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Cathodoluminescence of rare earth implanted AlInN

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AlInN layers implanted with europium and erbium ions are systematically studied and compared with similarly implanted GaN. Cathodoluminescence from four series of annealed samples shows that the Eu/Er emissions from AlInN are considerably broader than those from GaN, while the peak positions only change slightly. The rate of increase of cathodoluminescence intensity with annealing temperature, up to 1300 °C, is analyzed for all four series. For Eu the increase exceeds 10× in both hosts. Although some decomposition is observed for annealing at 1200 °C, well above the growth temperature, AlInN is shown to be a surprisingly robust host for rare earth ions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357343]

In recent years, rare earth (RE) doped III-nitride semiconductors have attracted considerable interest because of their potential application in light emitting devices. GaN has been widely used as a RE host.[1,2] AlGaN, with its wider band gap, has been shown to offer further advantages for RE doping.[3] AlInN materials offer potential as alternative wide gap RE hosts that can be lattice matched to GaN with 16%–17% InN fraction.[4,5] The band gap of $Al_{0.83}In_{0.17}N$ is about 4.3 eV.[4,6] In this letter we describe a systematic investigation of AlInN as a host material for RE light emission.

The optical properties of four series of Eu and Er implanted AlInN/GaN and GaN samples, each annealed at different temperatures in the range from 700 to 1300 °C, have been studied using cathodoluminescence (CL) spectroscopy and scanning electron microscopy (SEM). The variation of CL intensity with annealing temperature for each series is investigated and demonstrates that RE luminescence in the two hosts changes with the annealing temperature in very different ways.

A series of AlInN layers close to lattice match with GaN, each nominally 130 nm thick, was grown on GaN-on-sapphire buffer layers in an Aixtron 200-series metal organic vapor phase epitaxy (MOVPE) reactor.[6] The AlInN layer used for Eu implantation was grown at a set point of 840 °C with the InN fraction estimated at 15±2 at. %. That used for Er implantation was grown at 820 °C with the InN fraction estimated at 17±2 at. %. Epilayers of GaN, approximately 2 μm thick, were grown by MOVPE on *c*-plane sapphire at 1090 °C following a low temperature GaN buffer layer. Thin AlN caps were grown epitaxially on top of the GaN layers to protect the sample both during implantation and high temperature annealing.[7,8] The caps used for Eu and Er implantations were 20 nm of polycrystalline AlN and 11 nm of monocrystalline AlN, respectively.

Both Eu and Er ions were implanted into the AlInN/GaN bilayers using a 120 keV beam to a nominal dose of 1×10^{15} at./cm^2 with the RE beam tilted 10° away from the surface normal in order to minimize channeling of RE ions into the substrate.[9] For the thicker GaN layers, the RE ions were implanted at normal incidence through the cap with a higher beam energy of 300 keV but to the same nominal dose. The implanted samples were then annealed at different temperatures in the range from 700 to 1300 °C for 20 min in a conventional tube furnace filled with nitrogen gas at 4 bar overpressure. When the annealing temperature exceeds the growth temperature of the host materials, some decomposition is expected: principally, In loss for AlInN and N loss for GaN.

The CL of all samples was excited at room temperature in an electron probe microanalyzer modified to allow light collection through its optical microscope system using a cooled silicon charge-coupled device array.[10] The CL was collected and detected under the same conditions for each sample in order to aid comparison of relative intensities. The electron beam was defocused to 30 μm in diameter. A low beam energy of 3 keV was chosen to avoid penetration of the electrons through the AlInN layer into the underlying GaN layer and depth profiles measured using time-of-flight secondary ion mass spectrometry show that almost all of the RE ions are within the region excited by the electrons.[9] The higher implantation energy and density of the GaN, compared to the AlInN, result in a deeper penetration of the ions into the GaN and a shallower region excited by the 3 keV electrons. The estimated depth for deposition of 95% of the electron energy (65 nm) does, however, exceed the depth of the peak ion concentration (50–60 nm) and the majority of RE ions will be excited.

