

Room temperature visible luminescence from amorphous GaN:Tb deposited by DC magnetron sputtering

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The GaN and GaN:Tb thin films have been prepared by direct current (DC) planar magnetron sputtering deposition under the same conditions. GaN thin film was analyzed by photoluminescence (PL) measurements, Fourier Transform Infrared (FTIR) absorption and UV-Vis transmission. FTIR result indicates the main absorbance is Ga-N stretching vibration. From UV-Vis result the optical band gap of the film has been calculated as 3.85 eV and no yellow and green emission was observed in PL spectrum. The GaN:Tb film was characterized by X-ray diffraction (XRD) and photoluminescence (PL) spectra. XRD shows the structure of thin film as being amorphous. 4f transitions of Tb³⁺ visible green photoluminescence have been obtained at room temperature: ⁵D₄ - ⁷F₆ (497.0 nm), ⁵D₄ - ⁷F₅ (552.4 nm), ⁵D₄ - ⁷F₄ (594.2 nm), ⁵D₄ - ⁷F₃ (627.8 nm).

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1. Introduction

Semiconductors doped with rare earths (RE) can emit the specific rays of rare earths and could be used in optical communication, flat panel display and optical memory devices, etc. They can also be compatible with the modern integrated circuit (IC) technology. Since 1960s, the scientists put rare earths into elements and compound semiconductors. But the results were discouraging because the emission efficiency of the samples was very low and temperature quenching was very large.

Since 1990's, GaN:RE (Er, Pr, Tm and Eu) *epitaxial* films have been prepared by implantation or *in situ* deposition and photoluminescence (PL) and the electroluminescence (EL) properties of the films were studied^[1-13]. Important blue, green, red and IR emissions of rare earths from GaN:RE *epitaxial* films have been observed and the results pointed out that the luminous emitters made with the GaN:RE films exhibit high brightness, long life, good single colour, and low quenching effect [3, 8].

Up to now, GaN *epitaxial* layers made through any *epitaxial* method presented many defects. If amorphous GaN (a-GaN) has partial properties of crystalline GaN, it may replace crystal GaN in many fields, including the host material for rare earth doping. During the late 1990s a-GaN material attracted much attention in several labs [14-20]. Rare earths-doped a-GaN has also been reported [18-20]. Kang *et al* [18] have obtained infrared emission of a-GaN:Er. The emission lines of rare-earth ions were observed, also, by A.A.Andreev [19]. Aldabergenova *et al* [20] have prepared a-GaN:Tb at 350°C by co-sputtering

method and obtained the characteristic emission of Tb³⁺ ions. The feature green emission of Tb³⁺ is situated at 550 nm and agrees with the standard green of CIE. Much attention has been paid to Tb³⁺ doped materials, such as Tb doped GaN [19,21,22] and Tb doped AlN [23-26].

The sputtering method can be used to prepare large-area and uniform films. GaN film deposited by the sputtering method was been reported very early [27]. In this paper, a-GaN:Tb films have been prepared and green feature emission has been obtained without any post treatment.

2. Experimental

Gallium (Ga) target used highly pure metallic Ga (99.999 %), which was put into a 5 cm-diameter steel dish. The distance between the target and the substrate was 5 cm. GaN:Tb and GaN films were sputtered under the same growing conditions. A small Tb sheet was put on the surface of Ga when GaN:Tb was prepared. The background pressure was 3×10⁻³ Pa. The sputtering and reactive gas was nitrogen (99.999 % purity). There was no heating during the preparation, the working pressure was ~4 Pa, the sputtering power was 10 W and the deposited time was 3 hours.

The structure of a-GaN:Tb film was observed through X-ray diffraction (XRD) (Philips X'Pert) using Cu Kα (λ=0.154056 nm) target tube. The Fourier Transform Infrared (FTIR) absorption spectrum measurement of the film was carried out on a Nicolet NEXUS 670 spectrometer. PL measurement of GaN:Tb and GaN film were analyzed by SHIMADZU RF-540 fluorescence

spectrometer with a 325 nm line of a 15 mW He-Cd laser.

3. Results and discussion

Fig. 1 shows the XRD pattern of the GaN:Tb film. Two diffraction packs centering at $2\theta = 34^\circ$ and 60° were observed but without an obvious diffraction line, indicating that the film was of a typical amorphous structure. No diffraction line of Tb and Ga_2O_3 was found, indicating that Tb was doped uniformly in the film.

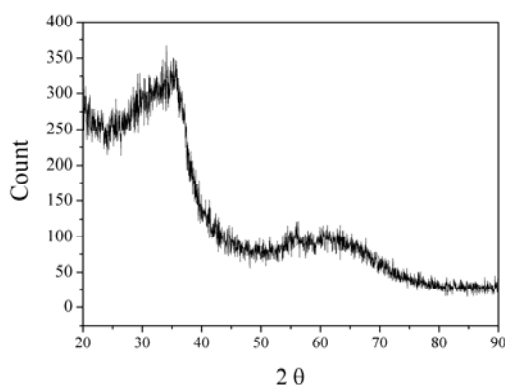


Fig. 1. XRD pattern of the GaN:Tb film.

