Blue Emission by Interstitial Site Occupation of Ce$^{3+}$ in AlN
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ABSTRACT: An AlN phosphor that was coactivated by Ce$^{3+}$ and Si$^{4+}$ ions was synthesized by gas pressure sintering (GPS) at 2050 °C for 4 h in a 0.92 MPa nitrogen atmosphere. The phosphor emits blue color with the Commission International de l’Eclairage (CIE) chromaticity coordinate of (0.15, 0.07), which is close to the National Television Standard Committee (NTSC) blue coordinate. The crystallization and cell parameters of the samples were investigated by Rietveld refinement and high-resolution transmission electron microscopy (HRTEM). Since the ionic size of Ce$^{3+}$ ions are much larger than that of Al$^{3+}$ ions, the locations of rare earth (RE) ions in the AlN lattice are unclear. An octahedral interstitial site inside the wurtzite structure is proposed to be the site for RE ions. The effect of Si substitution was verified by energy-dispersive X-ray spectroscopy (EDX) and solid-state nuclear magnetic resonance (ssNMR). Cathodoluminescence (CL) was examined under electron bombardment at different accelerating voltages. Nitride phosphor exhibited high brightness and favorable stability. This study reveals the superior characteristics of nitride compounds in field emission display (FED) applications.

KEYWORDS: field emission display, nitride phosphor, interstitial site

INTRODUCTION

Field emission displays (FEDs) are vacuum electron devices that operate in a similar principle as a cathode ray tube (CRT) does: electrons that are emitted from emitters are controlled to bombard the anode side that is coated with a phosphor layer. They attract considerable attention because of several excellent features such as thin-panel thickness, self-emissive, distortion-free image, wide viewing angle (170°), quick responses, and so on.1 FEDs are also expected as low power consuming devices because power is theoretically consumed only at the emitting part. The requirements of phosphors for FEDs are high stability under electron bombardment, high efficiency under excitation by accelerated electrons at a relatively low voltage, high conductivity, and good chromaticity. Currently the three primary color phosphors used are ZnS for blue and green emitting parts and Y$_2$O$_2$S for red color. However, sulfide host lattices have low chemical stability and a poor thermal stability, so they may easily contaminate emission tips and limit the device lifetime.2 Therefore, research of phosphors for FEDs has been of great interest.3

Recently, aluminum nitride has been studied extensively as a new class of phosphor host recently owing to its wide band gap, high efficiency, and excellent chemical stability.4 Activators such as Er$^{3+}$, Ga$^{3+}$, Cr$^{3+}$, Eu$^{2+}$, Tb$^{3+}$, Mn$^{2+}$, Pr$^{3+}$, and Ho$^{3+}$ have been reported to be doped into AlN by sputtering or chemical vapor deposition.5−12 However, most related studies have focused on amorphous thin films rather than polycrystalline powder materials, possibly because of the high melting point of AlN and the low solubility of activators in the host lattice.

Aluminum nitride is a semiconductor with a wide band gap of 6.2 eV. It has a wurtzite structure in which the cations are coordinated with four anions. The high stability and thermal conductivity of AlN enable it to be used as a light-emitting diode material.13 Reports on activator-doped AlN powder phosphors have focused on Eu$^{3+}$ ions. Earlier investigations of Eu$^{2+}$-doped AlN prepared by combustion synthesis showed green emission.14,15 Later experiments that involved AlN prepared by spark plasma sintering, carbothermal reduction, and gas pressure sintering demonstrated blue emission.16−20 This work demonstrates a new blue phosphor that is an AlN host lattice codoped with Si$^{4+}$ and Ce$^{3+}$ ions. The indigenous oxygen impurities in AlN precursor are examined. An adapted heating program is designed, and a small amount of carbon acting as a reductant was added to successfully remove the impurities. The crystal structures of AlN doped with Si$^{4+}$ and Eu$^{2+}$/Ce$^{3+}$ ions are also studied. Possible interstitial sites for Ce$^{3+}$ in the AlN lattice may exist.

