Resonant photoemission study of Eu doped GaN

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Rare-earth ions doped GaN is a promising material in application for light-emitting devices because of their unique optical properties. We have reported that the luminescence from Eu doped GaN shows sharp peak at 623 nm due to intra-atomic f-f transition assigned as $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion, and that the luminescence peak position, intensity and full width at half maximum of the peak are extremely stable with temperature.[1)]

It is well known that the stable oxidation state (ionic state) of Eu ion is divalent or trivalent depending on the chemical environment. The ionic states of Eu ions affect luminescent properties. The trivalent Eu generally shows red emission, and the divalent Eu mostly shows the luminescence in the blue light region. If the ionic states of Eu ions in GaN can be controlled, it may realize luminescence in another wavelength region.

The aim of the present work is to clarify the ionic states of Eu ions in GaN by carrying out resonant photoemission spectroscopy. Our results indicate that the divalent Eu ions are also present only at the surface of Eu doped GaN.

The Eu doped GaN was grown on sapphire (0001) substrate by gas-source molecular beam epitaxy using NH_3. Eu concentration was estimated to be about 2% by Rutherford back scattering spectrometry. The photoluminescence spectrum of Eu doped GaN shows dominant sharp emission at 623 nm with no band edge emission and with external quantum emission efficiency of about 0.2, as reported elsewhere.[1)] This means that only the trivalent Eu ions contribute to the luminescence from the sample.

Before the photoemission measurements, the sample surfaces were cleaned by ion bombardment and annealing in cycles under UHV conditions until no carbon and oxygen contaminations were detected by Auger electron spectroscopy. Even after this cleaning procedure, no degradation was observed in the luminescence property.

Figure 1 shows a series of energy distribution curves (EDC's) for Eu doped GaN in the valence band region for photon energies between 130 and 155 eV. The binding energy is measured with respect to the Ga 3d level. The valence band maximum is considered to be located at the binding energy of 18-20 eV in

this figure. It is evident that the photoemission cross section increases dramatically around 140 eV, which corresponds to the Eu 4d→4f excitation. Below 134 eV, there is no resonance and the spectra are fairly similar to those of undoped GaN. The contribution of Eu 4f component to each spectrum can be extracted by calculating difference spectra from EDC's taken on and off resonance. Using the spectrum taken under the incident energy of 130 eV as off resonance, the difference spectra were extracted and shown in Fig. 2. It should be noted that the density of states near the valence band maximum is resonantly enhanced only around 140 eV. This enhanced state corresponds to a final-state of $4f^6$ configuration of divalent Eu ions.[2] On the other hand, no distinct resonance of $4f^7$ configuration was observed, which means that only divalent Eu ions exist at the surface and that they do not contribute to the luminescence from Eu doped GaN. The existence of the divalent ions at the surface is often observed in Eu compounds. It has been considered that the change in the ionic state at the surface is caused by a decrease in cohesive energy due to the reduced coordination at the surface.[3] Though the divalent ions of Eu near the surface may be difficult to act as radiative center since the ions are in the depletion layer, it may be useful to understand the atomic structure of Eu near the surface in order to control the ionic state.

References

1) T. Maruyama et al., Jpn. J. Appl. Phys. 38 (1999) L1306.

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3) B. Johansson,, Phys. Rev. B 19 (1979) 6615.

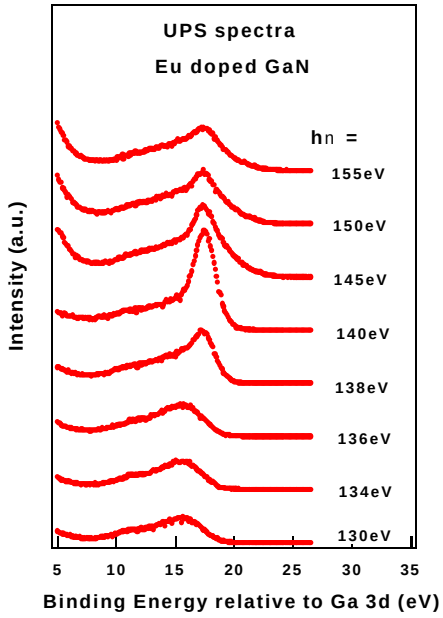

Fig. 1. Energy distribution curves (EDC's) of Eu doped GaN. The binding energy zero is the Ga 3d state.

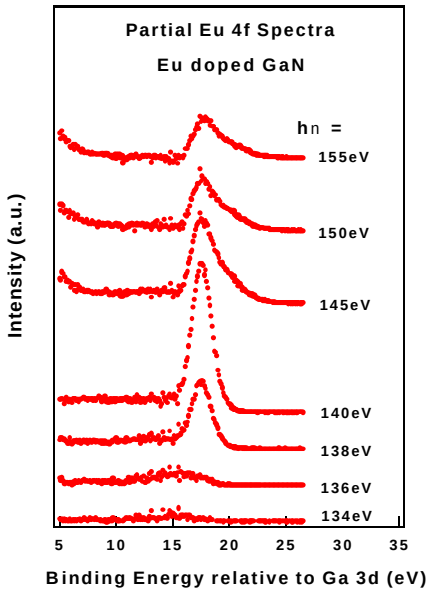

Fig. 2. Difference spectra obtained from the EDC spectra of Eu doped GaN taken on and off resonance.