Fig. 2 is the IR absorbance spectrum of the GaN. The line of 560.6 cm^{-1} refers to Ga-N bond stretching vibration absorption [28]. The absorption line of 605.5 cm^{-1} is due to vibration by which C substituted crystal Si. It is possible that C was a pollutant from substrate [29]. The 1107 cm^{-1} absorption line corresponds to Si-O bond vibration, which is from Si oxidation in atmosphere. Ga-O vibration was not observed in IR absorbance spectrum, neither was it found in $50\text{--}600\text{ cm}^{-1}$ IR spectrum (not shown here).

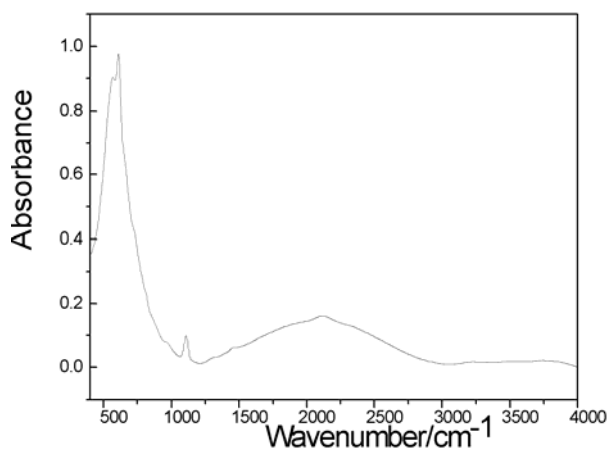


Fig. 2. FTIR absorbance spectra of the GaN film.

Fig. 3 shows absorption coefficient vs photons energy of the GaN film, based on the Tauc formula:

$$(\hbar\omega\alpha)^n \sim (\hbar\omega - E_g)$$

For indirect transitions $n=1/2$ and for direct ones $n=2$. From transmittance and reflectance spectra (not shown here), an absorption coefficient for the film as a function of photon energy has been calculated (Fig. 3) and the optical gap of the film was found 3.85 eV. Below the gap in Fig. 3, the curve is smooth and without absorption, and this indicates that there are few gap states in the gap of a-GaN.

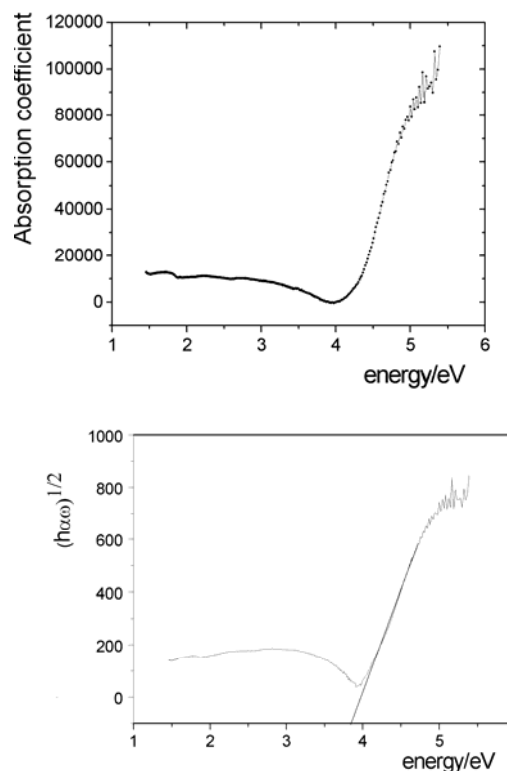


Fig. 3. Absorption coefficient vs photons energy of a-GaN film.

Fig. 4(a) presents the photoluminescence of a-GaN and a-GaN:Tb films at room temperature. Fig. 4 (a.Δ) shows photoluminescence of non-doped a-GaN. Yellow and green emission was not observed, as was reported in Reference [30] and this result is consistent with References [15,17,18]. Strong yellow and green emission of crystal GaN, which had grown with the MOCVD method, can be observed by naked eyes, but not for a-GaN. This indicates that there are few gap states in a-GaN and therefore there are few non-radiation channels in it.

Fig. 4 (a.■) shows the photoluminescence of the film a-GaN:Tb. Between 450 - 650 nm, four feature lines of Tb^{3+} ions were clearly observed: $^5\text{D}_4 - ^7\text{F}_6$ (497.0 nm), $^5\text{D}_4 - ^7\text{F}_5$ (552.4 nm), $^5\text{D}_4 - ^7\text{F}_4$ (594.2 nm) and $^5\text{D}_4 - ^7\text{F}_3$ (627.8 nm).