EXPERIMENTAL SECTION

Synthesis. Al$_{0.95}$N:Si$_{0.05}$xCe$_{3+}$(x = 0.01−0.15%) and Al$_{0.95}$N:Si$_{0.05}$.5Eu$_{3+}$ were prepared from AlN (Tokuyama Corp., type F), α-Si$_3$N$_4$ (Ube Industries, grade SN-E10, α/(α + β) > 95% by wt), Eu$_2$O$_3$ (Aldrich Inc., 99.9%), CeO$_2$ (Aldrich Inc., 99.9%), and C (graphite) as starting powders, using the gas pressure sintering (GPS)
method. For each composition, the amounts of AlN and that of α-Si₃N₄ were fixed to make the molar ratio of Al and Si equal to 95:5. The amount of CeO₂ was determined by the value of diffraction peaks corresponding to CeO₂. The amount of SiO₂ was calculated from the difference between the total mass of starting materials and the calculated mass of AlN and CeO₂.

The amount of graphite was determined by the value of mass gain during heating. For each composition, the amounts of AlN and graphite were weighed out stoichiometrically and mixed by grinding in an agate mortar.

Characterization. The composition and phase purity of the samples were studied by XRD measurements which were carried out at the high-energy beamline 01C2 at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu. The beamline was in transmission mode operated at an energy of 25 keV. The XRD pattern was recorded using the wavelength λ = 0.7749 Å at room temperature. The exposure time was 3 min, and the XRD patterns were obtained on the Mar 345-image plate detector. The crystal structure was refined by the Rietveld method using the General Structure Analysis System (GSAS) program. The photoluminescence (PL) spectra were obtained using a FluoroMax-3 spectrofluorometer at room temperature with a 150 W Xe lamp and a Hamamatsu R928 photomultiplier tube (PMT). The particle size and morphology of the samples were examined using a scanning electron microscope (SEM; Hitachi S2400), and the element composition was determined using an energy-dispersive X-ray spectroscope (EDX) that was attached to the SEM. Transmission electron microscopic (TEM) images and fast Fourier transform (FFT) patterns were attained using a Jeol JEM-2011 electron microscope equipped with a LaB₆ filament operating at an accelerating voltage of 200 kV. The high-resolution TEM (HRTEM) images were recorded using a Gatan 794 CCD camera. The cathodoluminescence (CL) measurements were made at room temperature, in an ultrahigh-vacuum chamber (10⁻³ Pa). A total of 0.12 g of phosphor powder was deposited on an aluminum plate (1 cm x 1 cm) with an adhesive conductive carbon tape by sedimentation with a dispersing agent. The CL properties were studied using a continuous electron-beam with a wavelength of 0.7749 Å at room temperature. The emission spectra and the photograph of the sample were recorded using a Hamamatsu C5094 spectrograph.

Solid-state nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DSX 300 MHz NMR spectrometer equipped with a 4 mm double-resonance magic-angle-spinning (MAS) probe head. The Larmor frequencies for 29Si and 27Al were 59.63 and 78.22 MHz, respectively. 29Si single pulse experiments were carried out using a π/3 pulse (3 μs), a recycle delay of 60 s, and a sample spinning rate of 5 kHz. 27Al signals were collected after a selective pulse (<π/6) of 3 μs with a recycle delay of 1 s and a spinning rate of 12 kHz. 29Si and 27Al chemical shifts were reported relative to external tetramethylsilane and 1 M aqueous Al(NO₃)₃, respectively.

RESULTS AND DISCUSSION

Indigenous Impurities of AlN. Oxygen is a common impurity in AlN crystals. The high solubility of oxygen in the aluminum nitride lattice affects its phase purity, lattice parameters, thermal conductivity, and optical properties. The AlN lattice may accommodate oxygen according to the formula Al₂O₃. For every three oxygen atoms incorporated, one aluminum atom vacancy is created. At high oxygen concentrations, extended defects such as polytypoids are formed. Figure 1a reveals that under 123 nm excitation, the AlN precursor emits a broad band emission that is centered in the UV region from 300 to 550 nm. This UV emission is ascribed to radiative recombinination of oxygen related impurities and Al vacancies. When the AlN precursor itself was fired to 2050 °C from room temperature at a constant heating rate of 10 °C/min, the emission peak shifted to a blue color centered at 470 nm. Figure 1b presents the emission and excitation spectra and the photograph of the sample. The impurities that are formed by oxygen are present in not only AlN but also in Si₃N₄, and the precursors of rare earth ions are oxides. Hence, completely removing the oxygen impurities from the precursors is important. Two solutions are introduced to the synthesizing process: (1) a small amount of carbon is added, and (2) the temperature is held at 800 °C for 3 h under vacuum. After the heating program was modified, the product that was obtained by firing the AlN precursor exhibited no emission under 365 nm UV light excitation (data not shown). The oxygen impurities from AlN and Si₃N₄ are assumed to be Al₂O₃ and SiO₂, respectively. The function of carbon corresponds to the following reaction equations:

\[ \text{Al}_2 \text{O}_3 + 3 \text{C} + \text{N}_2 \rightarrow 2 \text{AlN} + 3 \text{CO(g)} \]
\[ 3 \text{SiO}_2 + 6 \text{C} + 2 \text{N}_2 \rightarrow 3 \text{SiN}_4 + 6 \text{CO(g)} \]
\[ \text{CeO}_2 + 3 \text{C} + \text{N}_2 \rightarrow 2 \text{CeN} + 3 \text{CO(g)} \]

Figure 1. (a) Excitation (λ_ex = 400 nm) and emission spectra (λ_em = 132 nm) of AlN precursor. (b) Excitation (λ_ex = 470 nm) and emission spectra (λ_em = 310 nm) of firing the AlN precursor at 2050 °C, 4 h, and 0.92 MPa. The inset shows the picture of the sample under 365 nm UV light excitation.
The byproduct, carbon monoxide, is removed by the vacuum system. Because the amount of impurities is low, the 0.003 g of graphite is sufficient to the aforementioned amount of the precursors. The shifting of the emission color after heating is unclear.

**Crystal Structure and Luminescence Properties.** Figure 2 shows the XRD patterns of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$ ($x = 0.01–0.15$%). The diffraction peaks do not reveal any impurity phases, so the incorporation of small amounts of Si$^{4+}$ and Ce$^{3+}$ ions into the host lattice does not significantly distort the structure. The Rietveld refinement of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$ reveals that the compound has a hexagonal structure with the space group P6$_3$mc, and its cell parameters are $a = b = 3.1115(4)$ Å, $c = 4.9807(2)$ Å. The refinement process did not replace the rare earth ions with any of the elements in the host lattice because we believe that the differences between the ionic sizes of the host elements and rare earth ions Al$^{3+}$ (4CN, 0.39 Å) and Ce$^{3+}$ (6CN, 1.01 Å) are too large. During the refinement procedure, the occupancy parameters of all atoms were evaluated with reference to the nominal stoichiometry. The temperature factors were fixed for all substituted ions. Table 1 presents the structural parameters of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$.

The emission and excitation spectra of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$ ($x = 0.01–0.15$%) are asymmetric because of the spin–orbital coupling of the Ce$^{3+}$ ions with a full width at half maximum (fwhm) of 90 nm. The critical distance of energy transfer $R_c$ can be calculated by using the concentration quenching method where the critical distance between Ce$^{3+}$ ions can be estimated by the following formula:

$$ R_c = 2 \left( \frac{3V}{4\pi X N} \right)^{1/3} $$

where $V$ is the volume of the unit cell, $N$ is the number available for activators in the unit cell, and $X$ is the critical concentration. The value of $V$ obtained by Rietveld refinement is 41.76 Å$^3$. The value of $N$ is 0.25, which is estimated from the unit cell crystal structure. Accordingly, the critical distance $R_c$ is calculated to be 86.1 Å. The typical value of $R_c$ is approximately 15 Å, indicating that the incorporation of Ce$^{3+}$ ions in the AlN host does not involve substitution of the ions of the host lattice.

To elucidate the luminescent behaviors, an understanding of the structure of AlN host lattice is necessary. AlN crystallizes in a wurtzite structure with a cell volume no bigger than 45 Å$^3$. The metal atoms form a hexagonal closed packed arrangement (HCP), and the anions fill half of the available tetrahedral sites. Figure 4a shows the crystal structure of AlN drawn in an HCP arrangement; the unit cell is indicated by the thin black line. Previous investigations have suggested three sets of possible sites for the incorporation of Mn$^{4+}$ (or Mn$^{3+}$) ions into the AlN lattice. The first are interstitial sites with octahedral coordination, shown as yellow polyhedral. The second are interstitial sites with tetrahedral coordination, shown as red polyhedral. In the third case, Mn$^{4+}$ ions are substituted at the interstitial sites with tetrahedral coordination. Figure 4b shows the octahedron from a different view direction. The six surrounding N ions are all connected to four Al$^{3+}$ ions, and no Al–N bonds cross the octahedron. The length of the diagonal is 4.34 Å, enabling a Ce$^{3+}$ ion to be located at the center of the octahedral.