Figure 1 compares typical room temperature CL spectra from AlInN:Eu (below) and GaN:Eu (above) samples, both of which were annealed at 1100 °C. The emission lines are assigned to the intra 4*f*-shell transitions of Eu ions, i.e., $^5D_1$-$^7F_1$ (544 nm), $^5D_0$-$^7F_1$ (600 nm), $^5D_0$-$^7F_2$ (622 nm), $^5D_1$-$^7F_4$ (634 nm), and $^5D_0$-$^7F_3$ (664 nm). High-resolution CL and photoluminescence (PL) spectra and PL excitation data have been reported in our previous work.[9,11] The spectra are normalized to the peak of the strongest emission line at 622 nm. In fact, the GaN:Eu emission line at 622 nm comprises of several lines, which can be well resolved at low

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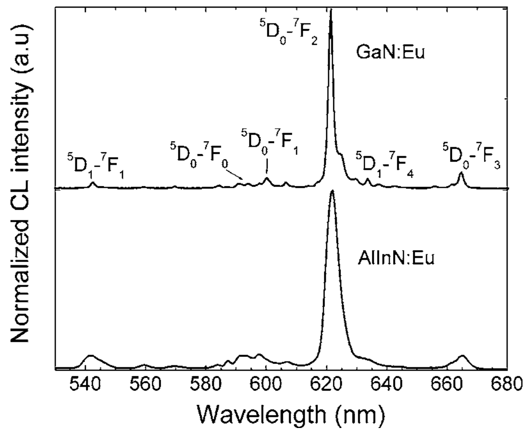

FIG. 1. Room temperature CL spectra of Eu implanted GaN and AlInN annealed at 1100 °C and normalized to the intensity at 622 nm.

temperatures and attributed to different Eu sites.[11]

All the Eu emission lines appear at roughly the same spectral positions for the two different hosts, with the strongest line showing only a very slight *redshift* for AlInN:Eu, compared to GaN:Eu. The main difference between the spectra is in the width of the emission lines. The full width at half maximum of the main peak increases from 2 nm for GaN to 5 nm for AlInN. Moreover, it is found that this broadening of the emission lines does not change with the annealing temperature, indicating that the local environment is not changed by the annealing. Hence, we conclude that it is alloy disorder that increases the width of Eu emission lines from AlInN. The local environment around Eu ions in the ternary alloy is less homogeneous than in the GaN host.

Figure 2 compares normalized room temperature CL spectra of Er implanted AlInN (below) and GaN (above) after both samples were annealed at 1100 °C. The emission at about 537 nm is assigned to the Er intra 4*f*-shell transition $^2H_{11/2}$-$^4I_{15/2}$, and that at 558 nm is assigned to $^4S_{3/2}$-$^4I_{15/2}$. Both of these emission lines are again composites ascribed to different Er sites in the host.[12] The AlInN:Er emission peaks, at 535.5 and 556.5 nm, are slightly *blueshifted* with respect to GaN:Er. As was the case for Eu implanted material, the Er related emission lines are broader for the AlInN host. The relative intensity of the spectral lines is clearly different in the two hosts. In addition, a broad yellow band is observed in AlInN:Er samples annealed at 1000 °C and above. This yellow band was also observed in some Er:GaN samples annealed at 1200 °C and above.

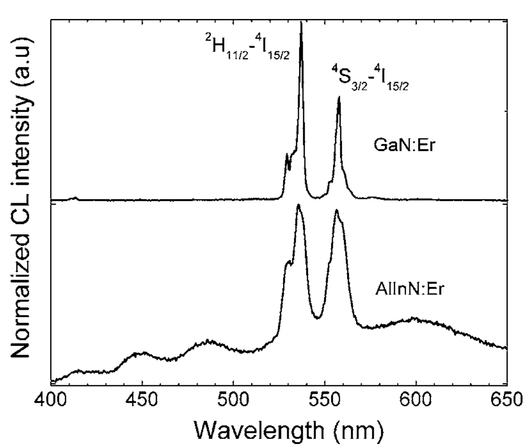

FIG. 2. Room temperature CL spectra of Er implanted GaN and AlInN annealed at 1100 °C and normalized to the intensity at 537 nm.

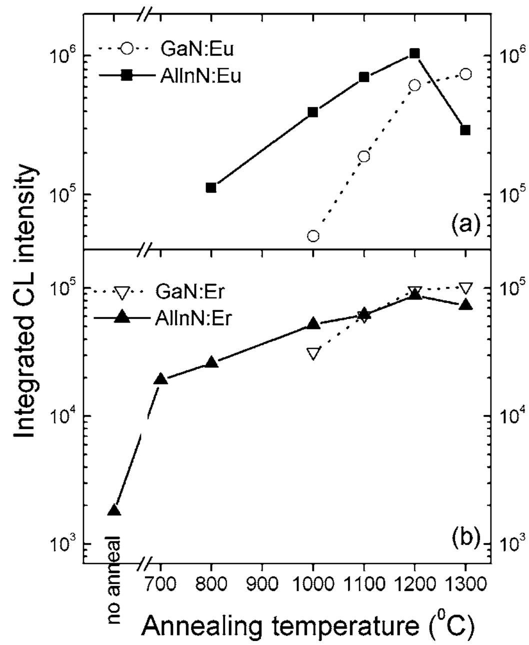

FIG. 3. Integrated room temperature CL intensity of (a) Eu implanted GaN and AlInN (b) Er implanted GaN and AlInN annealed at different temperatures and measured under the same conditions.

