

Dynamics of ultraviolet emissions in Tm-doped AlN using above band gap excitation

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We report on dynamics of ultraviolet (UV) emissions using above band gap excitation in Tm-doped AlN epilayers grown by solid-source molecular beam epitaxy. The UV and visible photoluminescence (PL) spectra were measured using the frequency quadrupled output from a Ti:sapphire laser. In the UV region, dominant emissions at 298 and 358 nm were observed under 197 nm excitation. Temperature dependence of the PL intensities of these emission lines reveals a binding energy of ~ 150 meV. The quenching of the UV emissions in AlN:Tm appears related to the thermal activation of the excitons bound to the rare-earth structured isovalent charge trap at 1.50 eV below the conduction band. © 2008 American Institute of Physics. [DOI: 10.1063/1.2970993]

The compound semiconductor AlN is a direct band gap semiconductor that has been recognized as an important material for electronic device applications.¹ Strong chemical bonds make it chemically inert in most environments and account for its radiation hardness. Because of its high thermal conductivity, large piezoelectric field, low electron affinity, and large dielectric constant, AlN has found application in stable x-ray production, surface acoustic wave devices, cold cathode, and transistor gate insulation.²⁻⁵ In addition, AlN's large band gap (6.1 eV) gives rise to optical transparency over a wide spectral range, from the infrared (IR) to the ultraviolet (UV).⁶ These properties make it an optimum host for the various emissions that are possible from lanthanide rare-earth (RE) ions. Significant research has been carried out on the incorporation of RE elements in III-N semiconductors and into the resulting optical properties.⁷⁻¹² Since RE ions have well-shielded 4*f*-electron shells, the 4*f*-transitions are nearly independent from the host materials. Potential applications of RE-doped AlN include full color displays and white lighting systems provided that the efficiency of these RE emissions can be improved. Thulium is an important RE element for such applications since in its trivalent charge state (Tm³⁺) there are prominent IR, visible, and UV emissions. It has also been reported that Tm-doped Al_xGa_{1-x}N ($x > 0$) alloys show room temperature ferromagnetism from the two unpaired electrons in its 4*f*-shell.¹³ Therefore Tm-doped AlN (AlN:Tm) could be a potential material for magnetic and optical functionality on a single chip.

The cathodoluminescence (CL) spectra of Tm-implanted AlN covering the wavelength range from 290 to 820 nm have been reported by Gruber *et al.*¹⁴ They observed more than 200 intra-4*f* Tm³⁺ transitions and identified about 100 transitions. Dorenbos and Van der Kolk¹⁵ developed a method to establish the 4*f* ground state energy for divalent and trivalent lanthanide relative to the valance and conduction band (CB) in AlGa_xN alloys. Their scheme predicts that the charge transfer band, from Tm³⁺ to Tm²⁺, is located at ~ 1.44 eV below the CB in AlN:Tm. A kinetic model of energy transfer from the host lattice to the localized core

excited state of RE structured isovalent (RESI) traps for RE ions was proposed by Lozykowski.¹⁶ According to this model the energy-transfer process occurs either through an Auger mechanism or from the exciton bound to RESI trap to the core states. The RESI centers of energies 0.72 and 1.41 eV have been measured from the thermal quenching of the CL intensities in Tm-implanted AlN films.¹⁷ However, there is no emission band at 298 nm in their CL spectra. Lee and Steckl reported¹⁸ the molecular beam epitaxy (MBE) growth of Al_xGa_{1-x}N:Tm alloys for $0 \leq x \leq 1$ and observed strong blue (466 and 475 nm) electroluminescence with increasing Al content up to $x \cong 0.8$. Hömmerich *et al.*¹⁹ measured the PL spectra of the same set of samples and also observed strong blue emission with increasing Al content. Using below band gap excitation at 250 nm, they reported a broad emission band near 300 nm.