Notably, without the incorporation of Si$^{4+}$ ions, no emission is detected from the AlN host which is singly doped with Ce$^{3+}$ ions. The role of Si$^{4+}$ ions is yet to be determined, although it has been studied previously.

By using EDX technique, the

![Image](image-url)
presence of Si$^{4+}$ ions is confirmed in Figure 5. The ratio of Si ions is close to 5%. The inset of Figure 5 displays the morphology of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$, which has a diameter of 10–15 μm. In this study, we suggest that the shorter ionic radius of Si$^{4+}$ ions (4CN, 0.26 Å) compared to that of Al$^{3+}$ (4CN, 0.39 Å) ions plays an important role when a small amount of Si$^{4+}$ ions replaces Al$^{3+}$ ions. In Figure 4b, the volume of the octahedron will be made larger when shorter Si–N bonds replace longer Al–N bonds. The replacement of Al$^{3+}$ ions by shorter Si$^{4+}$ ions results in enlarging the activator site has also been mentioned.32 Figure 6 compares the results concerning the Rietveld refinement of the three samples: AlN host, Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$, and Al$_{0.95}$N:Si$_{0.05}$0.5Eu$^{2+}$. The average length of the cation-N (Al–N and Si–N) bond decreases when the AlN host lattice is doped with small amounts of Si$^{4+}$ and rare earth ions.

Location of the doped Ce$^{3+}$ ions in the crystal was examined by HRTEM imaging of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$. It is obvious that the Ce$^{3+}$ doping is not in a random manner. Many layered defects were detected from the crystals, and these (ab) defect planes were separated without showing any relation along the c axis. A typical image is shown in Figure 7a. The d-spacing of the principal planes, marked as A, is about 4.83 Å, corresponding to the (001) planes of AlN structure. Two atomic fringes are observed in each unit cell along the c-axis. The defect layer, marked as B, has a spacing of 9.64 Å, containing 4 atomic fringes, implying that the Ce$^{3+}$ doping did not change the unit cell parameter, c, but changed the image contrast pattern significantly. Some short black linear domains were also observed as indicated by the short arrow in Figure 7a. These image patterns of the defects were not detected when viewing down the [001] direction.

Figure 7b is a HRTEM image on the [001] projection. Many dark spots can be seen in the image. In thick areas (top-right corner), these dark spots are randomly distributed. We believe these dark spots correspond to individual Ce$^{3+}$ in the octahedral interstitial sites. When an atom/ion occupies an interstitial site in a crystal, it will induce local lattice distortion. The distorted area, typically spherical with several atomic layers, is much larger than the atom/ion itself. Although the TEM resolution is not high enough to detect disordered individual atoms in a crystal, it is possible to give strong image contrast patterns from the distorted areas associated with these point defects, i.e., dark spots mainly contributed by the diffraction contrast. In Zhou’s previous work, excess oxygen anions occupying interstitial sites in perovskite33 and in silicate apatite34 gave similar dark-spot image contrast patterns. The bottom inset in Figure 7b is an enlarged image of the single dark spot marked by a circle. Local lattice distortion can be seen clearly. In the thin area of the crystal the concentration of the point defects is much higher and they become ordered forming a 3-fold superstructure along the [100] direction. The corresponding fast Fourier transform (FFT) pattern in the top inset shows extra spots in the [100] direction, confirming the 3-fold superlattice.

