Growth and Characterization of GaDyN/AlGaN Multi-Quantum Well Structures

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GaDyN single layer and GaDyN/AlGaN multi-quantum well (MQW) structures are grown on GaN templates by radio-frequency plasma-assisted molecular-beam epitaxy (RF-MBE). X-ray diffraction θ/2θ scan curves exhibited well-defined satellite peaks for the MQW structure samples. From analyzing extended x-ray absorption fine structure (EXAFS), majority of Dy atoms are found to be incorporated into substituting the Ga sites in the GaDyN with wurtzite structure, which has longer bond length than that of GaN. The lattice constant of the GaDyN is larger than that of GaN due to large radius of Dy ion. Two photoluminescence excitation bands are found at 342 and 581 nm, which are identified as the band-to-band transition in the GaDyN quantum wells and the inner-4f transition of Dy³⁺ ions, respectively. Ferromagnetism is confirmed in the magnetization versus magnetic field curves at 10 and 300 K for the both structure samples. It is found that the MQW sample has larger magnetic moment than the single layer sample. This enhancement of magnetic moment is realized due to a strong exchange interaction between confined electrons and Dy ions. [DOI: 10.1380/ejssnt.2012.499]

Keywords: Quantum wells; Molecular beam epitaxy; EXAFS; Lanthanides

I. INTRODUCTION

GaN/AlGaN multi-quantum well (MQW) structures have attracted much attention for application to optoelectronic devices. For example emission from well layer is expected for the active region of ultraviolet (UV) light emitting diodes [1]. On the other hand, rare earth (RE) element-doped semiconductors have been of considerable interest for their unique magnetic and optical properties. RE elements (such as Gd, Eu, Er, Dy) doped into wide band gap semiconductors lead to sharp emission lines from UV through the visible to the infrared because of 4f inner shell transition [2–4]. In the case of Gd, Eu and Er doped GaN, ferromagnetic properties are also indicated [2, 4, 5]. Therefore, RE-doped MQW structures are expected to be designed spin-polarized vertical-cavity surface-emitting laser (spin-VCSEL), which can be used in optical computing and reconfigurable optical interconnects. Dy³⁺ ion has the largest magnetic moment among RE elements (10.6 μB). It is expected that GaDyN exhibits much larger magnetization and magneto-optic effect, which can be easily observed compared with the other RE-doped GaN having same RE element concentration.

In this paper, GaDyN single layer and GaDyN/AlGaN MQW structures were grown on GaN templates by radio-frequency plasma-assisted molecular-beam epitaxy (RF-MBE). Their structural, optical and magnetic characterizations are investigated.

II. EXPERIMENTAL

The TEM image of the GaDyN/AlGaN MQW sample is shown in Fig. 2. GaDyN layers have dark contrast and AlGaN layers have bright contrast. This period matches the XRD profile. It is clearly seen that the flatness of heterointerface is good.

FIG. 1: (a) XRD profiles for the GaDyN single layer and the GaDyN/AlGaN MQW samples, and (b) expanded-scale profiles.

GaDyN single layer and GaDyN/AlGaN MQW samples were grown on the GaN templates by RF-MBE. GaN template with 2-μm-thick Si-doped GaN layers (n ~ 10¹⁸ cm⁻³) was grown on a c-plane sapphire substrate by metalorganic chemical vapor deposition (MOCVD). After growth of a thin GaN buffer on the GaN template, a
GaDyN single layer (130 nm) was grown at 650°C. The growth temperature for MQW sample was 720°C. The MQW structure consists of 30 cycles of a GaDyN well (1 nm) separated by an Al0.23Ga0.77N barrier (9 nm). After growth of MQW, a 3-nm-thick GaN cap layer was grown to prevent Dy oxidation.

