Formation of Nitrogen Vacancy Adjoining to Gd Ion Doped in GaN

Daijiro Abe, Kotaro Higashi, Shuichi Emura, Yi Kai. Zhou, Shigehiko Hasegawa and Hajime Asahi

The Institute of Scientific and Industrial Research, Osaka University
8-1 Mihoga-oka, Ibaraki
Osaka 567-0047, Japan
Phone: +81-6-6879-8406 E-mail: emura@sanken.osaka-u.ac.jp

1. Introduction
In semiconductors, imperfection generally prevents exploring the physical properties ideally. This is one of the factors to make the performance of the device poor. The efficiency of Photo- and electro-luminescence is reduced by imperfection. Transport characteristics become poor by the defect scatterings. However, some impurities are in practical use as high quality luminescence centers. Donner and acceptor dopants are also necessary defects in semiconductor devices. Besides, there can be still the rarely available imperfections. F-center, which is an anion vacancy, was very valuable to investigate the electronic behavior in solid and some devices like an infrared laser and an imaging plate are produced with F-centers.

GaN doped with Gd ions is one of the diluted magnetic semiconductors (DMS) represented by GaMnAs. At present, physics and the application of many DMS materials are on investigation [1 - 3]. The elucidation of the origin of the ferromagnetism in those DMS is still in ambiguity except the Mn-DMS. The carrier-mediate mechanism is a highly potential model based on a few experimental evidences [4, 5]. It seems that one more process of magnetic interaction in addition to the standard carrier-mediate model for the DMS GaGdN should be necessary to interact for the f-orbital electrons of the Gd ion with the carriers, because the f-orbital of the Gd$^{3+}$ ion in GaN lies in the deep energy level from the valence band of GaN. Recently, it has been theoretically proposed that the Ga vacancy in GaGdN carries the ferromagnetism in co-operation with the dopant ion Gd [6, 7]. X-ray absorption spectra around the Gd L$_{III}$ edge in GaGdN DMS are observed to survey nitrogen vacancy, and the analysis of the spectra is presented, where we quote a discussion on DMS GaGdN should be necessary to interact for the f-orbital electrons of the Gd ion with the carriers, because the f-orbital of the Gd$^{3+}$ ion in GaN lies in the deep energy level from the valence band of GaN. Recently, it has been theoretically proposed that the Ga vacancy in GaGdN carries the ferromagnetism in co-operation with the dopant ion Gd [6, 7].

X-ray absorption spectra around the Gd L$_{III}$ edge in GaGdN DMS are observed to survey nitrogen vacancy, and the analysis of the spectra is presented, where we quote a simulation technique by a code FEFF. We will roughly discuss on the formation of nitrogen vacancy adjoining to Gd ion Doped in GaN.

2. Preparation of GaGdN Epi-layers and Experimental Procedures

Preparation of GaGdN Epi-layers

The samples were prepared on a (0001) plane of a sapphire substrate laminated by an n-type GaN template by a radio-frequency plasma-assisted molecular beam epitaxy method. Elemental Ga, Gd and plasma-enhanced N$_2$ were used as sources. The growth temperature is 700°C, the nitrogen flow rate 1.5 sccm, the RF power 180 W, and the Gd cell temperature 1100°C. Two samples were grown with different Ga cell temperatures, which were arranged to be two different vapor pressures between $0.7 \times 10^{-7}$ Torr and $1.8 \times 10^{-7}$ Torr. Here, a sample grown under the higher Ga vapor pressure (Ga rich condition) is labeled as a “Type I” and a sample under lower pressure as “Type II”. The GaGdN layers are piled up for one hour, and finished by the thin (one minute growth) GaN cap layer. The epitaxial growth of layers well oriented perpendicularly to the growth direction is observed. The Gd concentration which was estimated from the peak hight of the XANES spectra in comparison with known samples is less than 0.5 atomic percent.

