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Structure and visible photoluminescence of Sm^{3+}, Dy^{3+} and Tm^{3+} doped *c*-axis oriented AlN films*

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Visible photoluminescence (PL) has been observed from rare earth (Tm, Sm and Dy)-doped AlN films grown by radio-frequency magnetron reactive sputtering. X-ray diffraction indicates that the films are *c*-axis-oriented hexagonal wurtzite type structure with an average crystal size of about 80–110 nm. Room-temperature PL spectra indicate that the blue emission is due to the transition of $^1D_2$ to $^3F_4$ and $^1G_4$ to $^3H_6$ intra 4f electron of Tm^{3+}, the yellow emissions of AlN:Sm are due to $^4G_{5/2}$ to the ^6H_J ($J = 5/2$, 7/2, 9/2, 11/2) and the reddish emissions of AlN:Dy correspond to the $^4F_{9/2}$ to ^6H_J ($J = 15/2$, 13/2, 11/2 and 9/2) and $^6F_{11/2}$ transitions.

Keywords: photoluminescence, III-V semiconductor, thin film growth

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Rare earth (RE) dopants exhibit optical properties that have led to many important photonic applications.[1] The emission wavelength involved in the intra-4f transitions of trivalent RE ions is relatively insensitive to the host and temperature because the 4f shell is shielded from its surroundings by the filled 5s and 5p shells. III-N semiconducting compounds, such as AlN and GaN, are of particular interest because of their direct band gap and high level of optical activity even under a condition of fairly high defect density, which would quench the emission in other narrower-gap III-V and wide-gap II–VI compounds. Since Steckl and Birkhahn[2] reported the visible luminescence of Er-doped GaN films, RE-doped GaN semiconductors have been extensively studied in recent years owing to the attempt to develop photoelectronic devices, which combine the electronic properties of GaN semiconductors with the luminescence features of RE ions.[3−8] Lozykowski *et al.*[3] reported the sharp visible cathodoluminescence of GaN doped with Dy, Er, and Tm by metal organic chemical vapour deposition (MOCVD). Gruber *et al.*[9] discussed the spectroscopic properties of Sm^{3+} in GaN in detail. Favennec *et al.*[10] also reported that the luminescence intensity of rare earth doped semiconductor decreased with the increase of temperature, and the decreasing rate is slower in larger band gap semiconductor. With a wide band gap, novel thermal, chemical, mechanical, acoustic and optical properties, AlN thin films have received considerable attention as promising candidates for thermal dissipation, dielectric and passivation layers, surface acoustic wave (SAW) devices and photoelectric devices.[11−14] Luminescence of Tb^{3+}, Eu^{3+}, Er^{3+} doped AlN has been widely discussed by many authors.[15−18] A suitable annealing temperature is often required for active RE ions in the implanted RE doped III-N films prepared by MOCVD or molecular-beam epitaxy (MBE). Magnetron sputtering technique is a low-cost, large-area, and easy-control method for film growth, since the RE doped films prepared by reactive sputtering do not need the annealing process. In the present paper, we report the visible photoluminescence (PL) of Sm^{3+}, Dy^{3+} and Tm^{3+} doped *c*-axis oriented AlN

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films grown by radio frequency (RF) reactive magnetron sputtering on Si (001) substrate.

Al (99.999%) was combined with 1 at% Sm, Dy or Tm(99.9% pure) by an argon arc melting and then pressed into a target 65 mm in diameter and 3 mm in thickness. AlN:RE films were deposited in 99.999% pure nitrogen and argon mixtures with a total flowing rate of 15 sccm in a planar magnetron RF sputtering system, and the Ar:N_2 ratio was fixed at 4:1. The target was placed above the substrate with the target-substrate distance kept at 30mm. RF power was 200 W. Silicon (0 0 1) wafers were used as substrates in this work. Before the deposition, the substrates were cleaned with 2% HF solution for 10 min, followed by rinsing in ethanol and distilled water in an ultrasonic bath. High-purity Ar gas was introduced into the chamber after the chamber was evacuated to below 8×10^{-4} Pa. Then the Al:RE target was pre-sputtered for 15 min. During pre-sputtering the RF power and Ar pressure were kept at 150W and 1 Pa, respectively. Then nitrogen gas was introduced into the chamber and reactive sputtering was initiated. The deposit time was fixed to 1h and the substrate was heated to 300 °C.