The sample crystalline quality was evaluated by X-ray diffraction (XRD) and transmission electron microscope (TEM) measurements. X-ray absorption fine structure (XAFS) measurements were performed at a beamline BL01B1 in Spring 8. The beamline BL01B1 is installed with a double-crystal monochromator with the alternative surfaces of (111), (311), and (511) of Si crystal and two mirrors for collimation of incident x-rays and for vertically focusing of monochromatized x-rays on a sample. The spectra were recorded with a solid-state detector (Ge:Li) with 19 elements. The X-ray energy was calibrated at the pre-edge of the Cu foil (12.7185 degrees). All measurements were carried out at room temperature. Photoluminescence (PL) measurements were conducted with the 325 nm line of a 27 mW He-Cd laser as an excitation light source. Magnetic properties were investigated by measuring magnetization as functions of magnetic field with a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSIONS

The XRD profiles of the GaDyN (1 nm)/AlGaN (9 nm) MQW and the GaDyN single layer samples are shown in Fig. 1(a) and expanded scale is shown in Fig. 1(b). No secondary phase such as DyN can be confirmed. The Dy concentration is evaluated about 6% by Energy Dispersive X-ray spectroscopy (EDX). GaN (0002) reflection peaks associated with the GaN templates appear almost at the same position in both samples. For the GaDyN single layer, a clear peak was observed at low angle side of the GaN (0002) reflection peak. This can be deduced that effective radii of Dy ions are larger than those of Ga ions [6], therefore lattice constant of GaDyN is larger than that of GaN. On the other hand, for the MQW sample, the observation of the satellite peaks indicates the successful growth of the MQW structure.

The local structure around Dy atoms in the GaDyN single layer and the GaDyN/AlGaN MQW structures were studied by XAFS measurements using Dy LIII-edge (7790 eV). XAFS oscillations $\chi(k)$ extracted from observed XAFS spectra, and the $\chi(k)$ function was multiplied by $k^3$ to compensate the damping of XAFS amplitude in the longer region. In order to obtain the radial distribution functions (RDFs) around Dy atoms, the $k^3\chi(k)$ functions were Fourier-transformed (FT). Absolute values of FT taken from the range of 2-12 Å$^{-1}$ in $k$-space of XAFS amplitudes were shown in Fig. 3. Results of GaN, NaCl-type DyN and Dy metal were also shown for comparison in the figure.

As results from Fig. 3, distances of 1st and the 2nd nearest-neighbor for the GaDyN and GaN samples are similar and differ from DyN and Dy metal obviously. Therefore majority of Dy atoms were considered to be incorporated into substituting the Ga sites of wurtzite structure of the GaDyN. The $k^3\chi(k)$ functions were Fourier-transformed (FT). Absolute values of FT taken from the range of 2-12 Å$^{-1}$ in $k$-space of XAFS amplitudes were shown in Fig. 3. Results of GaN, NaCl-type DyN and Dy metal were also shown for comparison in the figure.
TABLE I: The local structures around Dy and Ga in the GaDyN and GaN, respectively.

| Sample        | Atom type | Number of atoms | Distance (Å) | DW  | R value |
|---------------|-----------|-----------------|--------------|-----|---------|
| GaDyN single layer | 1st N     | 3.771           | 2.246        | 0.062 | 0.696   |
|               | 2nd Ga    | 8.431           | 3.302        | 0.055 | 1.166   |
| GaN           | 1st N     | 4.0             | 1.95         |      |         |
|               | 2nd Ga    | 12              | 3.18         |      |         |

DyN are 2.411 Å and 3.478 Å respectively. For the GaDyN sample compared with GaN, the bond lengths are elongated due to the incorporation of Dy atoms.

Figure 4(a) shows PL spectrum of the GaDyN/AlGaN MQW sample at 4 K. A sharp peak at 358 nm and a broad peak at around 550 nm were associated with the GaN template. A band-to-band emission at around 342 nm was observed from quantum wells at the higher energy side of the general GaN peak as shown in Fig. 4(b). The peak energy from GaDyN QWs is about 3.625 eV, which is almost similar to GaGdN/AlGaN QWs described in Ref. [8]. This peak energy is smaller than that of GaN/AlGaN QWs (3.664 eV). Although this emission intensity is very weak comparing with that from GaN template, it is shown that the quantum size effect exists in the GaDyN wells. In addition, an emission peak at 581 nm as shown in Fig. 5(c) is originated from the $^4F_{9/2}$–$^6H_{15/2}$ transition of Dy$^{3+}$ [3]. This sharp peak shows no shift with increasing the temperatures. This inner-$4f$ transition is suggested that energy transfer from GaN to Dy ions is occurred in the GaDyN wells [9]. For single layer sample, the emission at 581 nm corresponding to Dy ion inner-shell transition was also observed.

