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# Luminescence from praseodymium doped AlN thin films deposited by RF magnetron sputtering and the effect of material structure and thermal annealing on the luminescence

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**Abstract** Thin films of Praseodymium doped AlN are deposited on silicon (111) substrates at 77 K and 950 K by rf magnetron sputtering method. About 500–1000 nm thick films are grown at 100–200 watts RF power and 5–8 mTorr nitrogen, using a metal target of Al with Pr. X-rays diffraction results show that films deposited at 77 K are amorphous and those deposited at 950 K are crystalline. Cathodoluminescence studies are performed at room temperature and luminescence peaks are observed in a wide range from ultraviolet to infrared region. The most intense peak is obtained in green at 526 nm from amorphous films as a result from $^3P_1 \rightarrow {}^3H_5$ transition. In crystalline films the intense peak was obtain in red at 648 nm as a result from $^3P_0 \rightarrow {}^3F_2$ transition. Films are thermally activated at 1300 K for half an hour in a nitrogen atmosphere. Thermal activation enhances the intensity of luminescence. Two peaks at 488 nm and 505 nm merged after thermal activation, giving rise to a single peak at 495 nm.

## Introduction

Rare-earth-doped III-nitride semiconductor thin films are attracting increasing attention as phosphor materials for use in optical displays [1–3]. Recent progress toward nitride-based light-emitting diode and electroluminescent devices (ELDs) has been made using crystalline and amorphous GaN and AlN doped with a variety of rare-earth elements [1–3]. The electronic structure of the RE ions differ from the other elements and are characterized by an incompletely filled $4f^{\,n}$ shell. The 4*f* electrons lay inside the ion and are shielded from the surroundings by the filled $5s^2$ and $5p^6$ electron orbitals [4, 5]. When these materials are excited by various means, intense sharp-line emission is observed due to intra-$4f^n$-shells transitions of the rare-earth ion core [5–10]. Different factors can affect this emission from such phosphors.

Aluminum nitride (AlN) gets special attention due to its high thermal conductivity and stability, chemical inertness and band gap above 6ev which make it a promising candidate for the implementation of visible, infrared (IR) and ultraviolet (UV) light emitters [2, 11–14].

In the present work, the effects of material structure and thermal activation on the luminescence properties of praseodymium are studied when co-deposited in AlN host. The spectra obtained provide data in a broad range from 300 nm to 850 nm. Thus luminescence from these elements in UV, visible and IR are obtained and studied simultaneously.

## Experimental details

Thin films of AlN:Pr were prepared at 77 K and 950 K by rf magnetron sputtering of an aluminum target of 99.999% purity in a pure nitrogen atmosphere. Doping of thin films with Praseodymium (Pr) was accomplished by drilling a small hole (0.5 cm diameter) in the aluminum target (4.2 cm diameter) and placing a slug of Pr in the hole. Pr was then co-sputtered with the aluminum. The rf power was varied between 100 and 200 watts. All films

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were deposited onto 2 cm × 2 cm, or less, p-silicon (111) substrates. The background pressure in the chamber was $<3 \times 10^{-5}$ Torr. Liquid nitrogen was used to keep the temperature of the film at 77 K. The metallic substrate holder was designed such that it had a half inch diameter cylindrical hole from the top. The substrate was pasted on the metal base of the holder below the liquid nitrogen. Liquid nitrogen was constantly poured in the holder to provide a constant low temperature to the substrate during film growth. Special holder connected to an electric heater was used to provide high temperature to the substrate during growth to get crystalline films.

The as-deposited films were characterized for their characteristic emissions. The thickness of the films was between 500 nm and 1000 nm, measured with a quartz crystal thickness monitor in the growth chamber. X-rays diffraction (XRD) was used to determine the structure of the films.

Cathodoluminescence (CL) studies of the films were performed at room temperature in a vacuum chamber at a pressure of about $3 \times 10^{-6}$ Torr, which was maintained with an Alcatel CFF 450 turbo pump. Films were excited with electron beam energy of 2.85 kV and beam current of 100 $\mu$A. The films were placed an angle of 45° to the incident electron beam coming out of electron gun. The detector was placed at an angle of 45° to the film such that lines joining electron gun, the film and detector were making and angle of 90°. Luminescence from the films was focused onto the entrance slit of a SPEX Industries double monochromator with gratings blazed at 500 nm and detected at a Thorn EMI fast high gain photomultiplier tube with a range of 200–900 nm.

