Observation of a New Isoelectronic Trap Luminescence in Nitrogen δ-doped GaP

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1. Introduction
Single impurity centers in semiconductors are attractive as a candidate for solid-state single photon source with well-defined energy. Isoelectronic trap in gallium phosphide doped with nitrogen (GaP:N) has been used as a bright luminescent center for light emitting diodes in the green region. Recently single photon emission from a single nitrogen pair center (NN) in nitrogen δ-doped GaP has been demonstrated [1], and GaP:N is getting renewed attention. Although the isolated nitrogen or pairs of nitrogen has been an object of study for a long time, little is known about nitrogen clusters composed of more than three nitrogen atoms[2]. Since such a cluster may be also useful for a single photon source, they should be investigated in detail. Single impurity spectroscopy is a powerful tool for this purpose. In the present paper, we applied single impurity spectroscopy to nitrogen δ-doped GaP samples with various nitrogen density, and found a new peak which is most likely due to the excitons trapped by a NNN cluster.

2. Experimental Details

Samples
The samples were grown on undoped GaP(001) substrates by a low-pressure metal-organic chemical vapor deposition. Triethyglyllium (TEGa) and phosphine (PH₃) were used as sources for the GaP epitaxial layers, and dimethylhydrazine (DMHy) was used as a nitrogen dopant. To achieve a nitrogen δ-doping, the GaP buffer layer was subject to DMHy gas pulses of 5 s duration after stopping the TEGa and PH₃ flows, and it was subsequently capped with 200 nm-thick GaP. The sheet density of the δ-doped layer was measured by secondary ion mass spectroscopy (SIMS). We used samples with a nitrogen sheet density of 10¹¹-10¹² cm⁻².

Experimental Setup
The samples were kept in an optical cryostat at 30 K. An argon ion laser was used as the excitation light source. For time-resolved measurements, second harmonics of a ps-Ti:S laser was used. The luminescence image of the sample was collected with a microscope objective and was focused onto the entrance slit of an imaging spectrometer with focal length of 25 cm equipped with a charge-coupled device (CCD). For the detection of a single NN center, a pinhole was introduced at a location confocal to the sample plane. The lifetime of a single luminescence center was measured by time-correlated single photon counting technique using an avalanche photodiode based single photon counting module.

3. Results and Discussion

µ-PL spectra
Figure 1(a) shows typical µ-PL spectra obtained at different position on a sample. Sharp luminescence peaks due to the third neighbor pair (NN₃) and the forth neighbor pair (NN₄) have been demonstrated [1], and GaP:N is getting renewed attention. Their energies agree well with the values in literature[3] which are represented by the vertical dotted lines. In addition to well-known NN pair luminescence, we found a new peak labeled X, whose energy is between NN₃ and NN₄. This peak has almost the same luminescence intensity as NN's. Figure 1(b) shows the temporal change of a single X luminescence. The decay profile is well fitted by a single exponential decay with a decay time of 40 ns.

Luminescence image
Density dependence of the luminescence centers is important to know their origin. We have measured the luminescence image of the samples with different nitrogen density using the band pass filters tuned for the specific wavelength (NN₃, NN₄, NN₅ or X). Figure 2 (a) shows examples of the luminescence image of NN₄ for three samples with different nitrogen density. The diameter of the detection area is 12 µm on the sample surface. With increasing the nitrogen density, the number of observed spots increases drastically. The similar measurements were performed for
peak X (see Fig. 2(b)) in the identical sample used for NN_4. The number of spots are very small compared with NN_4; nevertheless it increases with the increase of nitrogen density, suggesting nitrogen-related origin for peak X.

The NN pair density can be calculated by the spots and the area of the detection circle. The densities of NN_4 pairs are plotted in Fig. 3 as a function of nitrogen density. Assuming a random distribution of nitrogen impurities in the δ-doping layer, the nitrogen pair density, \([\text{NN}_4]\), is given by \([3]\)

\[
[\text{NN}_4] = \frac{n_4 [N]^2}{2 S_0}
\]

where \(S_0\) is the surface density of phosphorous sites on GaP(001), i.e., \(6.7 \times 10^6 \mu\text{m}^{-2}\), because its lattice constant is 0.545 nm. \(n_4\) is the number of equivalent sites forming NN_4 around one specific N atom in the δ-doping layer. The experimental result for NN_4 is well explained by Eq. (1) which is represented by a solid line in Fig. 3. Similar measurements were performed for NN_3 and NN_5, and their densities (open circles) were also found to follow the square dependence. On the other hand, the density dependence of luminescence peak X can not be explained by the square low. Their density seems to be proportional to the cube of nitrogen density. We may, therefore, reasonably conclude that the new peak originates from excitons bound to a nitrogen cluster composed of three nitrogen atoms.

3. Conclusions

We observed a new luminescence peak in nitrogen δ-doped GaP by μ-PL measurement. The areal density of the new luminescence center was found to be proportional to the cube of the nitrogen density. They are most likely comes from excitons trapped by NNN triplets. Further study is needed to understand the configuration of nitrogen atoms in the NNN cluster.

References

