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$AlN:TbF_3$ Electroluminescence Thin Film Prepared by Radio-Frequency Magnetron Sputtering *

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High quality AlN thin films doped with TbF_3 were prepared by rf magnetron reaction sputtering. High purity Al metal and TbF_3 were used as target materials with N_2 and Ar as sputtering gases. The influence of preparation conditions on the photoluminescence brightness was studied, and the electroluminescence was found to have a similar dependence on the concentration of TbF_3 and substrate temperature. The characteristic emission of Tb^{3+} ions was obtained in an $AlN:TbF_3$ alternating current thin film electroluminescence device prepared with 600° C substrate temperature and 4.0 mol% concentration of TbF_3.

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Thin-film electroluminescence (TFEL) display panels are gaining large acceptance in information displays on account of their superior characteristics: all solid state, active emission, high contrast, wide view angle, high operational speed, wide operating temperature and long term reliability. However, full-color electroluminescence (EL) display has not yet been commercialized due to lack of good blue or white phosphors. The traditional EL host matrices, such as Ⅱ−Ⅵ sulphides or ternary compounds,[1] have a difficulty of charge compensation when they are doped with rare-earth ions, which will form unexpected defect energy levels and lower luminescence efficiency. The biggest challenge today is to find new EL materials to produce multi- and full-color EL display panels. Efforts have been made and more and more new matrices are being reported,[2] but there is no report about using AlN thin film for EL.

Aluminum nitride is a direct gap semiconductor with a 6.2 eV band gap, and has been used in many fields.[3,4] Doping rare-earth ions in AlN thin film, We expect that excitation probability of upper energy levels and efficiency of shorter wavelength emission will be higher than in other narrower band gap semiconductor. As an EL phosphor, AlN:Mn was reported in the 1950 s, but it was limited to the powder state.[5] In the 1970 s, low resistance AlN thin film blue-violet EL was obtained by direct current voltage excitation.[6] The resistance of AlN thin films prepared by radio frequency magnetron sputtering is higher than $10^{13}\ \Omega\cdot$cm and it is difficult to be excited by direct current voltage, so we developed an alternating current thin film electroluminescence (ACTFEL) device with a double insulating layer structure. We report here for the first time an ACTFEL device made of $AlN:TbF_3$ thin film.

$AlN:TbF_3$ thin film was prepared by rf magnetron reactive sputtering, on a sputtering machine Type JS450D, made in Bejing, China. High purity Al metal and TbF_3 were used as target materials with N_2 and Ar as sputtering gases at a total pressure of 1 Pa. The best ratio of N_2 to Ar is 1/4. Other ratios were tried but the crystallinity of the thin film became relatively worse. The sputtering power was 750 W, the target area 50 cm^2 and the distance from the target to substrate 6 cm. Before sputtering, high vacuum ($< 5 \times 10^{-5}$ Torr) is necessary because the existence of oxygen will destroy the crystallinity of the thin film. The substrate temperature ranged from 250 to 600°C and the concentration of Tb^{3+} ion in AlN thin film from 0.8 to 8.7 mol%. The dates of the concentration used were obtained with an analysis balance through analyzing the mass variation of target materials before and after the film was prepared. To determine the dependence of luminescence on different preparation conditions, the photoluminescence (PL) and excitation spectra were measured with 236 nm excitation by an MPT-4 fluorescence spectrometer (made in Japan). The ACTFEL device was designed with $AlN:TbF_3$ as the luminescent layer and SiO_2/Ta_2O_5 as double insulator in a stacked structure. The SiO_2 and Ta_2O_5 film were deposited by rf magnetron reactive sputtering in a chamber having two targets made of high purity Si and Ta metal. The area of each target was 38.5×9.4 cm. The SiO_2 film was deposited in conditions in which the total pressure of O_2+Ar mixture gas was 2 Pa, the partial pressure of O_2 20%, the rf power 1000 W, and the substrate temperature about 200°C. The Ta_2O_5 films were sputtered in an O_2+Ar atmosphere containing 35% O_2 with total pressure of 2 Pa. The power was 1500 W, and the substrate temperature about 300°C. The EL spectra were measured under 500 Hz sinusoidal wave voltage excitation by a monochromator with a photomultiplier (RCA Model 31034) connected to a recorder.