Thermal activation was accomplished by placing the flat films in a tube furnace at 1300 K in a nitrogen atmosphere for half an hour.

## Results and discussion

Figure 1 shows the CL spectrum of amorphous AlN:Pr in 250–850 nm range at room temperature. $Pr^{+3}$ emits in a very broad region covering UV, visible and IR regions of the spectrum. Dominant peaks were observed in red, green and blue region at wavelengths 648 nm, 526 nm, 488 nm and 505 nm from $^3P_0 \rightarrow {}^3F_2$, $^3P_1 \rightarrow {}^3H_5$ and $^3P_0 \rightarrow {}^3H_4$ transitions. Detail of all transitions is given in Table 1. Its is clear from this figure that green is the most dominant and intense emission from amorphous AlN:Pr. Further, the $^3P_0 \rightarrow {}^3H_4$ transition gives two peaks in blue, located close to each other at 488 nm and 505 nm.

Figure 2 gives the effect of thermal activation on the amorphous AlN:Pr films. Thermal activation has enhanced the luminescence from $Pr^{+3}$. Spectra before and after thermal activation are given here together. Along with the overall enhancement in luminescence, two obvious effects are observed. One, the blue and the red emissions are affected more than the green by thermal activation. The intensity of the green emission is 4.5 times higher than the blue emission and almost 4 times higher than red emission. However after thermal activation this ratio reduces to 1.1 for green and blue emission and 1.4 for green and red emissions, clarifying that the effect of thermal activation on the blue emission is 4 times and on the red emission is 3.5 times the effect on the green emission. Second, the two peaks in the blue region at 488 nm and 505 nm no more exist as separate peaks after thermal activation. Thermal activation has changed the two resolved peaks to a single peak at 495 nm.

Figure 3 provides CL spectrum of crystalline AlN:Pr in 300–850 nm range at room temperature. The intensity of luminescence in amorphous films can be compared to crystalline films by comparing this figure with Fig. 1. Unlike amorphous films the dominant luminescence is

