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Observation of defect complexes containing Ga vacancies in GaAsN

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Positron annihilation spectroscopy was used to study GaAsN/GaAs epilayers. GaAsN layers were found to contain Ga vacancies in defect complexes. The density of the vacancy complexes increases rapidly to the order of 10^{18} cm^{-3} with increasing N composition and decreases after annealing at 700 °C. The anticorrelation of the vacancy concentration and the integrated photoluminescence intensity suggests that the Ga vacancy complexes act as nonradiative recombination centers. [DOI: 10.1063/1.1533843]

Quaternary alloy $Ga_{1-y}In_yN_xAs_{1-x}$ is a novel material for low-band-gap applications on gallium arsenide.[1,2] The alloy is lattice matched to GaAs when $y \approx 3x$, and only a few percent of N ($x<0.05$) is needed to decrease the band gap below 1 eV due to huge band-gap bowing. This material is used in applications such as infrared lasers,[3] multijunction solar cells,[4] and heterojunction bipolar transistors.[5] Because of the large size mismatch between As and N atoms, high quality arsenide-nitride alloys are difficult to fabricate. The epitaxial growth is typically performed at the temperature range of 400 to 600 °C. The effects caused by N are more straightforward to study with the ternary alloy $GaAs_{1-x}N_x$. The addition of N affects the band structure of GaAsN mainly by decreasing the conduction band edge. However, also the valence band changes a little, and it has been recently shown that GaAsN/GaAs material system has type-I band alignment.[6,7] Various defects are formed in the material during the growth, and post-growth annealing can be used to eliminate some of them.[8,9] Intrinsic point defects identified in the arsenide-nitrides so far are an As_{Ga} antisite,[10,11] an N interstitial,[12–14] and a Ga vacancy.[14]

In this work, we have found evidence of vacancies in GaAsN alloy grown by metalorganic vapor phase epitaxy (MOVPE). We show these vacancies to be Ga vacancies (V_{Ga}) that exist in defect complexes. We have further studied the effect of annealing on the density of the Ga vacancies.

Positron annihilation spectroscopy[15] was used to detect vacancy-type defects in GaAsN epitaxial layers. A variable-energy positron beam was used to scan the depth profile. Positrons thermalize very fast in the sample and diffuse until they annihilate with electrons. At room temperature, positrons are effectively trapped by neutral and negatively-charged vacancy defects. The annihilation spectrum of trapped positrons differs from that of free positrons by smaller Doppler broadening of the annihilation line at 511 keV. Broadening is described by line shape parameters S and W determined as a fraction of counts in the central area and the wing area of the peak, respectively.[15] Thus, vacancies are detected as an increase in the low-momentum parameter S and a decrease in the high-momentum parameter W. The measurement is sensitive in the vacancy density range approximately from 10^{16} to 10^{19} cm^{-3}.

The GaAsN layers were grown by MOVPE on semi-insulating GaAs (001) substrates using TMGa, TBAs, and DMHy precursors and hydrogen carrier gas. A detailed description of the growth parameters can be found in Ref. 16. The samples consist of a 50-nm-thick GaAs buffer, a $GaAs_{1-x}N_x$ layer with a thickness of 170 nm and composition x ranging from 0 to 0.05, and a 3-nm-thick GaAs cap layer. One of the samples was cut in pieces, which were annealed in the MOVPE reactor for 10 min under different annealing conditions. The GaAsN layer thicknesses and compositions were determined by high-resolution x-ray diffraction using (004) reflection, and photoluminescence (PL) at a temperature of 10 K was used to characterize the optical quality of the layers. The unintentionally doped epilayers were p-type with hole concentrations between 10^{16} and 10^{17} cm^{-3} as determined by Hall measurements. The hole concentration decreased with increasing N composition, and the effect of annealing to the hole concentrations was negligible.

When nitrogen is introduced into the GaAsN epilayer, an increase in the S parameter and a decrease in the W parameter are observed at positron incident energies of 0 to 5 keV, indicating the presence of vacancy defects in the 170-nm-thick overlayer (Fig. 1). By increasing the nitrogen composition x of the $GaAs_{1-x}N_x$ layer higher than 1%, the value of the S parameter saturates. A p-type GaAs sample was used to obtain the reference levels $S_B=0.5374$ and $W_B=0.0361$ for the GaAs lattice.

