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Annealing Temperature-Dependent Luminescence Color Coordination in Eu-Doped AlN Thin Films

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Abstract

AlN was used as a host material and doped with Eu grown on Si substrate by pulsed laser deposition (PLD) with low substrate temperature. The X-ray diffraction (XRD) data revealed the orientation and the composition of the thin film. The surface morphology was studied by scanning electron microscope (SEM). While raising the annealing temperatures from 300˚C to 900˚C, the emission was observed from AlN: Eu under excitation of 260 nm excitation. The photoluminescence (PL) was integrated over the visible light wavelength shifted from the blue to the red zone in the CIE 1931 chromaticity coordinates. The luminescence color coordination of AlN: Eu depending on the annealing temperatures guides the further study of Eu-doped nitrides manufacturing on white light emitting diode (LED) and full color LED devices.

Keywords

Low-Temperature PLD Growth, Eu-Doped AlN Thin Film, White Light Emitting Diode

1. Introduction

Solid-state lighting white LEDs based on nitride materials have attracted much attention because of their high efficiency, small volume, long lifetime, and environmental friendliness [1] [2]. Generally, the nitride materials doped with rare earth (RE) ions were considered as promising materials for LED chips and phosphors owing to their high stability and flexible bandgap adjustment in the visible light range.

For the RE doped GaN, it has strong luminescence and high efficiency. However, the sharp blue light from a GaN emission is an inevitable weak point for the configuration of the white color. AlN is a promising material for the host material which has a wurtzite structure and a wide bandgap (6.0 eV) that can efficiently prevent a higher temperature quenching effect and provide higher energy photons for the RE ions. The defect luminescence around 360 nm of AlN combined with red emission from RE can provide warm white light. Within all the RE elements, Eu was considered as an excellent choice in fabricating RE-based photoluminescent layers because of their stable red emission at 610 nm from Eu^{3+} and green emission of Eu^{2+} [3]. For the AlN doped with Eu, it can be very difficult to realize the controlling emission color of the different valences of Eu. So far, Takeda *et al.* reported that Eu and Si co-doped AlN showed blue luminescence by UV and electron excitation [4]. Berzina *et al.* reported Eu caused luminescence was determinative over emissions of AlN native defects such as oxygen impurity [5]. O_N, V_{Al}, and their related complexes induced abundant mid-gap states in AlN which can transfer energy to the Eu as reported by Chen *et al.* [6].

This study used deposition with a YAG laser (355 nm) system to achieve the low-temperature Eu-doped AlN thin film fabrication. The luminescence color of the thin films was regulated by changing the annealing temperature. Under 260 nm excitation light, the luminescence color coordination was shifted from the red to the blue zone across the white light region according to the CIE color space.

2. Experiment and Characteristics

Eu doped AlN thin films were grown on Si (111) faced substrates by PLD. The 3rd harmonic line of a YAG laser (355 nm) was used for ablating the target with a typical laser fluence of 1 $J \cdot cm^{-2}$. The PLD target was the AlN ceramic target combined with 0.6 at% Eu_2O_3 made by TOSHIMA Manufacturing Co. Ltd. The AlN: Eu samples were grown in an N_2 atmosphere at 5×10^{-3} Torr. The substrate holder was heated to 150˚C before the growth procedure. The PLD growth time was 8.3 h. The nitrogen pressure played a critical role in growth which could reduce the speed of the plume particles to improve the morphology and supply sufficient nitrogen anions to decrease the vacancy of nitrogen in AlN [7]. The thickness of the layer was about 480 nm detected by FE-300 film thickness monitor. The as-prepared samples were post-annealed under different temperatures for 1 hour in N_2 atmosphere at normal pressure (1 atm). The annealing temperatures were 300˚C, 400˚C, 500˚C, 600˚C, 700˚C, 800˚C, and 900˚C. The preparation process of AlN: Eu was shown in **Figure 1** in schematic form.

