Effect of Structural Changes Induced by Annealing Atmospheres on Luminescence of Eu^{2+}, Eu^{3+}-doped AlN Thin Films

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Aluminum nitride (AlN) shows ultraviolet to blue luminescence ascribed to various defect levels (V_{Al}, V_N, i_{Al}, i_N). Europium (Eu) is widely used as a phosphor material, which generally occurs in a 3+ valence state. Eu^{3+} ions show sharp red emissions due to 4f-4f transitions, whereas Eu^{2+} exhibits broad green emission attributed to 4f-5d transitions. Therefore, Eu doped AlN (AlN:Eu) thin films are expected to be applications to white light-emitting diodes with the mixture of those tri-phosphors. The valence states of Eu, 2+ and 3+, is influenced by the local structure around Eu ions such as the number and type of neighboring atoms. Previous study has reported that the presence or absence of oxygen in the ligands of Eu ions affects the valence state of Eu and the color of the emission in AlN:Eu [1]. This paper discusses the effect of post annealing in different atmospheres (N_2, O_2) on change in the local fine structure and luminescent properties of AlN:Eu thin films.

The AlN:Eu thin films were fabricated on Si (111) substrates using the pulsed laser deposition under a pressure of 1.8×10^{-5} Torr. A ceramic target of AlN (1:1 molar ratio) and Eu_2O_3 (5 wt%) mixture was ablated by the third harmonic (355 nm) of a Q-switched yttrium aluminum garnet (YAG) laser. AlN:Eu thin films were post annealed under O_2 or N_2 gas at 700, 900, and 1100°C. The luminescent properties were characterized by photoluminescence (PL) under an excitation of a He-Cd laser (325 nm), while changes in the local structure around Eu^{2+} and Eu^{3+} were analyzed by X-ray Absorption Fine Structure (XAFS) measurements and their fitting.

Samples annealed in N_2 atmosphere exhibited PL spectra peaking around 400 nm from defect levels in AlN and around 500 nm attributed to Eu^{2+}as shown in Fig. 1. In contrast, samples annealed in O_2 atmosphere showed relatively stronger peak at 617 nm attributed to Eu^{3+} than those for AlN defects and Eu^{2+}. The Eu L_{III}-edge XANES of AlN:Eu are given in Fig. 2. According to the peak positions for EuS and Eu_2O_3 were located at 6977 eV and 6986 eV, respectively. Samples annealed in N_2 atmosphere showed both Eu^{2+} and Eu^{3+}, whereas Eu^{2+} was predominant at 1100°C. Conversely, samples annealed in O_2 atmosphere exhibited a transition to Eu^{3+} valence state with increasing annealing temperature.

These results suggest that the valence states of Eu ions in AlN:Eu can be controlled by selecting annealing atmosphere. Details including the number, type, and distance between Eu ions and neighboring atoms will be discussed.

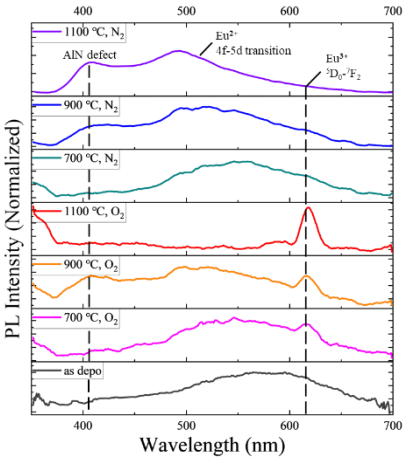

Fig. 1 PL spectra of AlN:Eu sample series annealed in N_2 and O_2 atmospheres at different temperatures.

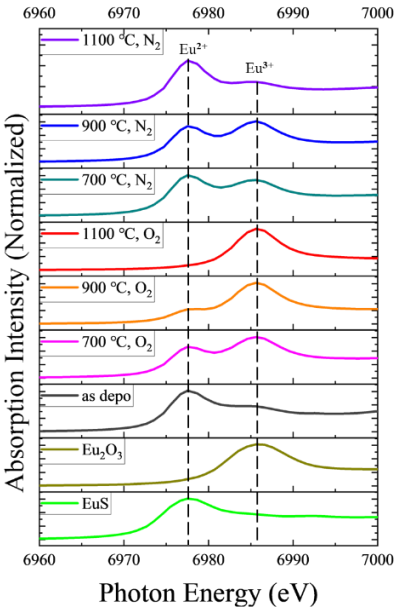

Fig. 2 XAFS of AlN:Eu sample series and standard samples, EuS (Eu^{2+}) and Eu_2O_3 (Eu^{3+}) powders.

References

[1] L. Yin, Q. Zhu, W. Yu, L. Hao, X Xu, F. Hu, and M. Lee, J. Appl. Phys. 111, 053534 (2012).