The linear dependency between the S and W parameters in our as-grown GaAsN epilayers (Fig. 2) shows that the change in the positron annihilation signal is caused by only a single type of a vacancy.[15] To identify this defect, we compare the slopes of the (S, W) data to those expected for V_{Ga} and V_{As}. The parameters of $S_{V,Ga}/S_B=1.019$ and $W_{V,Ga}/W_B=0.76$ were estimated for Ga vacancies by measuring the highly Si-doped and Si δ-doped GaAs samples, where complexes of V_{Ga} have been previously identified.[17,18] The parameters for neutral As vacancies have been estimated to be $S_{V,As}/S_B=1.030$ and $W_{V,As}/W_B=0.80$.[19] The (S, W) points of GaAsN layers appear between the values of GaAs

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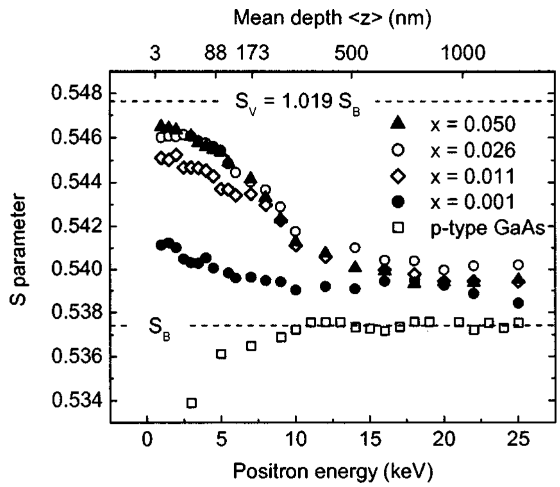

FIG. 1. Low-momentum parameter S as a function of positron incident energy in the as-grown $GaAs_{1-x}N_x$ samples. The reference value S_B of p-type GaAs and the characteristic value S_V of the V_{Ga} are drawn by dashed lines. The top axis shows the mean depth of positron penetration corresponding to the positron incident energy.

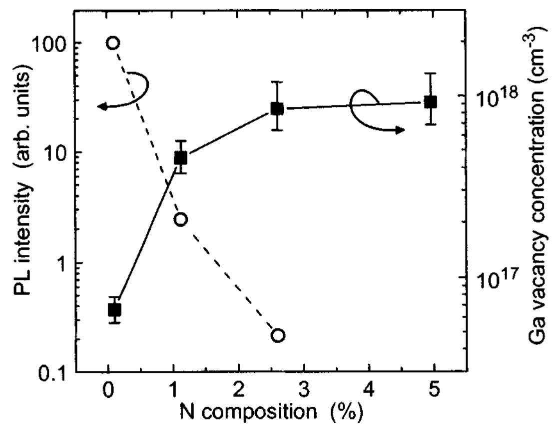

FIG. 3. Integrated PL intensity at 10 K and V_{Ga} concentration of as-grown 170-nm-thick $GaAs_{1-x}N_x$ epilayers as a function of N composition.

lattice and Ga vacancy, which allows us to identify the defects as Ga vacancies. In fact, As vacancies are not typically seen by positron annihilation spectroscopy in p-type and semi-insulating GaAs, because of their positive charge.[15]

According to electron irradiation studies, isolated Ga vacancies are not stable in the GaAs lattice at temperatures above 300 °C.[20] Thus, the vacancies in our samples grown at $>$500 °C probably belong to defect complexes with some other defects or impurities. The C and H impurity concentrations in MOVPE-grown GaInNAs are typically 10^{17}–10^{18} cm^{-3} and 10^{18}–10^{20} cm^{-3},[8,21] respectively. However, the complex of V_{Ga} and C impurity is unlikely due to the negative charge of both of them and vacancies decorated by hydrogen are usually not positron traps.[22] Molecular-beam-epitaxy-grown GaAsN has been shown to contain interstitial nitrogen (N_i).[12–14] However, we consider it unlikely that complexes of N_i and V_{Ga} could be stable, since the N interstitials could easily annihilate the Ga vacancy. The As_{Ga} antisite is another typical defect arising at group-V-rich growth conditions, and it has already been identified in GaAsN.[10,11] Indeed, the densities of positive As_{Ga} and negative V_{Ga} have been found to correlate in As-rich low-temperature-grown GaAs,[23] suggesting that they form neutral complexes.[24] We thus infer that the complexes involving V_{Ga} constitute intrinsic defects, and their likely assignment is that formed of the acceptor V_{Ga} and donor antisites such as As_{Ga} or N_{Ga}.

The vacancy concentration of an epilayer can be estimated by applying a positron trapping model with a single type of vacancies.[15] Figure 3 shows the experimental V_{Ga} concentration and the integrated PL intensity at 10 K of the GaAsN samples. The V_{Ga} concentration increases with N composition up to the order of 10^{18} cm^{-3}. Interestingly, the V_{Ga} concentration anticorrelates with the intensity of the photoluminescence.

A post-growth thermal annealing process is typically used to enhance the optical quality of the arsenide-nitrides. Figure 4 shows the S parameter data of the $GaAs_{0.975}N_{0.025}$ layers annealed at different conditions. Annealing at 650 °C decreases the S parameter and the sample annealed at 700 °C exhibits an even more pronounced effect. The S parameter, however, remains high compared with the vacancy-free level S_B.