Rigaku-Smart Lab 3 kW-Rigaku XRD was used to detect the structure of the thin films grown on the silicon substrate. The surfaces of the AlN thin films were characterized using a Sigma500 field emission SEM equipped with energy dispersive X-ray spectroscopy (EDS) from ZEISS, UK. The PL spectrum of samples was using a UV–visible spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan)

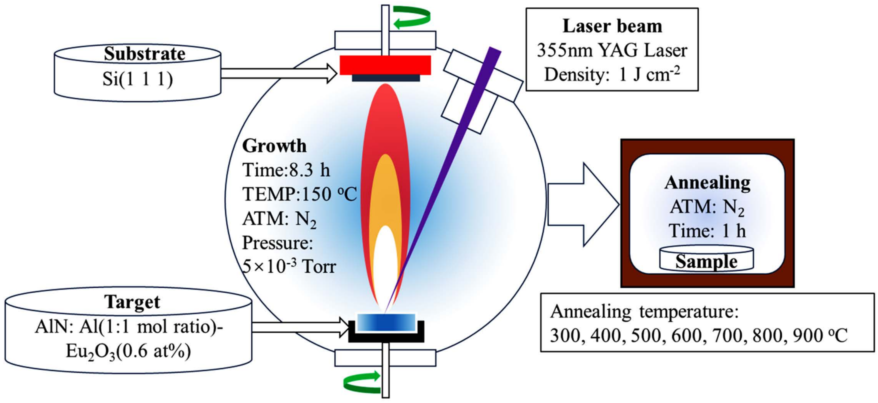

Figure 1. Schematic diagram of the AlN: Eu preparation process.

on ~500 nm thick films of the respective materials under the optimal excitation wavelength of 260 nm. All the measurements were carried out at room temperature.

3. Results and Discussion

The orientation and structure of the thin film were confirmed by XRD. The two plots marked as 600˚C and 900˚C in **Figure 2** are 2θ-ω profiles of the AlN overlayers annealing under 600˚C and 900˚C respectively. In these profiles, the sharp peaks located at 32.3, 35.9, and 39.0 degrees are respectively the diffractions of AlN (100), AlN (002), and AlN (101) [8]. The 28.3 and 58.7 2θ degrees peaks are related to the diffraction peaks of Si (111) and Si (222). [9]. The XRD peak position of AlN is well-matched with the standard JCPDS file (File No. 25-1133). The observed dominant peak belonging to (002) plane in samples represented that the AlN films preferred to grow along the c-direction on Si (111) substrate. The full width at half maximum (FWHM) values of AlN (002) in the sample 600 and 900˚C are 374.4 and 381.6 arcsec. The limited crystallite size gives broader peak. The smaller FWHM values indicated the better crystalline quality possessed by the sample calcined under 600˚C [10].

In order to investigate the surface of Eu-doped AlN layer annealing at 900˚C, the SEM was performed to characterize the morphology of the samples. **Figure 3** shows the top-view SEM image of the AlN thin film on the Si (111) substrate grown at identical conditions with other samples. Some irregular island-like and dot-like features were observed to partly cover the surface of the AlN layer in the SEM image shown in **Figure 3(a)**. To figure out the composition of the droplets and irregular shape islands, the signals of O, N, Eu, Al, and Si observed in the EDS spectrum were detected from two rectangular areas respectively including two different shape nanostructures on the AlN layer in **Figure 3(b)** and **Figure 3(c)**. The Eu M_α and Al $K_{\alpha 1}$ signals of the EDS intensity mapping spectra detected in the rectangular area of SEM images are shown in **Figure 3(b)** and **Figure 3(c)**, respectively. The high-intensity Eu M_α signal was detected in the bright region of EDS. The high density dots were at the same position of the irregular island in the image of SEM. The relatively high-intensity Al $K_{\alpha 1}$ signal was detected in Figure 3(c). As shown in EDS elemental spectrum from Figure 4(a), there are three kinds of cations detected, Eu ions, Al ions, and Si ions. Due to the detection depth of EDS about 1 μm which is much deeper than the top layer, the signal from the Si substrate emerged in the EDS mapping scan. Compared to the EDS scan mapping results of the Si $K_{\alpha 1}$ and Eu M_{α}, the Al $K_{\alpha 1}$ has the highest signal at the same position as the droplets on the AlN thin film surface. These results show that droplets are formed by laser melting aluminum and then solidify on the surface [11] [12] [13]. The smaller, irregularly shaped material is europium oxide, which has not integrated into the aluminum nitride lattice proved by the EDS result.