X-ray diffraction (XRD) data were collected on a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation (50 kV × 250 mA) and a graphite monochromator. A step scan mode was employed with a step width of $2\theta = 0.02°$ and a sampling time of 1s in the range of 2θ from 30 to 65 °.

The XRD patterns of RE doped AlN films are shown in Fig.1, showing a strong peak at 2θ about 36° which is the (002) peak of wurtzite type structure AlN. It indicates that the grown RE doped AlN films have a c-axis oriented wurtzite type structure. Figure 1 also shows a very weak peak at 2θ about 33° which is (100) peak of AlN. The (002) FWHMs of Tm^{3+}, Sm^{3+} or Dy^{3+} doped AlN films are 0.331°, 0.345° and 0.346°, respectively. Based on the well known assumption that the Cauchy component of the XRD profile is solely due to crystallite size and that the Gaussian contribution arises from strain, information on the micro-structural features related to the observed broadening of XRD peaks of RE doped AlN films is obtained by means of the single-line method.[19] After the correction of the instrumental broadening to the XRD profiles, the average crystal size is calculated according to the follow formula:

$$D = \lambda/(\beta_C \cos\theta), \qquad (1)$$

where β_C is the integral breadth of the Cauchy components of the broadened profile after the instrumental broadening correction; D is a volume-weighted average effective domain size along [hkl]. The peakfit V4.11 program was used to determine the integral breadth and FWHM based on the Voigt function. The calculated average sizes along [002] of Tm^{3+}, Sm^{3+} or Dy^{3+} doped AlN films are about 110, 79 or 83 nm, respectively.

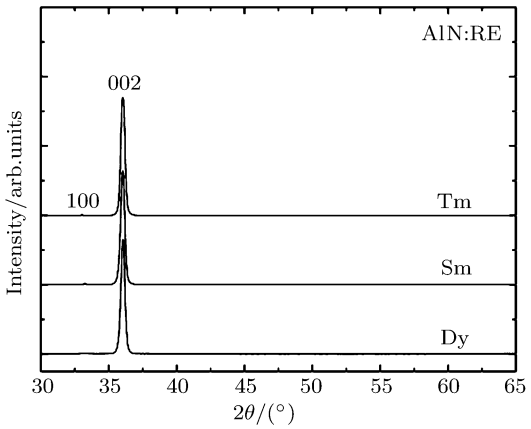


Fig.1. X-ray diffraction profiles of Tm, Sm or Dy doped AlN films.

Figure 2 shows scanning electron microscope (SEM) cross-sectional images of AlN:Tm films performed at XL30 S-FEG. For AlN:Sm and AlN:Dy, the SEM images are not shown, which are almost the same as that in Fig.2. SEM shows that the films are fibrous-like crystallites. The morphology of the films can be explained by the zone model proposed by Thornton.[20] The thickness of the films is about 4.0 μm.

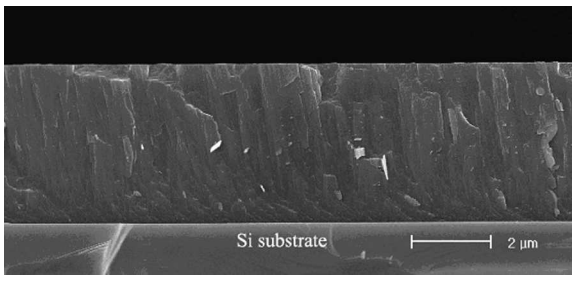


Fig.2. The SEM cross-sectional image of AlN:Tm films grown on silicon substrates.