Magnetic property of the single layer and the MQW samples at 300 K was shown in Fig. 6. The magnetic field was applied perpendicular to the sample surface.

Diamagnetic component from the substrate were subtracted out and the data were normalized with the volume of the GaDyN. Saturation magnetization per unit volume of the MQW sample shows 4 times larger than that of the single layer sample. This phenomenon was also observed in GaGdN/GaN superlattice samples. We have previously reported that the GaGdN/GaN superlattice samples having thinner GaGdN layers showed larger magnetic moment [10, 11]. This enhancement of magnetization is understood as carrier-induced ferromagnetism. In the GaDyN/AlGaN MQW structure, carriers (electrons) are also strongly confined in GaDyN wells because of high barrier height of AlGaN. These confined electrons can strongly couple with f electrons of Dy ions, therefore, enhanced carrier-induced ferromagnetism are expected.

IV. CONCLUSIONS

GaDyN single layer and GaDyN/AlGaN MQW samples were grown by using RF-MBE method. The lattice constant of the GaDyN is larger than that of GaN. High crystalline quality was confirmed by TEM observation for the MQW sample. Analysis of the local structure around Dy ions shows that the Dy occupies the Ga substitutional site in the samples. The emissions corresponding to the $^4F_{9/2}$–$^6H_{13/2}$ transition of Dy$^{3+}$ and the band-to-band transition in the GaDyN wells were observed.

Ferromagnetic behavior was confirmed for both samples at room temperature. The saturation magnetization of the MQW sample shows about 4 times larger than that of
FIG. 6: M-H curves for the GaDyN single layer and the GaDyN/AlGaN MQW samples.

the single layer sample. This implies that the magnetism can be controlled in the quantum structures and more unique properties are expected to be found.

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[1] H. Haratizadeh, B. Monemar, and H. Amano, Phys. Status Solidi A 203, 149 (2006).
[2] N. Teraguchi, A. Suzuki, Y. Nanishi, Y. K. Zhou, M. Hashimoto, and H. Asahi, Solid State Commun. 122, 651 (2002).
[3] H. J. Lozykowski, W. M. Jadwisienczak, and I. Brown, Appl. Phys. Lett. 74, 1129 (1999).
[4] J. K. Hite, G. T. Thaler, R. Khanna, C. R. Abernathy, S. J. Pearton, J. H. Park, A. J. Steckl, and J. M. Zavada, Appl. Phys. Lett. 89, 132119 (2006).
[5] J. M. Zavada, N. Nepal, C. Ugolini, J. Y. Lin, H. X. Jiang, R. Davies, J. Hite, C. R. Abernathy, S. J. Pearton, E. E. Brown, and U. Hommerich, Appl. Phys. Lett. 91, 054106 (2007).
[6] X.J Li, Y.K. Zhou, M. Kim, S. Kimura, N. Teraguchi, S. Emura, S. Hasegawa, and H. Asahi, Chin. Phys. Lett. 22, 463 (2005).
[7] V. Katchkanov, J. F. W. Mosselmans, K. P. O'Donnell, E. Nogales, S. Hernandez, R. W. Martin, A. Steckl, and D. S. Lee, Optical Mater. 28, 785 (2006).
[8] M. Almokhtar, S. Emura, Y. K. Zhou, S. Hasegawa, and H. Asahi, Phys. Status Solidi C 9, 737 (2012).
[9] T. Kawasaki, A. Nishikawa, N. Furukawa, T. Terai, and Y. Fujiiwara, Phys. Status Solidi C 7, 2040 (2010).
[10] Y. K. Zhou, S. W. Choi, S. Kimura, S. Emura, S. Hasegawa, and H. Asahi, J. Supercond. Nov. Magn. 20, 429 (2007).
[11] S. W. Choi, Y. K. Zhou, M. S. Kim, S. Kimura, S. Emura, S. Hasegawa, and H. Asahi, Phys. Status Solidi A 203, 2774 (2006).