In this work, we report on PL studies of the UV emissions of AlN:Tm epilayers grown by MBE on Si substrates. Dynamics of the UV emissions have been measured using above band gap excitation at 197 nm. Dominant emissions at 298 and 358 nm were observed and the temperature dependence of these lines reveals a binding energy of about 150 meV. Using Haynes' rule,²⁰ the quenching of both transitions is controlled by the thermal activation of the excitons bound to a charge trapping center located ~ 1.50 eV below the AlN CB. The experimental data indicate that this center is the RESI trap that allows excitonic energy to be transferred to the 4*f*-electron states resulting efficient UV emissions.

AlN:Tm epilayers of 0.5 μm thickness were grown on *p*-type Si (111) substrates by solid-source MBE using elemental Al and Tm sources in conjunction with a rf-plasma source supplying atomic N.¹⁸ The typical growth rate was 0.5–0.6 $\mu\text{m}/\text{h}$. The Tm concentration was between 0.2 and 0.5 at. %. All films were capped with an undoped AlN layer. No indication of the formation of second phases was found based on x-ray diffraction measurements. AlN:Tm epilayers were characterized by deep UV PL spectroscopy. Above- and below band gap excitations were done by frequency quadrupled and tripled Ti:sapphire laser sources. The deep UV PL system consists of a 100 fs Ti:sapphire laser with an average power of about 3 (100) mW at 197 (263) nm (rep-

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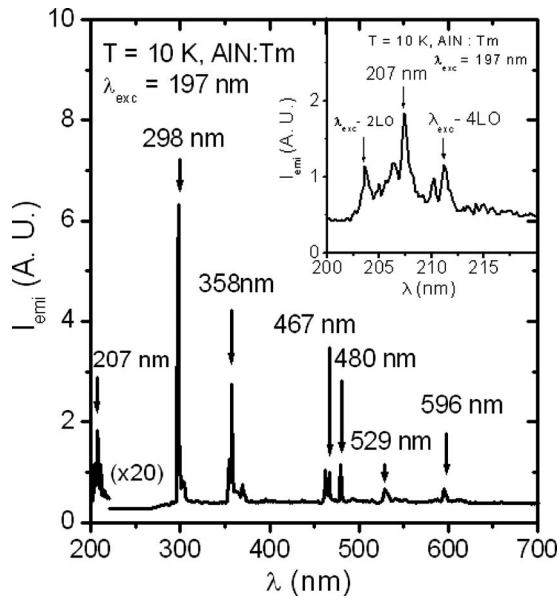


FIG. 1. The 10 K PL spectrum of Tm-doped AlN epilayer for $\lambda_{\text{exc}} = 197$ nm. The inset shows a high resolution short range PL spectrum, which exhibits the FX peak at 207 nm.

etition rate of 76 MHz) and a monochromator (1.3 m).²¹

Figure 1 shows the low temperature PL spectrum of AlN:Tm under 197 nm excitation. Prominent emission lines were observed at 298 and 358 nm due to transitions from 1I_6 to ground (3H_6) and 3F_4 states, respectively. Inset of Fig. 1 shows the high resolution short range PL spectrum that exhibits a band edge emission at 207 nm (5.99 eV) due to the free exciton (FX) transition and longitudinal optical (LO) phonon replicas at 204 ($\lambda_{\text{exc}} - 2\text{LO}$) and 212 nm ($\lambda_{\text{exc}} - 4\text{LO}$). Since the FX binding energy in AlN is around 0.08 eV,^{6,22,23} the band gap of AlN on Si at 10 K is thus around 6.07 eV (5.99 eV + 0.08 eV). Redshift of the band edge emission energy shows that AlN on Si has tensile strain. It is consistent with a previous study which shows the tensile strain on AlN/Si.²⁴ In addition to strong UV emissions and weak band edge transitions, visible intra-4f Tm^{3+} transitions at 463, 467, 480, 529, and 596 nm were also observed. There were no intra-4f Tm^{3+} transitions in the infrared region. A