The chemical composition of the AlN:RE films was analysed by x-ray energy dispersions spectrum (EDX). The EDX of AlN:Tm is shown in Fig.3. For AlN:Dy and AlN:Sm, the EDX are not shown which are similar to that in Fig.3. Figure 3 reveals the presence of Al, N, O, Tm and Au. Au signals originate from the electric coating Au layer. A relative weak oxygen peak in the spectrum possibly originates from the unavoidable surface oxidation. Due to the low

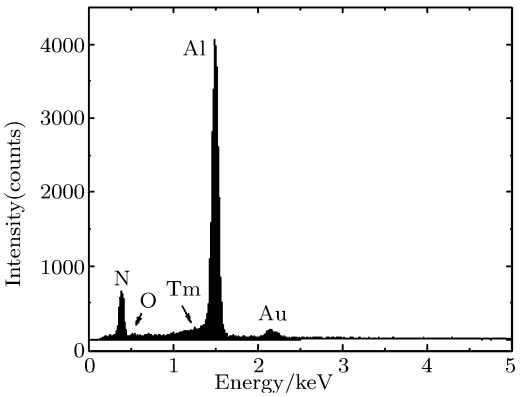


Fig.3. The EDX spectrum of AlN:Tm film.

content, RE peak in the spectrum is inconspicuous, but the higher background on the left of the Al peak indicates the existence of RE. Quantitative analysis of the spectrum gives a composition in atomic percent of 51.3 for Al, 47.0 for N and 1.7 for O. The result shows that the atomic ratio of Al to N is close to 1:1.

Room temperature (300K) PL of AlN:RE films was obtained using a He–Cd laser 325nm as an excitation source(Accent RPM2000). The PL spectra of AlN:RE are shown in Fig.4.

