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Photoluminescence from $\text{Al}_x\text{In}_{1-x}\text{N}$ layers doped with Tb^{3+} ions

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Abstract. $\text{Al}_x\text{In}_{1-x}\text{N}$ films ($0 \leq x \leq 1$) have been sputter deposited and annealed, both without and with terbium co-doping, to obtain a series of matrices whose band gap energies span the range from around 2 eV to 6 eV. The terbium green luminescence spectra (excitation wavelength 230 nm, i.e. 5.4 eV) are measured at room temperature as a function of the aluminium content (band gap route) and of the terbium concentration (concentration route). The green luminescence assumes a maximum of the integrated intensity at a band gap energy of 4.1 eV ($x = 0.7$) which can be argued to result from a resonant energy transfer from the host matrix into the Tb luminescence centres. Furthermore, the dependence of this maximum integrated intensity as a function of the Tb concentration, i.e. of the average distance between the Tb centres, suggests the energy transfer from the host material into the Tb luminescent centres to be due to dipole-dipole interaction via an exciton bound to the centre.

1. Introduction

Thin semiconductor films in large areas, such as for solar cells or thin film transistor arrays in displays, are generally produced by rapid deposition methods. Apart from chemical vapor deposition, which generally requires higher temperatures, magnetron sputtering is frequently used. Sputtering is applicable at any temperature, preferentially at room or modestly elevated temperatures because of economical reasons. Common to these methods is the fact that single crystalline material cannot be obtained. In most cases one obtains amorphous or nanocrystalline films whose structures can subsequently be improved by annealing causing crystallization and grain coarsening.

Crystal defects can impair the electronic and optical properties of semiconductor materials. This disadvantage is especially prominent in the ‘classical’ semiconductors like Si, Ge or the families of the IV-IV, II-VI and III-V semiconductor compounds, e.g. [1] and references therein. Interestingly enough, the III-nitride family (more precisely IIIA-nitride), i.e. GaN, InN, and AlN and its ternary and quaternary compounds, are much more tolerant to crystal defects [2]. Therefore this III-N family is very interesting for being investigated with regard to optoelectronic properties especially as it also offers a broad range of band gaps from less than 2 eV (InN) to a little larger than 6 eV (AlN) with the same crystal structure.

In this paper we report on an investigation of the luminescent properties of a series of $\text{Al}_x\text{In}_{1-x}\text{N}$ compound films ($0 \leq x \leq 1$) doped with Terbium in varied concentrations of one to a few at-%. Measurements of the intensity of the characteristic green Tb luminescent lines are discussed as a function of the annealing temperature, of the Tb concentration, and of the In content, i.e. the band gap of the host. The observed dependence of the appearance of a luminescence intensity maximum with increasing annealing temperature can be understood in terms of formation and decay of efficient Tb luminescence centres, e.g. [3,4], the formation of a luminescence maximum as a function of the band

gap energy can be understood in terms of a resonance model of the energy transfer from the excited host electronic system into the Tb luminescence centres [5,6].

2. Experimental procedures

2.1. Film deposition and annealing

All $\text{Al}_x\text{In}_{1-x}\text{N}:\text{Tb}$ -films in the composition range $0 \leq x \leq 1$ were deposited by reactive co-sputtering in an ATC 1500-F (AJA International) magnetron system. The Al-In composition and the Tb concentration were adjusted by respective deposition rates (controlled by the selected sputtering powers) from Al-, In-, and Tb targets. Only in the case of rather In-poor films, the In target was replaced by an Al target onto which some In wires were placed. The substrates were kept floating in temperature at room temperature, with the utmost temperature excursion during sputtering reaching around 40°C. In each deposition run three different substrates have been used (in order to match the different experimental requirements of the following measurements): sapphire (0001), Si (001) covered with 50 nm amorphous silicon oxide (SiO_x), and Si (001) covered with 50 nm a- SiO_x covered with 50 nm a- SiN_x . Two experimental strategies are followed. For the *concentration route*, AlN samples with different Tb concentrations between 1 and 5 at.%, and for the *band gap route* $\text{Al}_x\text{In}_{1-x}\text{N}:\text{Tb}$ samples ($0 \leq x \leq 1$) with practically constant Tb concentration (around 1 at.%) have been prepared. The layers had a thickness of about 400-500 nm, occasionally also around 100 nm.

All samples were annealed after deposition. The AlN films (*concentration route*) are isochronically annealed in the range of 100 to 1100°C under 1 bar of nitrogen in steps of 100°C (from 800°C in 50°C), each annealing step took 20 minutes. Because of the low nitrogen pressure a loss of InN occurred in these samples, so that their band-gap was investigated again after annealing. The AlInN films (*band gap route*) are annealed at 660°C (melting temperature of Al) for 20 minutes at 8 bar of nitrogen. The samples on sapphire were annealed for 20 min at 1100°C under 1 bar nitrogen.