Solid-state NMR (ssNMR) is adopted to study the substitution of Al$^{3+}$ ions by Si$^{4+}$ ions and the environmental change that occurs with the addition of activators. Figure 8a shows the measured $^{27}$Al spectrum of AlN precursors, Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$ and Al$_{0.95}$N:Si$_{0.05}$0.5Eu$^{2+}$. The chemical shift is 112 ppm, which is close to the value for AlN$_4$ in the literature. The measured peaks for the two phosphors doped with RE and Si$^{4+}$ ions are broadened to both higher and lower field. The unpaired electrons from the Ce$^{3+}$ and Eu$^{2+}$ ions can establish an additional magnetic field at the Al$^{3+}$ nucleus, giving rise to broadening of the NMR spectrum.35 The greater broadening of the peak for the Eu$^{2+}$-doped sample could be the result of a higher concentration of the activators and more unpaired electrons from the Eu$^{2+}$ ions. The $^{29}$Si spectrum in Figure 8b confirms the incorporation of Si$^{4+}$ ions. The spectrum includes two peaks: the peak at −48 ppm is assigned to the SiN$_4$...
tetrahedra and that at −22 ppm is associated with the AlN 21R polytypoid. Notably, from the Al0.95N:Si0.05,0.5Eu2+ sample, the peak at −22 ppm dominates, whereas from the Al0.95N:Si0.05,0.05Ce3+ sample, the peak at −48 ppm dominates. This result agrees with that obtained by Takeda et al., who discovered stacking faults in the Eu2+-doped sample.31 The peak from the AlN 21R polytypoid in the 27Al spectrum is at 112 ppm and is strongly shielded by the signal from the AlN4 tetrahedral.

Figure 6. Rietveld refinement of the XRD patterns of (a) Al0.95N:Si0.05,0.5Eu2+, (b) Al0.95N:Si0.05,0.05Ce3+, and (c) AlN host lattice. (d) The average cation–N bond lengths of parts a–c.

Figure 7. (a) HRTEM image of Al0.95N:Si0.05,0.05Ce3+ showing a typical layered defect along the c-axis. The inset is an enlarged image of the marked defect area. A and B indicate the d-spacings of the normal (001) planes and the defect layer, respectively. (b) An image viewed down the [001] direction. The top inset is the corresponding FFT pattern, indexed onto the hexagonal unit cell of AlN. The bottom inset is an enlarged image of the circle-marked area.

Figure 9a shows the cathodoluminescence (CL) emission spectrum. It is obtained using an electron beam with an energy of 5 kV and current of 500 pA. Al0.95N:Si0.05,0.05Ce3+ phosphor emits blue color with a peak at 390 nm. The asymmetric peak from the AlN 21R polytypoid in the 27Al spectrum is at 112 ppm and is strongly shielded by the signal from the AlN4 tetrahedral.
can be deconvoluted into two Gaussian components with peaks at 382 and 408 nm. The spin–orbital splitting of the 4f ground state of Ce$^{3+}$ ion is 1700 cm$^{-1}$ apart.$^{37}$ Figure 9b plots the brightness of the sample versus anode voltage. The brightness does not saturate because the depth of penetration of incident electrons into a phosphor particle increases with voltage. Unlike in solid-state lighting, blue and yellow can be combined to generate pseudo white light. Display devices require three primary colors (blue, green, and red). The quality of the display increases as the color coordinates more closely approach to the National Television Standard Committee (NTSC) coordinates. The splitting of spin–orbitals of Ce$^{3+}$ ions broadens the emission spectrum of Al$_{0.95}$N:Si$_{0.05}$Ce$^{3+}$. The Commission International de l’Eclairage (CIE) chromaticity coordinate of Al$_{0.95}$N:Si$_{0.05}$,0.05Ce$^{3+}$ is (0.15, 0.07), which is closer to the value of NTSC blue (0.15, 0.08) than that of Al$_{0.95}$N:Si$_{0.05}$,0.5Eu$^{2+}$ (0.13, 0.12). Figure 10 plots the corresponding CIE coordinates of the three samples.

**CONCLUSIONS**

In summary, a blue-emitting AlN phosphor that is coactivated by Ce$^{3+}$ and Si$^{4+}$ ions was synthesized by gas pressure sintering. The indigenous oxygen impurities from the precursors were successfully removed by adding carbon and a modified heating program. The crystal structures were investigated in detail by XRD, Rietveld refinement, SEM, and HRTEM. EDX and solid-state NMR $^{29}$Si and $^{27}$Al data were used to study the incorporation of Si$^{4+}$ ions and the change in the environment. The locations of the activators in the AlN host lattice are proposed. The cathodoluminescence (CL) emission spectrum is obtained by electron bombardment under various conditions. The nitride phosphor shows good stability. The as-synthesized Al$_{0.95}$N:Si$_{0.05}$0.05Ce$^{3+}$ has a CIE coordinate closer to that of NTSC blue than those of Al$_{0.95}$N:Si$_{0.05}$0.5Eu$^{2+}$, revealing that Al$_{0.95}$N:Si$_{0.05}$0.05Ce$^{3+}$ is an alternative blue phosphor for field emission displays.

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