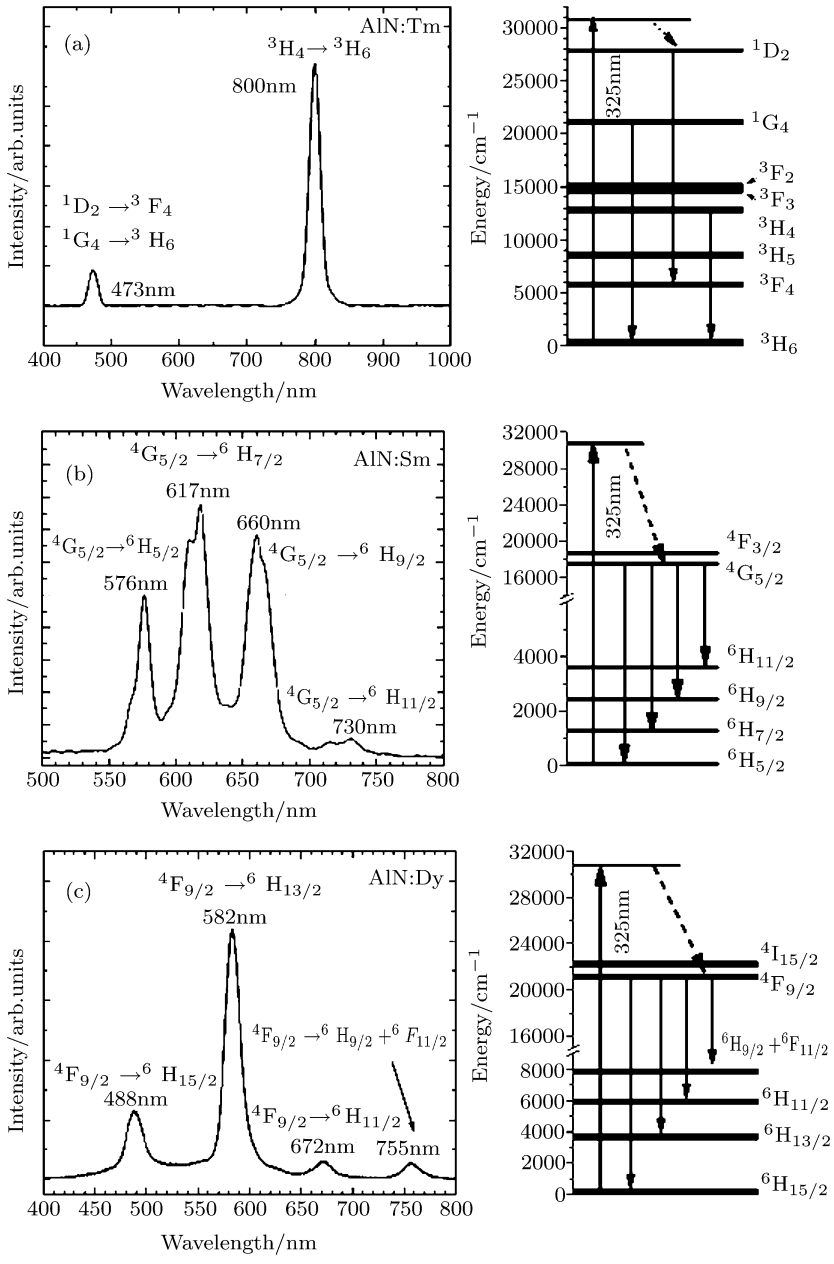


Fig.4. The PL spectra of AlN:RE films and the transition schematic: (a) AlN:Tm; (b) AlN:Sm; (c) AlN:Dy.

PL emission peaks for AlN:Tm are observed in the blue region ($\sim$ 473 nm) and in the infrared region (IR, $\sim$ 800nm). Lee *et al* reported that there exists only one emission peak at 465nm in the blue region for GaN:Tm, but for $Al_{1-x}Ga_xN$:Tm two emission peaks are observed at 465 and 478nm which are associated with Tm^{3+} 4f–4f transitions from $^1D_2$ to $^3F_4$ (465 nm) and from $^1G_4$ to the ground state $^3H_6$ (478 nm).[21] Due to the resolution of the instrument, the $\sim$ 473 nm emission observed in our system also corresponds to the combination of the two transitions, and the IR emission at $\sim$ 800 nm corresponds to the $^3H_4$ to $^3H_6$ transition. Three strong and one weak emission bands are observed for Sm^{3+} doped AlN films at $\sim$ 576, $\sim$ 617, $\sim$ 660 and $\sim$ 730 nm in the yellow to red region at room temperature (Fig.4(b)). According to the energy level scheme of Sm^{3+} in GaN [9] we attribute these emissions to the transitions of $^4G_{5/2}$ to ^6H_J (J = 5/2, 7/2, 9/2, 11/2). The intensities of the three emissions for ^6H_J (J = 5/2, 7/2, 9/2) are comparable. The PL spectrum of AlN:Dy is shown in Fig.4(c), four emission bands are observed in the green ($\sim$ 488 nm), the yellow ($\sim$ 582 nm), and the red ($\sim$ 672 nm and $\sim$ 755nm) regions. The $\sim$ 582 nm emission is obviously the strongest which is due to the transition of $^4F_{9/2}$ to $^6H_{13/2}$. The $\sim$ 672 nm band is assigned to the Dy^{3+} intra 4f transition of $^4F_{9/2}$ to $^6H_{11/2}$. The other PL peaks correspond to the following transitions: $^4F_{9/2}$ to $^6H_{15/2}$ (at $\sim$ 488 nm) and $^4F_{9/2}$ to $^6H_{9/2}$ + $^6F_{11/2}$ (at $\sim$ 730 nm).

Figure 5 shows the combined emission colour of Tm^{3+}, Sm^{3+} and Dy^{3+} doped AlN using the Commission International de l'Eclairage (CIE) chromaticity diagram 1931 system. Using the integral intensity of each emission peak, we have calculated the coordinates of the mixed emission. The mixed colour of AlN:Tm is blue with the CIE coordinates of (0.116, 0.074, 0.810). The CIE coordinates for AlN:Sm is (0.621, 0.378, 0.001) with reddish orange colour and the wavelength is about 600 nm; and the CIE coordinates for AlN:Dy is (0.485, 0.440, 0.075) with yellow colour and the wavelength is about 583 nm. The wavelength of the complementary colour for the AlN:Sm emission is about 482 nm. It reveals that the Sm and Tm co-doped AlN:film with a proper doping-content ratio might have a mixed emission with a nearly white colour.