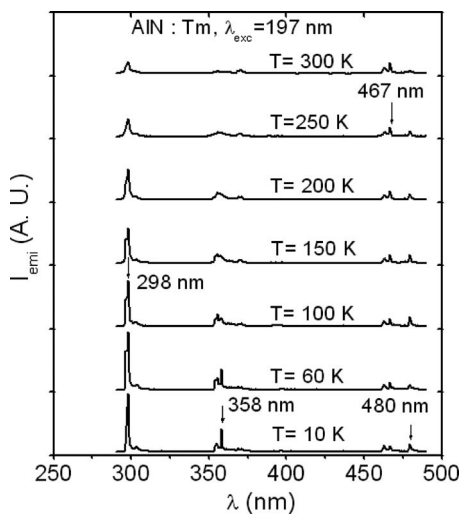


FIG. 2. The PL spectra of AlN:Tm measured from 10 to 300 K for $\lambda_{\text{exc}} = 197$ nm.

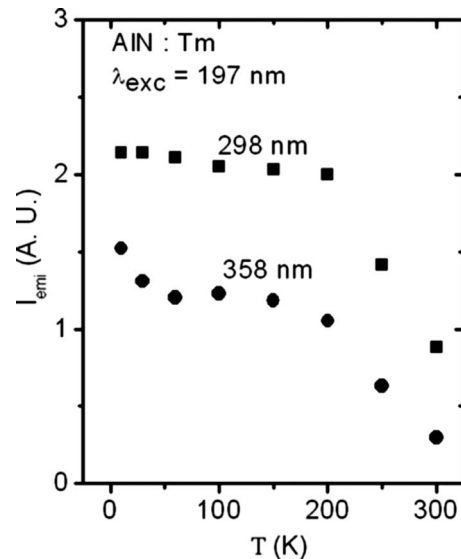


FIG. 3. Dependence of the integrated PL intensities of 298 and 358 nm intra-4f Tm^{3+} transitions on the sample temperature.

broad and strong emission peak at 315 nm and a sharp emission line at 480 nm were observed under below band gap excitation with a 263 nm laser line (not shown).

Figure 2 shows the temperature evolution of the PL spectra over a temperature range from 10 to 300 K. Emission at 467 nm is almost temperature independent and the 480 nm emission line has very small thermal quenching. However, UV emissions at 298 and 358 nm show distinct thermal quenching behavior, as shown in Fig. 3. Although the PL intensity (the area under the PL emission curve) is quenched at higher temperatures, the transition linewidth does not exhibit thermal broadening with increasing temperature from 10 to 300 K. There may be some contribution to the observed linewidths due to the monochromator slit width.

The Arrhenius plot of the PL intensities of 298 [Fig. 4(a)] and 358 nm [Fig. 4(b)] emission lines were measured in AlN:Tm for the temperature range between 60 and 300 K. As

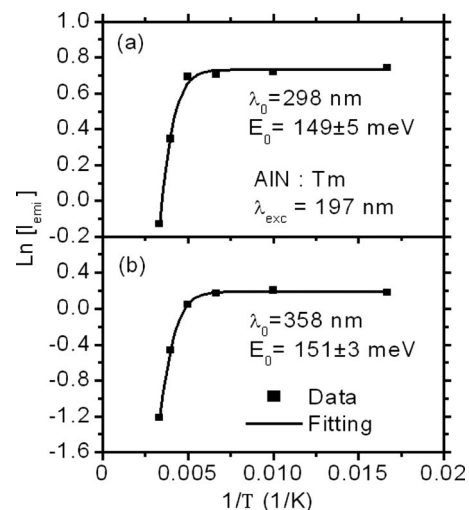


FIG. 4. The Arrhenius plot of the integrated PL intensity of (a) 298 and (b) 358 nm emissions in the temperature range between 60 and 300 K. The solid lines are best fits to the experimental data. The fitted values of activation energies are 149 ± 5 and 151 ± 3 meV for 298 and 358 nm transitions, respectively.