Experimental Procedures

X-ray absorption spectroscopic (XAS) measurements of X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS) were performed at a beamline BL9A in PF, KEK. The synchrotron radiation storage ring run at electron energy of 2.5 GeV and in an electron current of 450 mA in top-up operation. The beamline BL9A is installed with a Si (111) double-crystal monochromator and a pseudo-conical shape mirror for collimation of incident X-rays. Monochromatized synchrotron radiation was focused on the sample by a second pseudo-conical shape mirror with a 1 mm x 1 mm beam size. The X-ray energy was calibrated at the pre-edge of the Cu foil (12.7185 degrees). The spectra were detected with a solid-state detector (SSD, Ge:Li) with 19 elements. A high purity (99.95%) aluminum pipe was set just before the specimen to block detector reception of elastic and inelastic scattering by air in the X-ray path to the specimen. The XANES spectra were taken with 0.8 eV step in energy and 3 seconds per each point in accumulation time. Measurements were performed at room temperature. The observed spectra were analyzed by a code REX2000.

3. Results and Discussion

To find the nitrogen vacancy, we mainly observed the XANES spectra at the L$_{III}$ edge of the dopant Gd ion and furthermore XAFS spectra to obtain the local structure around the Gd ion. XAS has an advantage of the element specification. XANES indicates the energy region from the threshold of the absorption edge to several ten eV in the absorption spectrum, where multi-scattering process dominantly reflects on the absorption spectrum. Therefore, vacancies may be detectable, while it is very difficult to ex-
tract the information on vacancies from the XAFS spectra and the standard analysis. We found two types of XAFS spectra at the Gd $L_{III}$-edge, depending on the growth parameters. Figures 1(a) and 1(b) show the XANES spectra. Figure 1(a) gives the spectrum from “Type I”, in which the remarkable features (indicated by arrows) as a shoulder peak at 7253 eV and as a small hump at 7268 eV are recognized. On the other hand, figure 1(b) does not present any spectrum structures at those energy regions, and shows the same spectrum shape as other Gd compounds. The sharp peak, called as a white line, in the spectrum from “Type II” slightly shifts to higher energy by about 2 eV than that of “Type I”.

![Fig. 1 XANES spectra at the Gd $L_{III}$-edge of GaGdN epi-layers.](image)

Fig. 1 XANES spectra at the Gd $L_{III}$-edge of GaGdN epi-layers. (a) is recorded from the “Type I” sample and (b) from the “Type II” sample. The intensity is in arbitrary unit.

To inspect the origin of the spectrum variety between the samples “Type I” and “Type II”, the simulation by a code FEFF is carried out with three types of the coordination environment around the Gd ion to the second nearest neighbors: (a) the complete set the coordination environment with $C_{6v}$ symmetry, (b) one nitrogen vacancy at the first nearest neighbor, and (c) one Ga vacancy at the second nearest neighbor. We find the similar spectra for the coordination environment types (a) and (c) in the simulation spectra to the observed one of the “Type I”. The “Type II” spectrum is nearly same as the coordination environment of the types (b). Consequently, the simulation results suggest that the sample presenting the “Type II” spectrum contains the nitrogen vacancy adjoining the dopant Gd ion.

X-ray diffraction (XRD) profiles were taken to confirm the situation of the coordination environment described above. XRD profiles of both “Type I and Type II” strongly support our finding in the XANES analysis. The profile of “Type I” gives a peak originated from GaGdN and no relaxation of the lattice constant in GaGdN. “Type II” profile shows no additional peak, leading to the relaxation of the GaGdN lattice to that of GaN template (substrate) and as a result, suggesting that the vacancies are created. It is worth to note that the lattice of GaN is much larger than the host GaN. The details will be presented in the conference and its proceeding.

Formation of the nitrogen vacancy adjoining to the Gd dopant ion may be qualitatively explained by the facts that nitrogen ion is more favorable to combine chemically with Ga ion than Gd ion, and that the ionic radius of Gd ion is much bigger (about 1.6 times) than Ga ion. The suitable model for the formation of the nitrogen vacancy adjoining to the dopant ion Gd is under consideration.

4. Conclusion

We find two kinds of the coordination environment around the dopant ion Gd that is the complete set and one vacancy adjoining to the Gd ion, depending on the growth parameter. XRD profiles strongly support this finding.

Acknowledgements

X-ray spectra were measured at Photon Factory (beam-line BL9A) in KEK in cooperation with Institute of Material Structure Science through Proposals 2008G019, 2008G675, 2009G657 and 2010G567. This work is partially supported by a Grant-in-Aid for Scientific Research in Priority Areas “Development of New Quantum Simulators and Quantum Design” (contact number 17064014) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References