Figure 1 shows the relation of PL brightness with substrate temperature, with experimental points at 250, 300, 450, 545, and 600℃. In all samples, the Tb^{3+} ion concentration in the AlN thin film was

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controlled on the level of 4.0 mol%. It can be seen that the PL brightness increases rapidly with increasing substrate temperature. In our previous experiments, the crystallinity of AlN thin films improved with increasing substrate temperature, the reason being that aluminum has a much stronger affinity for oxygen than for nitrogen in low temperature, but with increasing temperature at some point affinity for nitrogen becomes stronger.[7] In our vacuum condition ($< 5\times10^{-5}$ Torr), the existence of oxygen will destroy the crystallinity of the thin film in low temperature regions while with increasing temperature the destruction will be lowered. It is obvious that the improved crystallinity with increasing temperature contributes to the increasing of PL brightness. We also prepared another series of samples under a 600°C substrate temperature with the concentration of Tb^{3+} ions varying in the range of 0.8 to 8.7 mol%, and the results are shown in Fig. 2. The optimum Tb^{3+} ion concentration in AlN thin film is found to be about 4.0 mol%, higher than that in ZnS thin film.[8] The reason for this may be that the difficulty of charge compensation in AlN is small in comparison with ZnS.

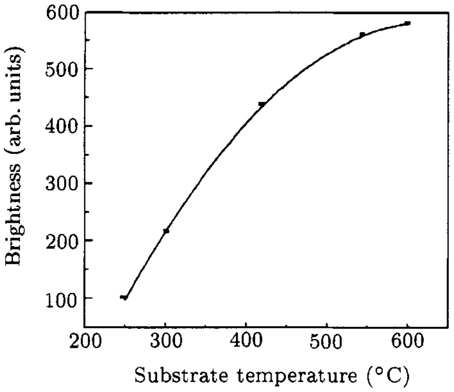

Fig. 1. Dependences of PL brightness of AlN:TbF_3 films on substrate temperatures. The brightness was measured at 236 nm excitation.

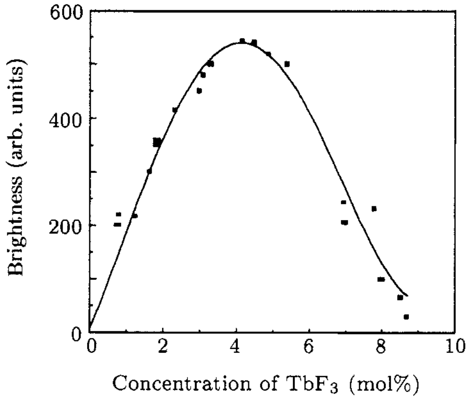

Fig. 2. Dependences of PL brightness of AlN:TbF_3 film on concentrations of Tb^{3+} ion. The brightness was measured at 236 nm excitation.

Figure 3 shows the stacked structure of an AlN:TbF_3 ACTFEL device. The AlN:TbF_3 thin film is prepared with a substrate temperature of 600°C and Tb^{3+} ion concentration of 4.0 mol%. Two layers of insulator are chosen for the sake of obtaining high brightness and stability.[9] The EL spectrum is shown in Fig. 4. The emission spectrum of AlN:TbF_3 consists of four groups of lines peaked around 490 nm ($^4D_4-{}^7F_6$), 545 nm ($^5D_4-{}^7F_5$), 590 nm ($^5D_4-{}^7F_4$) and 625 nm ($^5D_4-{}^7F_3$). Emission from $^5D_3$ energy level of Tb^{3+} is not observable in our experiment.

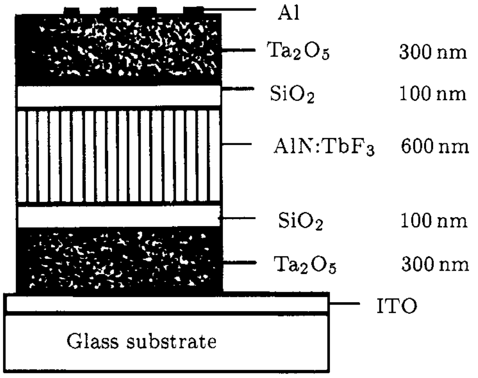

Fig. 3. structure of AlN:TbF_3 ACTFEL device.