**Fig. 1** CL spectrum of amorphous AlN

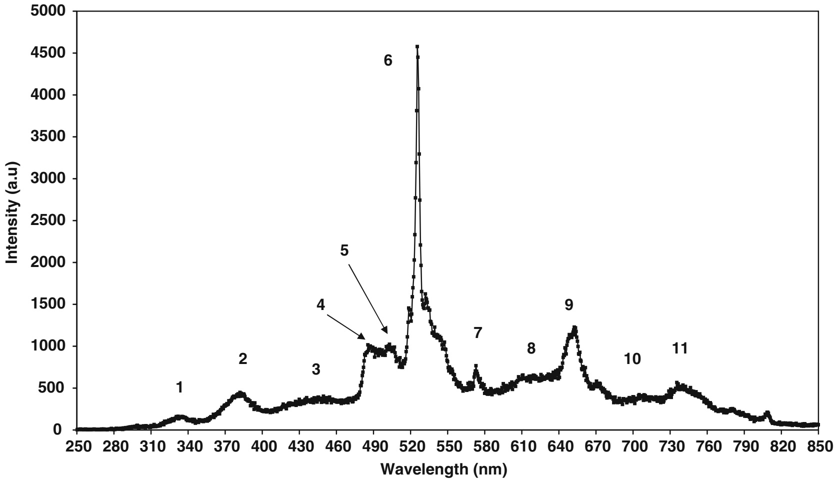

**Table 1** Summary of $Pr^{+3}$ ion emission from amorphous AlN:Pr

| Number | Transition | Wavelength (nm) | $R.I_n$. non-annealed samples | $R.I_a$. annealed samples | $R.I_a/R.I_n$ |
|---|---|---|---|---|---|
| 1 | $^1S_0 \rightarrow {}^1D_2$ | 335 | 0.036 | 0.113 | 3.14 |
| 2 | $^1S_0 \rightarrow {}^1I_6$ | 385 | 0.098 | 0.240 | 2.45 |
| 3 | $^3P_2 \rightarrow {}^3H_4$ | 439 | 0.085 | 0.174 | 2.047 |
| 4 | $^3P_0 \rightarrow {}^3H_4$ | 488 | 0.216 | 2.220 | 10.277 |
| 5 | $^3P_0 \rightarrow {}^3H_4$ | 504 | 0.224 | | |
| 6 | $^3P_1 \rightarrow {}^3H_5$ | 526 | 1.000 | 2.412 | 2.412 |
| 7 | $^3P_0 \rightarrow {}^3H_5$ | 573 | 0.167 | 0.375 | 2.245 |
| 8 | $^3P_0 \rightarrow {}^3H_6$ | 618 | 0.140 | 0.942 | 6.73 |
| 9 | $^3P_0 \rightarrow {}^3F_2$ | 652 | 0.268 | 1.800 | 6.71 |
| 10 | $^3P_0 \rightarrow {}^3F_3$ | 710 | 0.092 | 0.575 | 6.25 |
| 11 | $^3P_0 \rightarrow {}^3F_4$ | 738 | 0.117 | 0.632 | 5.40 |

Where $R.I_n$ means relative intensity of non-annealed samples and $R.I_a$ means relative intensity of thermally annealed samples

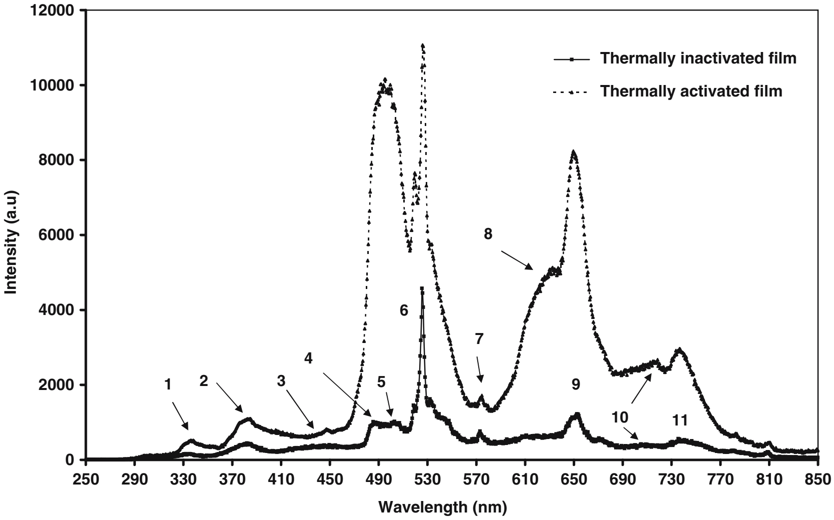

**Fig. 2** Comparison of thermally activated and in-activated amorphous AlN:Pr films

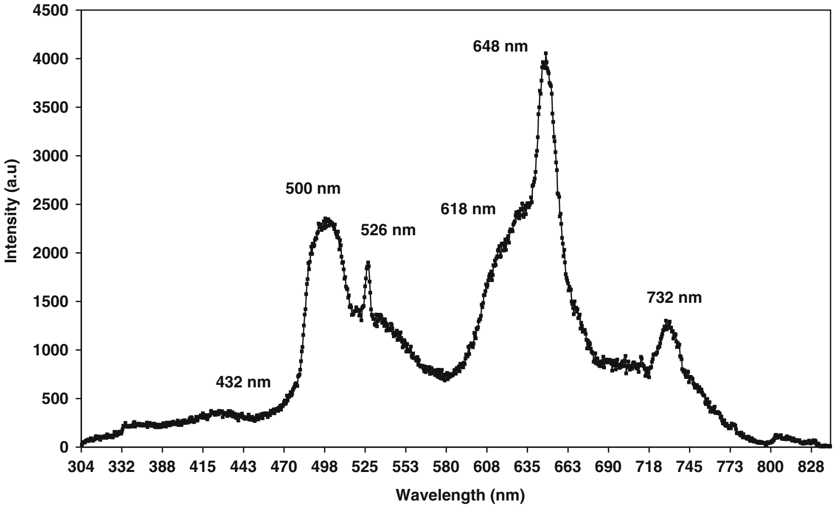

**Fig. 3** CL spectrum of crystalline AlN:Pr films

observed in red at 648 nm and 618 nm from $^3P_0 \rightarrow {}^3H_6$ and $^3P_0 \rightarrow {}^3F_2$ transitions followed by the blue emission at 500 nm. The two resolved peaks at 488 nm and 505 nm have also been replaced by a single broad peak at 500 nm. The dominant green emission of amorphous films is totally dominated by the red emission by a factor more than 2.