Figure 5 shows the PL efficiency and the V_{Ga} concentra-

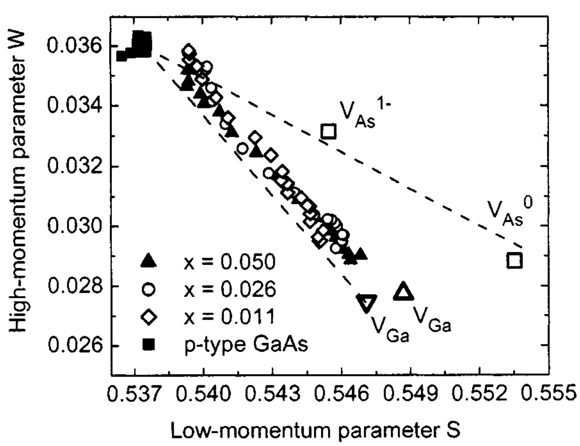

FIG. 2. High-momentum parameter W as a function of low-momentum parameter S for as-grown $GaAs_{1-x}N_x$ samples. Characteristic W and S parameters for V_{As} (□) and V_{Ga} (△) are from Refs. 18 and 22, respectively, and parameters for V_{Ga} (▽) are measured in this work. The dashed lines are guides for the eye.

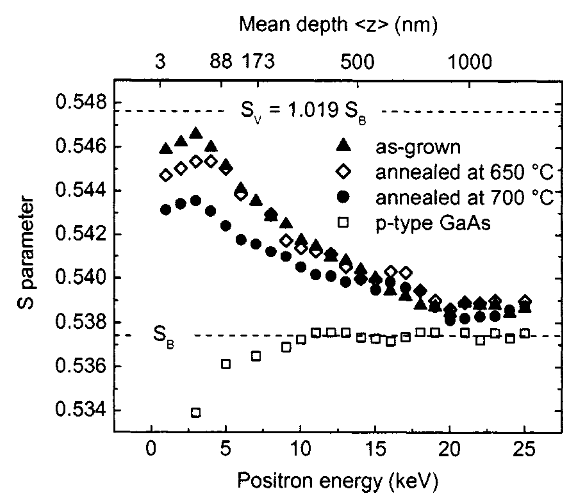

FIG. 4. Low-momentum parameter S as a function of positron incident energy in $GaAs_{0.975}N_{0.025}$ samples annealed at different temperatures. Other features are identical with Fig. 1.

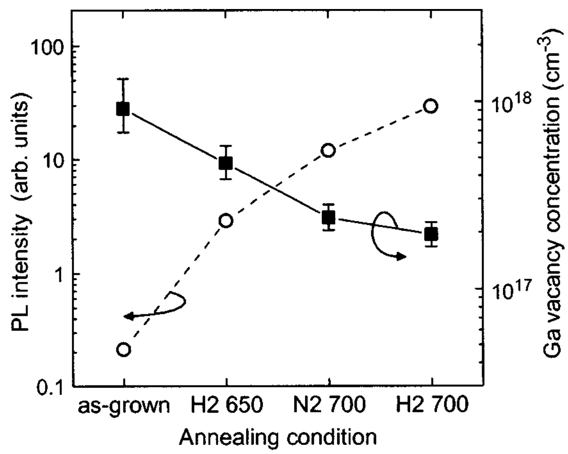

FIG. 5. Integrated PL intensity at 10 K and V_{Ga} concentration of 170-nm-thick $GaAs_{0.975}N_{0.025}$ epilayers annealed at different conditions. The lines are guides to the eye.

tion of $GaAs_{0.975}N_{0.025}$ annealed at different temperatures. The maximum PL efficiency is obtained by annealing for 10 min at 700 °C under H_2 carrier gas flow and TBAs excess ambient in the MOVPE reactor.[16,25] This procedure reduces the V_{Ga} density by a factor of 5 compared to that found in as-grown material. The ratio between the V_{Ga} concentration and the PL intensity is about the same as in the as-grown GaAsN layers with increasing N composition. The anticorrelation of the V_{Ga} density and the PL intensity thus suggests that the defect complexes containing the Ga vacancies act as nonradiative recombination centers in GaAsN.

In summary, we have found vacancies in MOVPE-grown GaAsN that are attributed to Ga vacancies in defect complexes. The density of the vacancies was found to increase rapidly up to the order of 10^{18} cm^{-3} with increasing N composition, and to decrease by a factor of 5 after the thermal annealing procedure optimized for the PL intensity. The anticorrelation between the vacancy density and the integrated PL intensity suggest that the defect complex acts as a nonradiative recombination center.

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