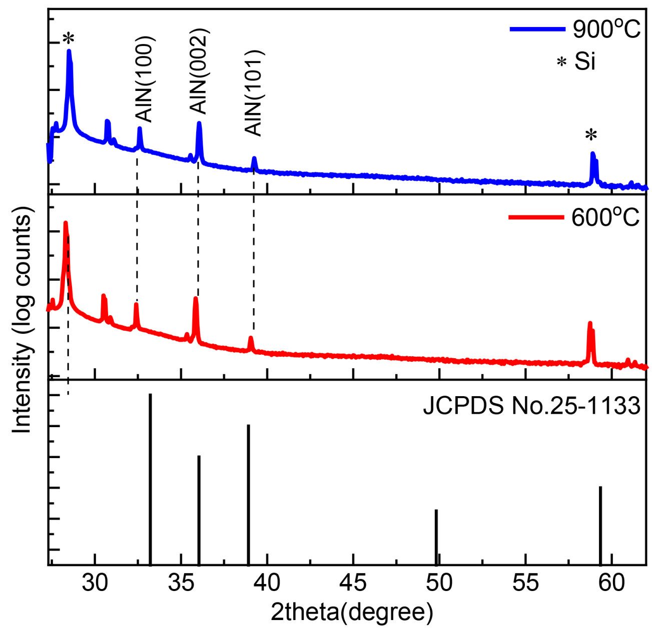

Figure 2. XRD patterns for AlN: Eu samples annealing at 600˚C and 900˚C. Standard JCPDS card No. 25-1133 is shown for comparison.

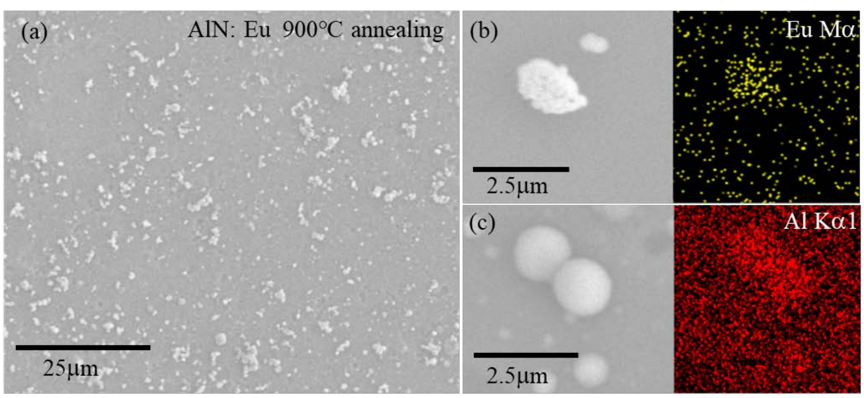

Figure 3. (a) The SEM plane-view images of the AlN: Eu thin film deposited on the Si (111); (b) the Eu Mα and (c) Al $K_{\alpha 1}$ signals detected in the part region of the EDS image in Figure 3(a).

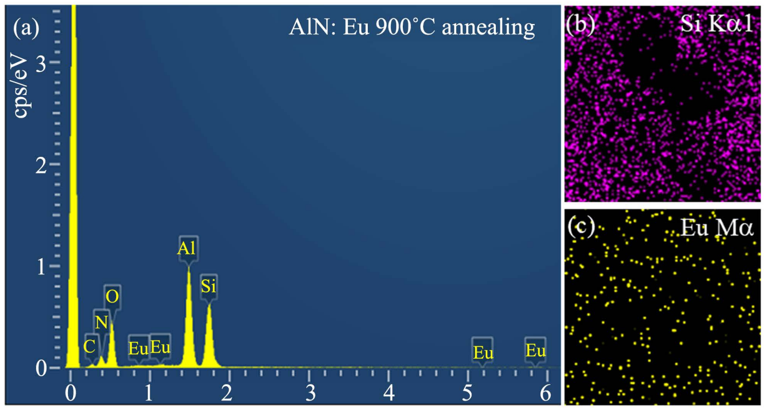

Figure 4. (a) EDS elemental spectrum of AlN: Eu sample under 900˚C annealing temperature. (b) Si $K_{\alpha 1}$ signals and (c) Eu Mα detected in the region of the EDS image in **Figure 3(a)**.

The PL measurement under room temperature was executed with 260 nm excitation on all the AlN doped Eu samples annealing temperatures from 300˚C to 900˚C in order to investigate the variation of the optical properties. The 260 nm excitation wavelength was chosen due to 613 nm emission peak show the best absorption at 260 nm according to photoluminescence excitation (PLE) result in **Figure 5**. By monitoring the emission at 613 nm, two excitation peaks were detected. Two peaks located at 260 nm and 567 nm which were related to the defect of AlN and Eu^{3+} ions respectively. Note that all the PL spectra were measured under identical set-up conditions.