The variation with annealing temperature of the integrated CL intensities of the main RE emission lines is shown in Fig. 3. Figure 3(a) shows that the integrated CL intensity (610–635 nm) of AlInN:Eu increases by one order of magnitude as the annealing temperature is increased from 800 to 1200 °C. It is noticeable that the integrated CL intensity of AlInN:Eu is several times stronger than that of GaN:Eu except for 1300 °C annealing, although it must be remembered that a smaller portion of RE ions will be excited in the GaN as described above. Moreover, some of our as-implanted AlInN:Eu samples emit red light whereas GaN:Eu does not show any emission at all prior to annealing. Below 1300 °C, the integrated CL intensity increases exponentially with the annealing temperature $[I_{CL}=I_0\exp(T/T_0)]$ with a characteristic temperature T_0 of 175 K. The CL intensity drops, however, when the annealing temperature is increased to 1300 °C.

For GaN:Eu samples, the CL also increases by one order of magnitude with increasing annealing temperature from 1000 to 1300 °C as reported in Ref. 7. However, the increase from 1200 to 1300 °C is below the trend of the data. SEM images show that the sample annealed at 1300 °C has a more seriously damaged surface than that annealed at lower temperature. This shows that the polycrystalline AlN cap, used here for GaN:Eu, is not as robust as the monocrystalline cap used in previous studies.[8]

Figure 3(b) shows that the integrated CL intensity (510–580 nm) of AlInN:Er samples increased by a factor of about 5 in the annealing temperature range from 700 to 1200 °C. With the exception of the as-implanted and 1300 °C annealed sample, the integrated CL intensity again increases exponentially with a characteristic temperature of 330 K. The drop of the CL intensity for the sample annealed at 1300 °C is also due to decomposition of the ternary alloy, as mentioned above. It is worth mentioning again that the

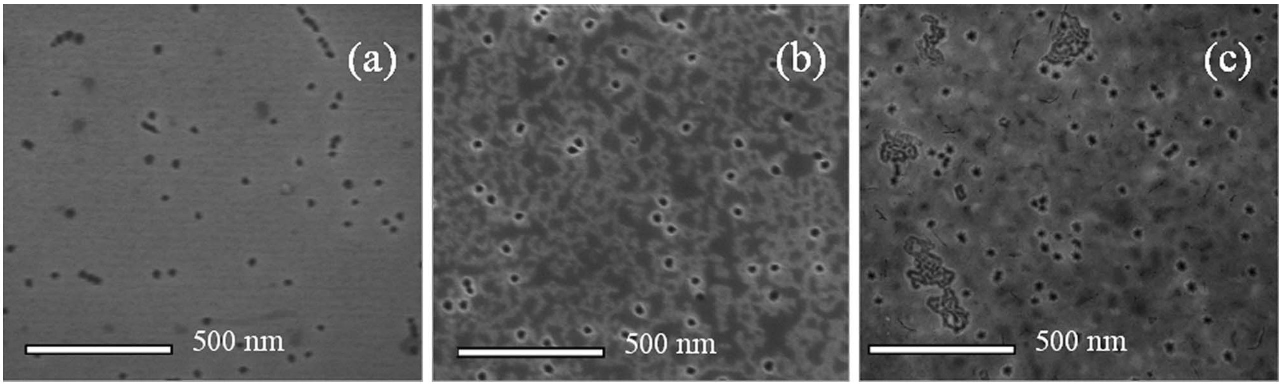

FIG. 4. High-resolution SEM images of Eu implanted AlInN/GaN bilayers annealed at (a) 1000 °C, (b) 1200 °C, and (c) 1300 °C.

as-implanted AlInN:Er was found to emit green light whereas GaN:Er did not show any emission before annealing. The integrated CL intensity of AlInN:Er is very close to that of GaN:Er annealed at the same temperatures.

