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Structural characterization of Eu-doped GaN by transmission electron microscopy

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The structural properties of Eu-doped GaN films grown on sapphire (0001) substrates by molecular beam epitaxy were studied using cross sectional transmission electron microscopy (TEM). The Eu concentration was estimated to be about 2at.% by Rutherford backscattering spectrometry and energy dispersive X-ray spectroscopy. Selected area diffraction patterns of the film showed a hexagonal structure, and no other anomalous patterns such as from Eu and EuN were observed. The high resolution TEM observation of the films showed a high density of stacking faults which was hardly observed in undoped GaN, bending layers and a small portion of cubic phase. The causes of the formation of stacking faults and bending of layers are discussed.

Key words: GaN, TEM, HRTEM, XRD, EDS, Rare Earth (Eu).

Introduction

Rare earth (RE) element doped GaN has significant potential for applications in optical devices since it shows sharp and intense luminescence. The emission wavelength and the intensity are insensitive to the environmental temperature, and the emission wavelength can be designable, extending from the infrared to the ultraviolet region depending on the RE element [1-5]. Since the room temperature intensity of the luminescence from the RE ion strongly depends on the band-gap energy of the host material [6-9], GaN is one of the promising materials as a host material. Among the various RE elements, Eu seems to be the most interesting, since it yields a red luminescence around 622 nm which has not been realized in commercially-available light emitting diodes (LED's) from nitride-based materials [10]. We have reported single crystalline growth of Eu-doped GaN with a the Eu concentration up to 2 at% and nearly temperature-independent red luminescence at 622 nm originating from the intra $4f$–$4f$ transition of the Eu^{3+} ion [4,5]. There are several reports about optical processes and the incorporation sites of Eu in GaN [5,11-14]. The red luminescence was analyzed and determined to be generated through trap-level-mediated energy transfer from the host GaN, and the external emission efficiency was estimated to be about 0.18 at room temperature when the Eu concentration was about 2 at.% [15,16]. Most of Eu ions in GaN are reported to be incorporated into Ga lattice sites. The results revealed that Eu-doped GaN is a potential material for the active layer of a LED. However, the structural properties of Eu-doped GaN are not yet clear. In this paper, we report on the crystallographic structure of Eu-doped GaN with a Eu concentration of 2 at% studied by transmission electron microscopy.

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Experimental

The Eu doped GaN films were grown by gas source molecular beam epitaxy (GSMBE) using uncracked ammonia gas as the nitrogen source. Metallic Ga of 6N purity and Eu of 3N purity were evaporated using conventional Knudsen effusion cells. Uncracked ammonia gas of 6N purity was introduced to the growth surface through a nozzle made from a stainless steel tube. The sapphire (0001) substrate was nitrided for a few minutes before the growth of a GaN buffer layer which was grown at 600°C. After annealing the buffer layer, Eu doped GaN was grown at 700°C. The film thickness was typically 0.8 μm. The Eu concentration in the GaN was measured by an energy dispersive X-ray spectro- meter (EDS) and Rutherford backscattering spectrometry (RBS).

TEM observations were carried out using a JEM-3100F (JEOL) with an acceleration voltage of 300 kV. The specimens for the cross-sectional TEM observation were prepared as follows; the specimen was thinned down to 100 μm by mechanical grinding followed by dimpling down to 10 μm. Then electron transparency was achieved by ion milling at 5 kV or a focused ion beam for undoped GaN and Eu doped GaN, respectively. TEM observations were carried out the incident electron beam parallel to a <1120> axis. X-ray diffraction (XRD) measurements were carried out with a θ-2θ mode using both Cu $K\alpha_1$ and $K\alpha_2$ radiations.

Results and discussion

Fig. 1 shows XRD profiles of Eu-doped GaN and undoped GaN for reference. The peak position of the Eu-doped GaN slightly shifted to a lower angle possibly due to the large atomic radii of Eu incorporation resulting in an increase in the lattice constant. The full width at half maximum (FWHM) of the diffraction peak of Eu-doped GaN is almost 1.5 times larger than that of undoped GaN, indicating that Eu-doped GaN is of lower crystalline quality compared with the undoped sample. No other anomalous diffraction peaks were observed; therefore the possibility of segregation such as of Eu and EuN can be excluded.