In **Figure 6**, the PL spectra in the wavelength regions from 300 nm to 650 nm consists of several main peaks located at 328 nm, 363 nm and 613 nm. According to EDS measurements, oxygen was the main impurity in the AlN thin film. While raising the annealing temperature, the intensity of AlN defects emission at 363 nm and Eu luminescence peak at 613 nm was increasing. On the contrary, the peak around 328 nm has lower intensity compared to 363 nm peaks after 800˚C. The 328 nm peak could be attributed to the transition from shallow donors to $(V_{Al}\text{-}O_N)^{2-}$. During the annealing process, oxygen atoms would escape from the defects caused by lattice expansion and O ions migration in the crystal lattice. The $(V_{Al}\text{-}O_N)^{2-}$ defects would change to V_{Al} because of the breakaway of oxygen which make the V_{Al} related defects emission take a red shift to 363 nm [6] [14]. As the annealing temperature increases, the escape of oxygen ions from the AlN layer was enhanced so that the V_{Al} defect took a dominant place in the thin film. The peak around 363 nm is gradually stronger than the peak at 328 nm as shown in the **Figure 6** [6].

The long energy band tail from 450 nn to 550 nm can be due to the Eu^{2+} emission from 5d to 4f [15]. As the transition between $4f^6 5d$ and $4f^7$ of Eu^{2+} ion can be strongly affected by the crystal lattice environment, such as covalence, polarizability, crystal field strength, bond length, atom coordination numbers, and crystal symmetry. The peak of $^5D_0$ - $^7F_2$ of Eu^{3+} ions is located at 613 nm. The short peak near 589 nm was also due to the transition from $^5D_0$ to $^7F_1$ [16].

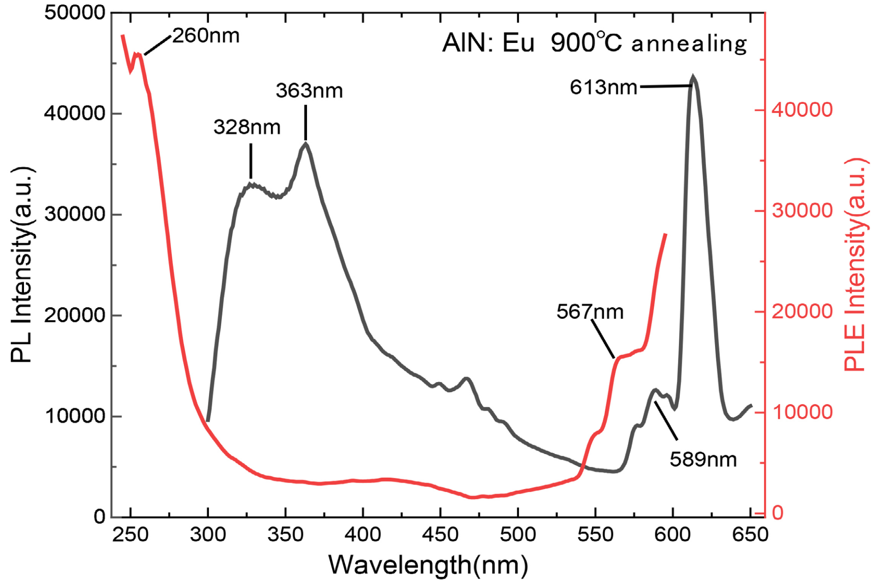

Figure 5. PLE spectrum of AlN: Eu sample under 900˚C annealing temperature.

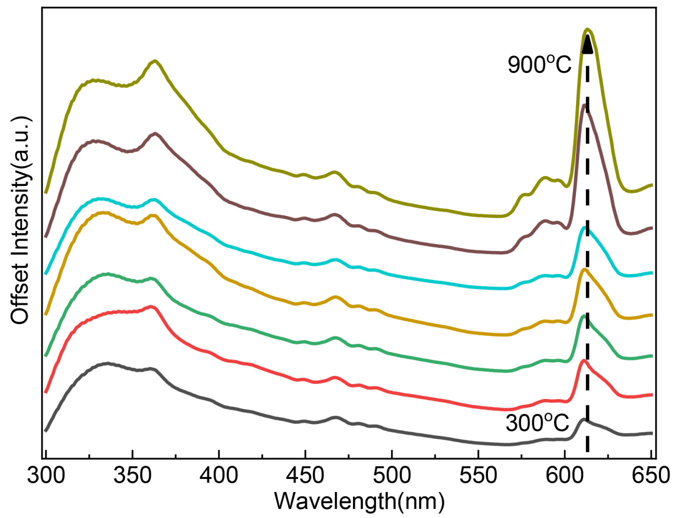

Figure 6. The luminescence of AlN: Eu under the 260 nm excitation in room temperature.