Careful analysis of crystalline film indicates that the luminescence from this crystalline film is more similar to the luminescence from thermally activated amorphous film.

Analysis of amorphous and crystalline AlN:Pr films show that crystalline films are good for applications in the red region of the spectrum while amorphous films are useful for applications in the green color [2, 13–15]. Both are equally important for blue color applications.

The significant increase in the intensity of luminescence from $Pr^{+3}$ ions by thermal activation has got a good explanation. Luminescence occurs from $Pr^{+3}$ ions and not from $Pr^{+2}$ or $Pr^{+1}$. During the film deposition it is most likely that some of $Al^{+3}$ of AlN may be replaced by $Pr^{+3}$ but there are also chances for imperfections and defects giving rise to $Pr^{+2}$ and $Pr^{+1}$. These ions do not contribute to luminescence. Smaller the number of these ions, more will be $Pr^{+3}$and hence luminescence will be higher. When these films are activated thermally at a higher temperature then a few or more of $Pr^{+2}$and $Pr^{+1}$ ions, ionize further to convert to $Pr^{+3}$ ions giving path to enhanced luminescence [16–18].

## Conclusion

Thin films of amorphous and crystalline AlN:Pr were deposited by rf magnetron sputtering. Films were characterized for their morphology and luminescence properties by XRD and CL. Effect of material structure and thermal activation was studied. The luminescence from amorphous and crystalline films is not similar in intensity. Both kind of films emit in a broad range covering UV, visible and infrared region. Green emission is dominant in the amorphous films while red is the most intense emission from crystalline films. Thermal activation enhances the luminescence of amorphous films.

## References

1. Caldwell ML, Martin AL, Dimitrova VI, Van Patten PG, Kordesch ME, Richardson HH (2001) Appl Phys Lett 78(9):1246
2. M Maqbool, Richardson HH, Kordesch ME (2005) Mater. Res. Soc. Symp. Proc. vol. 831 Article E8.12.1, Materials Research Society
3. Maqbool M, Richardson HH, Van Patten PG, Kordesch ME (2004) Mat. Res. Soc. Symp. Proc. 798:8.5.1–8.5.5, Materials Research Society
4. Suyver JF, Kik PG, Kimura T, Polman A, Franzo G, Coffa S (1999) Nucl Instr Meth Phys Res B148:497
5. Lozykowski HJ, Jadwisienczak WM, Brown I (2000) J Appl Phys 88(1):210
6. Gruber JB, Zandi B, Lozykowski HJ, Jadwisienczak WM (2002) J Appl Phys 91(5):2929
7. Lozykowski HJ (1993) Phys Rev B48:17758
8. Morrison CA, Wortman DE (1992) Opt Mater 1:195
9. Tsang WT, Logan RA (1986) Appl Phys Lett 49:1686
10. Steckl AJ, Birkhahn R (1998) Appl Phys Lett 73:1700
11. Levinshtein M, Rumyantsev S, Shur M (eds) (2001) Properties of advanced semiconductor materials, GaN, AlN, InN BN, SiC, SiGe. Wiley, New York
12. Vetter U, Zenneck J, Hofsass H (2003) Appl Phys Lett 83:2145
13. Chao LC, Steckl AJ (1999) Appl Phys Lett 74(16):2364
14. Zavada JM, Mair RA, Ellis CJ, Lin JY, Jiang HX, Wilson RG, Grudoski PA, Dupuis RD (1999) Appl Phys Lett 75(6):790
15. Birkham R, Garter M, Stickl AJ (1999) Appl Phys Lett 74(15):2161
16. Overberg M, Abernathy CR, MacKenzie JD, Pearton SJ, Wilson RG, Zavada JM (2001) Mater Sci Eng B81:121
17. MacKenzie JD, Abernathy CR, Pearton SJ, Hommerich U, Seo JT, Wilson RG, Zavada JM (1998) Appl Phys Lett 72(21):2710
18. Wang SZ, Yoon SF, He L, Shen XC (2001) J Appl Phys 90(5):2314