Fig. 2 (a) shows a cross sectional bright field image of undoped GaN layer grown on a sapphire (0001) substrate. The dark lines developing from the interface between the substrate and GaN to the growth surface can be assigned as threading dislocations as has been reported in many articles [17-19]. These dislocations are found to originate at the interface between the GaN and substrate. The generation of the threading dislocation has been proposed as from the inversion domain boundaries and stacking mismatch boundaries [20]. The dislocation density was estimated to be about 10^9~10^{10} /cm^2 from the micrograph. Fig. 2 (b) shows the selected area diffraction (SAD) pattern from undoped GaN. As can be seen in the figure, hexagonal GaN growth was confirmed. Fig. 2(c) shows a high-resolution cross-sectional image from the undoped GaN layer. The inset shows an enlargement of the area indicated. A hexagonal atomic arrangement is regularly observed.

Figs. 3 (a) and (b) show cross-sectional TEM micrographs from a Eu-doped GaN sample with a concentration of 2 at.% and its SAD pattern, respectively. Many tones of dark streak and spots were observed in the TEM image, which may be caused by a slight disordering in $[11\bar{2}0]$ lattice direction, that is, a twist structure. Although

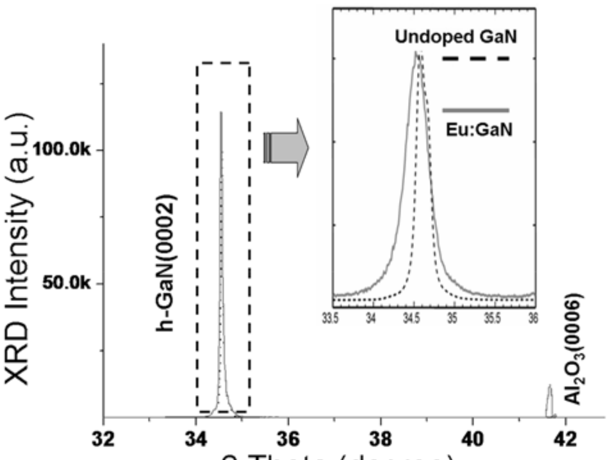

Fig. 1. XRD profiles of Eu-doped GaN with a Eu concentration of 2 at.% (solid line) and that of undoped GaN (dotted line).

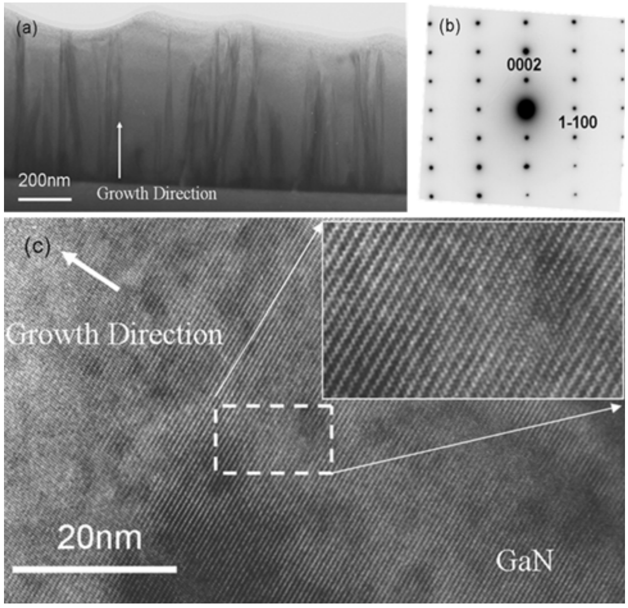

Fig. 2. Cross-sectional TEM micrographs of undoped GaN on sapphire (0001) substrate (a), SAD pattern from undoped GaN (b) and HRTEM image of undoped GaN (c).