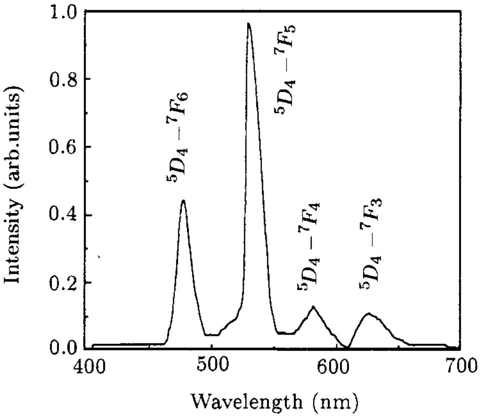

Fig. 4. EL spectrum from AlN:TbF_3 ACTFEL device. The concentration of Tb^{3+} ion in AlN film is about 4.0 mol% and the substrate temperature is 600°C.

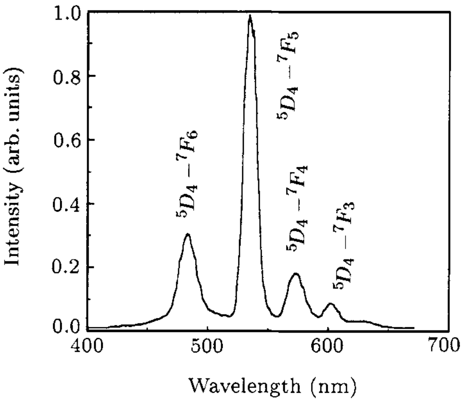

Fig. 5. PL spectrum from AlN:TbF_3 film. The concentration of Tb^{3+} ion is about 4.0 mol% and the substrate temperature is 600°C. The excitation wavelength is 236 nm.

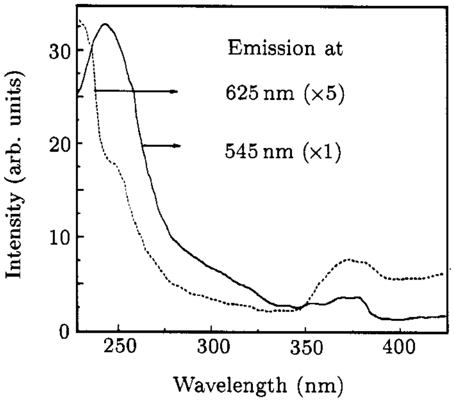

Fig. 6. PL excitation spectra from AlN:TbF_3 film. The concentration of Tb^{3+} ion is about 4.0 mol% and the substrate temperature is 600°C.

In order to study the possible excitation processes of EL in AlN:TbF_3 films, the PL and excitation spectrum are measured and shown in Figs. 5 and 6, respectively. The film is prepared in the same experiment with the EL device. The PL spectrum of AlN:TbF_3 thin film has similar emission peaks to those in EL spectrum, which are ascribed to the same transitions. Measuring the emission from $^5D_4 - {}^7F_5$ (peaked at 545 nm) and $^5D_4 - {}^7F_3$ (peaked at 625 nm), gave two excitation spectra, as shown in Fig. 6. Here, two excitation peaks are observed; one is stronger at 236 nm and maybe ascribed to excitation of the near band edge, the other is weaker at 380 nm. The solid excitation spectrum (measuring the emission from $^5D_4 - {}^7F_5$) is five times the height of the dashed one (measuring the emission from $^5D_4 - {}^7F_3$). In short, the luminescence processes are due to excitation of energy levels near the band edge at first, then energy is transferred to the Tb^{3+} ions. The excitation mechanism of AlN:TbF_3 is different from that of ZnS:TbF_3 thin film, which mainly involves direct excitation of the Tb^{3+} ions.[10] The difference in mechanism between AlN:TbF_3 and ZnS:TbF_3 are explained by the difference of crystal field environments. AlN is hexagonal while ZnS is Zincblende. AlN thin film prepared by radio frequency magnetron sputtering has some N vacancy energy levels, which can cause cathodoluminescence peaked at 370 nm. Thus the 380 nm peak in the excitation spectrum may be caused by N vacancy energy levels, followed by energy transfer from the N vacancy to the Tb^{3+} ion, and also may include the excitation $^7F_6 - {}^5D_3$ of the Tb^{3+} ion.

In summary, high quality AlN:TbF_3 thin films has been prepared by rf magnetron reaction sputtering. The influence of substrate temperature and doping concentration on the luminescence of AlN:TbF_3 thin film has been studied. The brightness increases with the substrate temperature. The optimal concentration of Tb^{3+} ions in AlN is about 4.0 mol%, higher than that in ZnS. The excitation mechanism as determined by the PL and excitation spectrum appears to be energy transfer from levels near the band edge to the Tb^{3+} ions. ACTFEL devices has been designed and green EL of AlN:TbF_3 thin film has been reported for the first time.

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