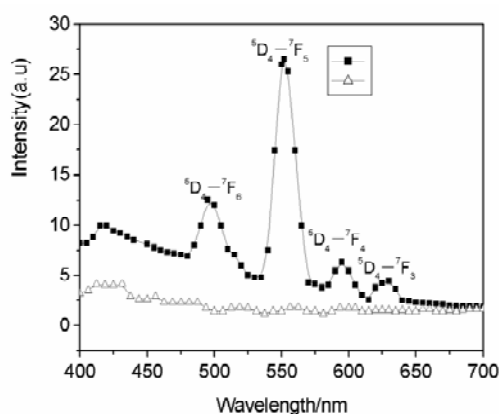


Fig.4(a) PL of a-GaN:Tb (■) and a-GaN (Δ) films at room temperature.

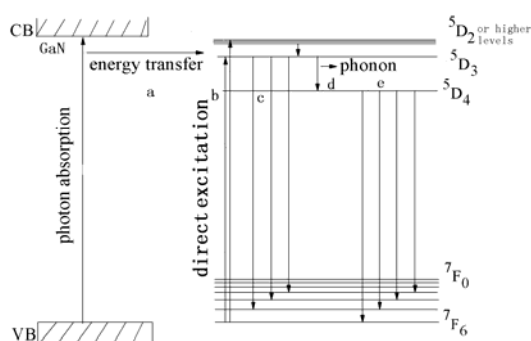


Fig.4(b) Relevant energy levels and energy transfer in the PL of GaN:Tb film.

Without any post treatment, green emission of Tb^{3+} ions was obtained, probably due to the fact that pure N_2 (not other gas) was used as the sputtering and reactive gas. The film, being N rich, has broad optical gaps and few gap states [15,18], hence few non-radiation channels. Fig.4(b) shows relevant energy levels and energy transfer in the PL of GaN:Tb film. There may be three possible energy transfer processes in GaN:RE [31, 32]. Rare earths ions can introduce electron or hole traps in III-V semiconductors and act as donors or acceptors. We call this kind of traps as isoelectronic structured impurities. The isoelectronic cationic structured substitutional impurities (Here id RE^{3+} ions) could lead to efficient emission in many rare-earth-doped materials [31]. The RE^{3+} ions also could introduce structured isoelectronic substitutional traps in III-V semiconductors. The isoelectronic traps can attract either electrons or holes. The isoelectronic trap is charged after an electron or hole was captured. The charged trap could capture an opposite carrier by Coulomb interaction and form a bound exciton. Then energy transfers from exciton to intra-4f electron of

RE^{3+} ions and excites them to high levels. This is one route of energy transfer. The second mechanism is the energy transfer from a free exciton near a trap to localized states by inelastic scattering process. The third method is the energy transfer from free electron or hole to the core electrons by trap occupied by electron or hole (process “a” in Fig. 4(b)). RE^{3+} ions absorb energy and bound to high levers then generate radiative transition (processes “c” and “e” in Fig. 4b). In order to obtain efficient radioactive recombination, the phonon coupling should be low. Luckily, the phonon density of a crystal material is larger and its energy distribution wider than that of an amorphous material. Tb^{3+} ions bound from high excited states to low states. Tb^{3+} ions transfer energy to the crystal lattice with the assistance of phonons, but this effect will be lower in an amorphous material. Thus visible green emission of Tb^{3+} could be observed at room temperature. Also, part of Tb^{3+} was excited to $^5\text{D}_3$ and or higher levels (process “b” in Fig. 4(b)) in a direct optical way and then bounds to ground states and emits light.

The gap of a host material for rare earths doping is much wider and the quenching effect much lower. The optical gap of a-GaN is 3.85eV and it is quite wide, being another reason why emission of Tb^{3+} ions was observed at room temperature.

Centered at 417.0 nm there is an emission packet in Fig. 4(a.■), which may be a transition between $^5\text{D}_3 - ^7\text{F}_6$ of Tb^{3+} ions in the PL spectrum (process c in Fig.4(b)). Though available information about the defects of a-GaN is limited, it can be inferred from the strong light emission of a-GaN:Tb that a-GaN is proper host material for rare earth doping.

4. Conclusions

The GaN:Tb and GaN thin films have been prepared by DC planar magnetron sputter deposition under the same growing conditions. XRD shows the GaN:Tb film as amorphous and FTIR shows that the main absorbance is Ga-N stretching vibration. From UV-VIS result the optical band gap of the film has been calculated as 3.85 eV. Without any post treatment, four feature green lines of Tb^{3+} ions have been clearly observed at room temperature: $^5\text{D}_4 - ^7\text{F}_6$ (497.0 nm), $^5\text{D}_4 - ^7\text{F}_5$ (552.4 nm), $^5\text{D}_4 - ^7\text{F}_4$ (594.2 nm) and $^5\text{D}_4 - ^7\text{F}_3$ (627.8 nm). GaN thin film was also analyzed by PL measurement and no yellow and green emission was observed.

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