In **Figure 5**, the excitation peak at 260 nm corresponds to the emission peak belonging to the V_{Al} at 328 nm with a stokes shift about 0.98 eV. The luminescence induced by energy transfer of $^5D_0$ - $^7F_2$ of Eu^{3+} ions show the best absorption energy of 4.77 eV (260 nm). The result indicates that after the electrons were excited by incident energy and captured by the defect energy level, the recombination energy of excitons was transferred to Eu^{3+} ions. The energy transition from AlN defect energy level to Eu^{3+} ions proves that Eu is successfully doped in AlN host material [6].

The series of PL spectrum of AlN: Eu thin film annealing under 300˚C to 900˚C excited by 260 nm have been integrated by the following function in the visible wavelength from 380 nm to 750 nm,

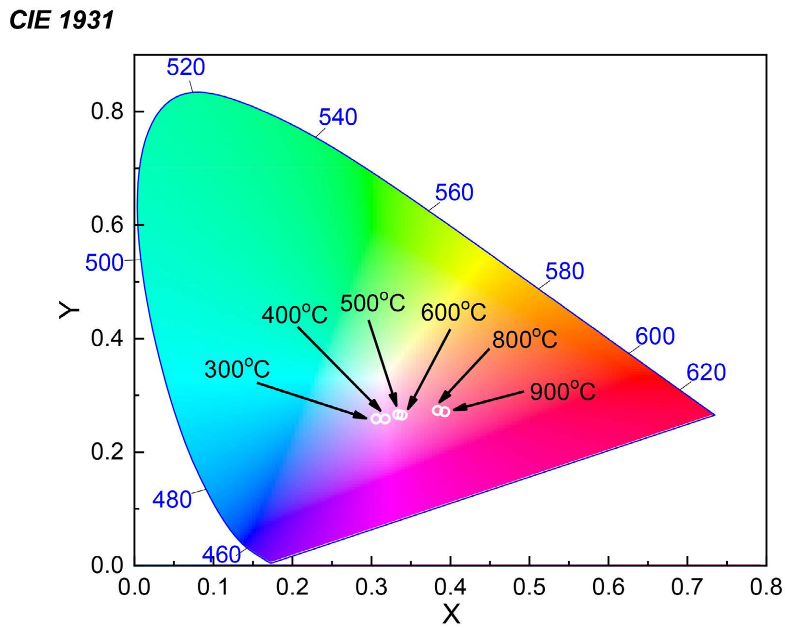

Figure 7. The coordination of integrated PL spectrum of AlN: Eu samples annealing at 300˚C, 400˚C, 500˚C, 600˚C, 800˚C, and 900˚C under the CIE 1931 color space.

$$X = \int f(\lambda)\bar{x}(\lambda)\mathrm{d}\lambda \tag{1}$$

$$Y = \int f(\lambda)\bar{y}(\lambda)\mathrm{d}\lambda \tag{2}$$

$$Z = \int f(\lambda)\bar{z}(\lambda)\mathrm{d}\lambda \tag{3}$$

where $f(\lambda)$ is the spectra, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are CIE 1931 color matching functions [17]. The coordination derived from these functions can be seen in **Figure 7**. The combined color of thin film luminescence under excitation 260 nm can be tuned from blue to red color zone by rising the annealing temperature from 300˚C to 900˚C. The chromaticity coordinates (x, y) of the sample under the annealing temperature of 300˚C, (0.29, 0.24) take a linear movement to (0.38, 0.27) when raising the annealing temperature to 900˚C.

4. Conclusion

A series of aluminum nitride films dominated by (001) crystal phase (c-direction) were successfully grown on Si (111) substrate by low-temperature PLD method. The surface quality was measured through SEM revealing the presence of AlN droplets and europium oxide adhering to the surface of the AlN layer. From the PL spectrum excited by the 260 nm light source, we observed that, as the annealing temperature raising, the AlN exhibited defects luminescence peak at 363 nm related to the defect of V_{Al} which was enhanced by oxygen escape. By integrating the PL intensity in the visible light range, the CIE 1931 chromaticity coordinates shifts from the blue region to the red region by increasing the annealing temperature. This demonstrates that effective control of the annealing temperature can fine-tune the luminescent properties of Eu-doped AlN. The economical and low temperature PLD grown AlN: Eu thin film has great potential as white LED materials.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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