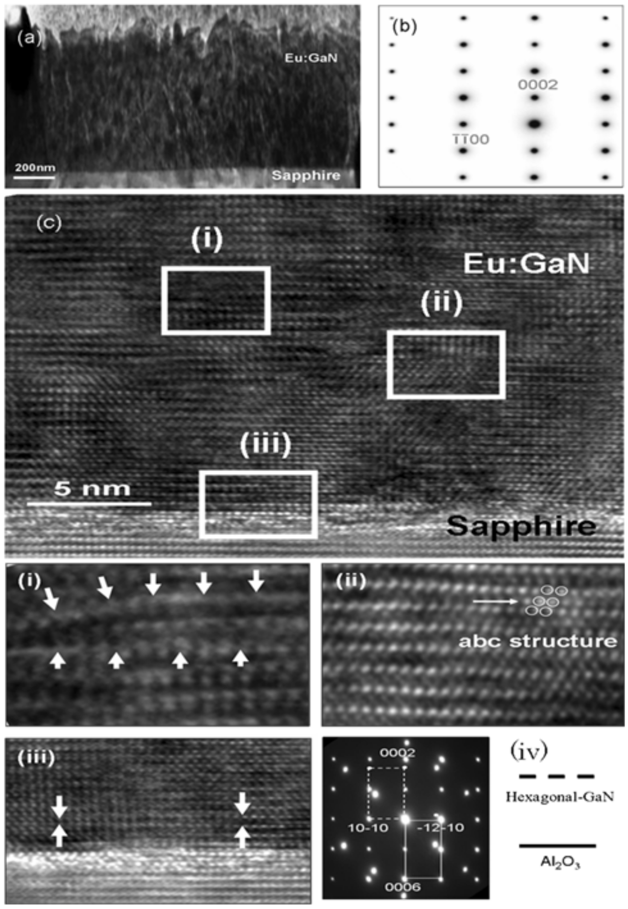

Fig. 3. Bright field image of a Eu-doped GaN film on Al_2O_3 (a), SAD pattern along the $[11\bar{2}0]$ zone axis from Eu-doped GaN(b), HRTEM image of Eu-doped GaN film near the interface(c). Enlarged images for the area indicated in Fig.3 (c) corresponding to (i), (ii) and (iii). A SAD pattern taken from the interface (iv).

the Eu- doped GaN is slightly twisted, the SAD pattern shows a hexagonal structure without extra spots. These results indicate that the Eu-doped GaN sample with a Eu concentration of 2 at% has a hexagonal phase without the formation of a secondary phase such as Eu and EuN which is consistent with the results from XRD.

A cross sectional high-resolution TEM image of the Eu-doped GaN sample is shown in Fig. 3(c). Disordering of atomic rows was observed in the entire region. Fig. 3 (i), (ii) and (iii) are enlarged images of the corresponding areas shown in Fig. 3(c). As shown in Fig. 3 (i), stacking irregularities such as broken and bent atomic row can be observed. The formation of a cubic phase was detected as shown in Fig. 3 (ii). These results indicate that a high density of stacking fault, which was rarely observed in undoped GaN was generated by Eu doping. As the atomic radius of Eu is 1.5 times larger than that of Ga, the Eu-doped GaN film contains large stresses. The stresses caused by Eu doping are considered to be relaxed by introducing stacking irregularities.

Fig. 3(iii) shows a cross sectional TEM image near the interface. The whitish intermediate layer, which is probably formed by the nitridation of the sapphire substrate, is observed. Fig. 3 (iv) shows a SAD pattern taken from the interface. The relation of epitaxial axes can be analyzed as sapphire [11$\bar{2}$0] parallel to Eu-doped GaN [1$\bar{1}$00] and sapphire (0001) parallel to Eu-doped GaN (0001) just the same as for undoped GaN on sapphire substrate.

Conclusions

The structural properties of Eu-doped GaN with a Eu concentration of 2 at% grown by molecular beam epitaxy on sapphire substrates were studied by cross sectional TEM observations. It was found that segregation such as Eu and EuN were not formed from the XRD and SAD observations. The Eu-doped GaN has a hexagonal structure with the epitaxial relationship of sapphire [11$\bar{2}$0]//Eu doped GaN [1$\bar{1}$00] and sapphire (0001)// Eu doped GaN (0001). A high density of stacking irregularities, however, which was not observed in undoped GaN, was detected for the doped samples. The formation of a high density of stacking irregularities may be caused by the incorporation of larger radius Eu which will induce significant stresses.

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