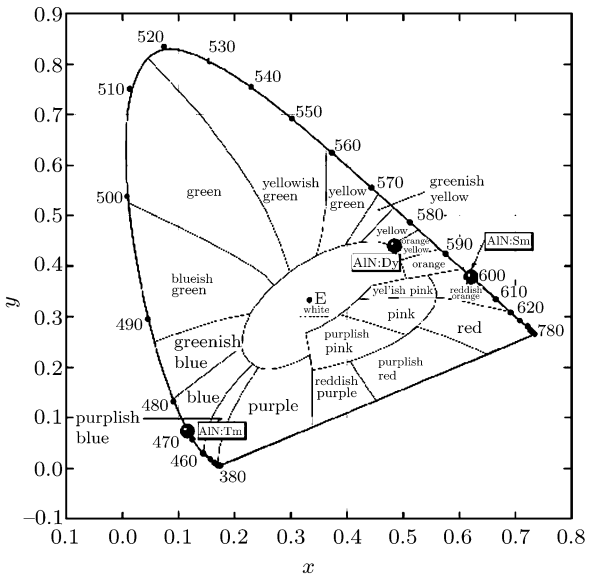


Fig.5. CIE 1931 x-y chromaticity diagram showing the locations of the mixed emissions of rare earth -doped AlN films.

In summary, the c-axis oriented AlN:RE (RE = Tm^{3+}, Sm^{3+} and Dy^{3+}) films have been grown by RF magnetron reactive sputtering. AlN:Tm film has a shows blue emission at $\sim$ 473 nm, AlN:Sm film has a mixed colour of reddish orange and AlN:Dy film has a yellow colour. The experimental results of the present study demonstrate the potential for fabricating visible light optoelectronic devices using RE-doped AlN thin films grown by sputter deposition.

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References

[1] Steckl J and Zavada J M 1999 *MRS Bull.* **24** 16
[2] Steckl J and Birkhahn R 1998 *Appl. Phys. Lett.* **73** 1700
[3] Lozykowski H J, Jadwisienczak W M and Brown I 1999 *Appl. Phys. Lett.* **74** 1129
[4] Zhang C G, Bian L F and Chen W D 2005 *Chin. Phys.* **14** 2141
[5] Jadwisienczak W M, Lozykowski H J, Perjeru F, Chen H, Kordesch M and Brown I G 2000 *Appl. Phys. Lett.* **76** 3376
[6] Lee D S and Steckl A J 2001 *Appl. Phys. Lett.* **79** 2450
[7] Liu Q L, Bando Y, Xu F F and Tang C C 2004 *Appl. Phys. Lett.* **85** 4890
[8] Song S F, Zhou S Q, Chen W D, Zhu J J, Chen C Y and Xu Z J 2003 *Acta Phys. Sin.* **52** 2558 (in Chinese)

[9] Gruber J B, Bahram Zandi, Lozykowski H J and Jadwisienczak W M 2002 *J. Appl. Phys.* **91** 2929

[10] Favennec P N, L'Haridon H, Salvi M, Moutonnet D and Le Guillou Y 1989 *Electron. Lett.* **25** 718

[11] Kumar A, Chan H L , Weimer J J and Sanderson L 1997 *Thin Solid Films* **308/309** 406

[12] Giardini A G, Mele A, Di Palma T M, Flamini C, Orlando S and Teghil R 1997 *Thin Solid Films* **295** 77

[13] Tanaka N, Okano H, Usuki T and Shibata K 1994 *Jpn. J. Appl. Phys.* **33** 5249

[14] Edgar J H, Carosella C A , Eddy C R and Smith D T 1996 *J. Mater. Sci. Mater. Electronics* **7** 247

[15] Lu F, Carius R, Alam A, Heuken M and Buchal C 2002 *J. Appl. Phys.* **92** 2457

[16] Jadwisienczak W M, Lozykowski H J, Berishev I, Bensaoula A and Brown I G 2002 *J. Appl. Phys.* **89** 4384

[17] Okano H, Takahashi Y, Tanaka T, Shibata K and Nakano S 1992 *Jpn. J. Appl. Phys.* Part 1 **31** 3446

[18] Liu Q L, Tanaka T, Hu J Q, Xu F F and Sekiguchi T 2003 *Appl. Phys. Lett.* **83** 4939

[19] De Keijser T H, Langford J I, Mittemeijer E J and Vogels A B P 1982 *J. Appl. Cryst.* **15** 308

[20] Thornton J A 1977 *Annu. Rev. Mater. Sci.* **7** 239

[21] Lee D S and Steckl A J 2003 *Appl. Phys. Lett.* **83** 2094