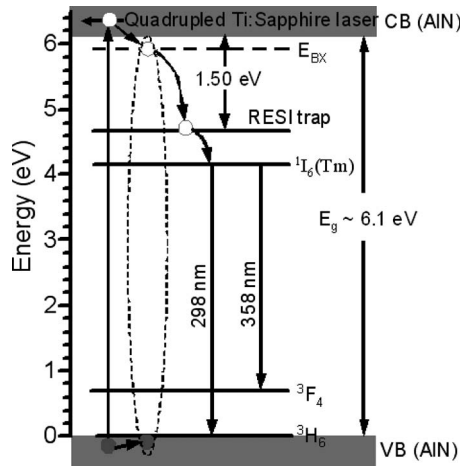


FIG. 5. Diagram of energy levels and intra-4*f*-shell Tm^{3+} transitions in AlN:Tm illustrating the excitation path and the resulting UV emissions. E_{BX} is the binding energy of the exciton bound to RESI trap and the BX is indicated by the dashed ellipse.

shown in Fig. 4 the solid lines are the least-squares fit of the data with equation

$$I_{\text{emi}} = \frac{I_0}{1 + ce^{-E_0/kT}}, \quad (1)$$

where c is a constant and E_0 is the activation energy. The fitted value of E_0 is ~ 150 meV for both transitions.

Atomic covalent radii of Tm^{3+} ions are larger than atomic radii of Al that they are replacing, and the electronegativity of Tm (1.25 Pauling unit) is smaller than Ga (1.61 Pauling unit) for which they substitute. The difference in size and electronegativity creates a short range potential, which can trap free charge carriers. Such RESI charge traps capture free carriers.^{15–17} Two different charge trap centers that result in intra-4*f* Tm^{3+} transitions in Tm-implanted AlN were measured by Lozykowski and Jadwisienczak.¹⁷ However, no 298 nm emission is present in their CL spectra. A recent theoretical model predicted a charge transfer band at 1.44 eV below the CB in AlN:Tm.¹⁵ The RESI trap captures individual free carriers or a FX forming a bound exciton (BX). The energy of the BX can be transformed to excite the 4*f*-state of Tm^{3+} ions. With increasing temperature, the BX will either dissociate or it will transfer energy to the lower excited state thereby decreasing the PL emission intensity. The thermal quenching of the PL intensities of the UV transitions at 298 and 358 nm results to the E_0 of ~ 150 meV. However, there are no significant changes in the visible PL intensities with temperature (see Fig. 2). Based on the experimental data, the measured value of E_0 has been assigned to the binding energy (E_{BX}) of the exciton bound to a RESI trap. Using Haynes' rule, the binding energy of the exciton-neutral-impurity complex is about 10% of the impurity binding energy if we neglect the central-cell correction.²⁰ The expected energy level of the RESI trap is 1.50 eV. Thus, the thermal quenching of the UV transitions in AlN:Tm is due to thermal dissociation of the excitons bound to RESI charge trap at 150 meV below the CB. Above band gap excitation results in efficient UV emissions due to shallow level of the exciton bound to the RESI traps.

From our experimental results, we have constructed an energy level model involving 1I_6 , 3F_4 , and 3H_6 states of a Tm^{3+} ion in AlN, as shown in Fig. 5. It also shows intra-4*f*-shell UV emissions and excitation paths. We have taken the low temperature band gap of AlN/Si to be 6.10 eV and have placed BX and RESI trap level at ~ 0.15 and 1.5 eV below the AlN CB, respectively.

In summary, AlN:Tm epilayers were grown by MBE and their optical properties were probed by deep UV PL. Using 197 nm excitation intra-4*f* Tm^{3+} transitions from 1I_6 to 3H_6 and 3F_4 states were observed at 298 and 358 nm, respectively. Thermal quenching of the PL intensities of the both 298 and 358 nm transitions results to an E_0 of 150 meV, which is assigned to the E_{BX} of the exciton bound to a RESI charge trap. Using Hayne's rule, the estimated value of the ground state energy level of the RESI trap in AlN:Tm is 1.50 eV, which is close to the recently reported theoretical value of 1.44 eV. The data indicate that the quenching of the UV emissions in AlN:Tm is controlled by the thermal activation of the excitons bound to the RESI charge trap.

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