By way of comparison, the optimized integrated CL intensity of Eu luminescence from both hosts is similar and one order of magnitude stronger than Er luminescence in the same hosts, as shown in Fig. 3.

The SEM images of AlInN:Eu in Fig. 4 give clues to explain the rapid reduction in CL intensity of the AlInN sample annealed at 1300 °C. Figure 4(a) shows that AlInN:Eu annealed at 1000 °C has a very clear and homogeneous background with some pits distributed across the surface, which are also seen in the as-grown samples. When the anneal temperature is increased to 1200 °C, the background of the SEM image in Fig. 4(b) shows a mixture of dark and relatively light regions. The pits are larger with more contrast around their edges than those in Fig. 4(a). This suggests that some decomposition of the AlInN has occurred. However, the CL intensity of Eu emission still increases in spite of this deterioration of the sample. In Fig. 4(c), the SEM image of AlInN:Eu annealed at 1300 °C shows some extra features and the CL intensity in this sample is much reduced.

Wavelength dispersive x-ray (WDX) measurements of the composition of AlInN:Er reveal that the InN fraction is constant at 17% when the annealing temperature is ≤1100 °C. A slight decrease, to 16% InN, is observed for the sample annealed at 1200 °C. Severe decomposition with significant In loss (measured InN fraction down to 10% accompanied by an increased Ga signal) was observed for samples annealed at 1300 °C. The measured Al and N fractions remain the same in all samples. Thus, surprisingly, AlInN is able to withstand annealing at up to 400 °C above the growth temperature. Further studies, including spatially mapped CL and WDX, are in progress and may clarify these effects.

In summary, CL from four series of Eu and Er implanted AlInN and GaN samples, annealed in a wide temperature range from 700 to 1300 °C, has been investigated. The Eu and Er emission lines for AlInN hosts are broadened compared to GaN host and the peak positions are slightly changed. Variation of the CL intensity of the four series of samples with the annealing at different temperatures has been demonstrated and compared. The integrated RE CL intensity increases exponentially with annealing temperature in both cases, but does so faster for AlInN:Eu whose characteristic temperature is about half of that for AlInN:Er. CL from the AlInN host survives annealing at temperatures up to 400 °C above the growth temperature.

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[1] A. J. Steckl and J. M. Zavada, MRS Bull. **24**, 33 (1999).
[2] A. J. Steckl, J. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Q. Wang, and R. Jones, IEEE J. Sel. Top. Quantum Electron. **8**, 749 (2002).
[3] A. Wakahara, Y. Nakanishi, T. Fujiwara, A. Yoshida, T. Ohshima, and T. Kamiya, Phys. Status Solidi A **202**, 863 (2005).
[4] J. F. Carlin, C. Zellweger, J. Dorsaz, S. Nicolay, G. Christmann, E. Feltin, R. Butté, and N. Grandjean, Phys. Status Solidi B **242**, 2326 (2005).
[5] I. M. Watson, C. Liu, E. Gu, M. D. Dawson, P. R. Edwards, and R. W. Martin, Appl. Phys. Lett. **87**, 151901 (2005).
[6] S. Hernandez, K. Wang, D. Amabile, E. Nogales, D. Pastor, R. Cusco, L. Artus, R. W. Martin, K. P. O'Donnell, and I. M. Watson, Mater. Res. Soc. Symp. Proc. **892**, FF23–04 (2005).
[7] K. Lorenz, U. Wahl, E. Alves, S. Dalmasso, R. W. Martin, K. P. O'Donnell, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **85**, 2712 (2004).
[8] E. Nogales, R. W. Martin, K. P. O'Donnell, K. Lorenz, E. Alves, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **88**, 31902 (2006).
[9] R. W. Martin, D. Rading, R. Kersting, E. Tallarek, E. Nogales, D. Amabile, K. Wang, V. Katchkanov, C. Trager-Cowan, K. P. O'Donnell, I. M. Watson, V. Matias, A. Vantomme, K. Lorenz, and E. Alves, Phys. Status Solidi C **3**, 1927 (2006).
[10] R. W. Martin, P. R. Edwards, K. P. O'Donnell, E. G. Mackay, and I. M. Watson, Phys. Status Solidi A **192**, 117 (2002).
[11] K. Wang, R. W. Martin, K. P. O'Donnell, V. Katchkanov, E. Nogales, K. Lorenz, E. Alves, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **87**, 112107 (2005).
[12] V. Dierolf, C. Sandmann, J. Zavada, P. Chow, and B. Hertog, J. Appl. Phys. **95**, 5464 (2004).