased concentration of the N-related defects.

Summary

In summary, the thermal annealing effects on the change of atomic configuration in GaInNAs system were investigated by XPS. Examination of As 3d core level revealed that the concentration of the N-related defects such as N-As split interstitials and (N_{As}-As_{Ga}) complex were decreased after annealing. Thus, the XPS data directly showed that the alteration of the atomic configuration related to the N induced defects during annealing causes the improvement of crystallinity in GaInNAs system after annealing.

Acknowledgments

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