2.2. Film structure, composition and optical properties

The structure and the Al content, x , of the samples were investigated by X-ray diffraction (XRD, D5000, Siemens, Cu- K_α -radiation, Bragg-Brentano-geometry). The spectra showed the wurtzite structure throughout, and indications of cubic phase or other phases were absent. Specifically the region $2\Theta = 40 - 52^\circ$ (Θ : diffraction, or Bragg angle) comprising the characteristic 102-peak of the hexagonal wurtzite phase was characterized to determine its shift with Al content, x . This shift is significant for the lattice parameter and can, by the use of Vegard's law, be converted into the Al concentration. As an independent method the band gap energy is also utilized for characterization of the chemical composition.

The microstructure of the films has been characterized by transmission electron microscopy in a Philips CM 200 microscope operated at 200 kV accelerating voltage. Plan view and cross-sectional samples prepared by grinding and ion milling have been investigated. The chemical composition has been determined in detail by X-ray photoelectron spectroscopy (Thetaprobe of Thermo-VG, Al- K_α -radiation). Oxygen distributed homogeneously across the thickness of the films is the main impurity.

The optical properties are evaluated from transmission spectra (samples deposited on sapphire) taken with a dual-beam spectrometer Cary 5000 (Varian) in the wavelength range 280 – 800 nm. The excitation light (Xenon-lamp) had a wavelength of 230 nm. A 280 nm-edge filter was used to avoid signals from the excitation source.

3. Results and Discussion

3.1. Terbium luminescence in dependence of the band gap energy

A number of research activities have shown that annealing of sputter deposited semiconductor films, Si or AlN, can lead to a considerable improvement of the luminescence intensity of rare earth ions, say Tb^{3+} as in the present case, contained in these films [7,8]. Figure 1 shows the integrated intensities of

the green line family $^5D_4 \rightarrow ^7F_J$ from all of the $\text{Al}_x\text{In}_{1-x}\text{N}:\text{Tb}$ films as a function of the band gap of the host as measured after annealing at 660°C . Examples of the spectra are displayed in figure 2. The three spectra relate to the large square data points in figure 1. It is obvious that the run of the intensity curve exhibits a pronounced peak at the band gap energy of 4.1 eV and an intensity increase again towards the high band gap energy end. In order to interpret the peak, the microstructure has been investigated (see the three micrographs in figure 3). One can see that the layers are made up by fibre like grains with an average diameter of around 50 nm, essentially standing upright on the substrate. There is no noticeable change of this structure with Al content, i.e. with band gap. We may therefore rule out a microstructural origin of the intensity peak in figure 1. In view of the rather sharp peak in the intensity, a resonant excitation process, i.e. a resonant energy transfer from the host's matrix to the luminescent Tb centre, leading to this peak can be envisaged. In fact, measurements by photo luminescence excitation spectroscopy have indicated that a direct optical excitation of the Tb centres occurs at a negligible rate only [6].

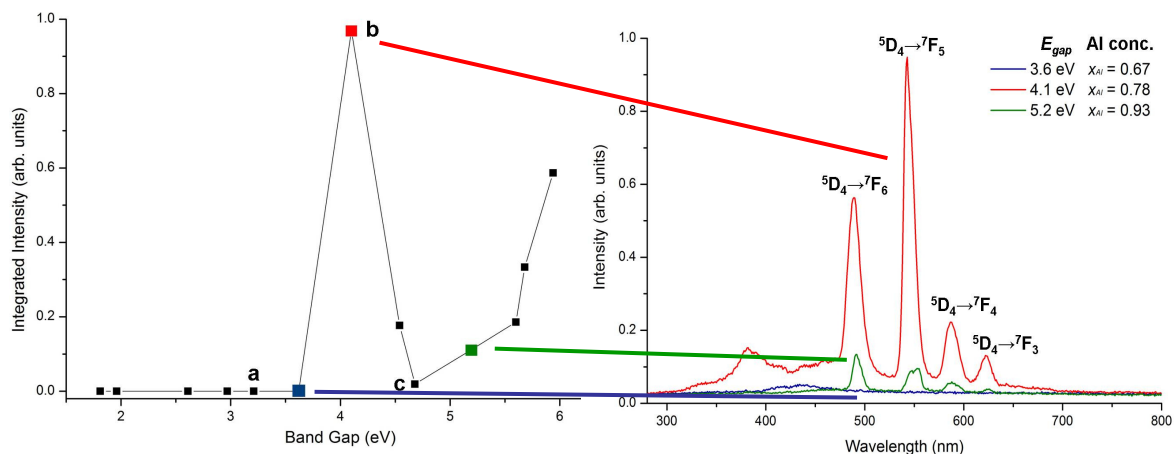


Figure 1. Integrated intensities of the Tb green luminescence lines in dependence of the host band gap energy. The intensity peaks at around the band gap energy of 4.1 eV. The coloured squares indicate the spectra pertaining to figure 2. The lettered data points indicate the respective film microstructures in figure 3.

Figure 2. Examples of Tb luminescence spectra measured from hosts having band gap energies given in the inset. Measurements after a 20 min anneal at 660°C in atmosphere.

A rather transparent explanation for the occurrence of the intensity maximum relies on the work of Lozykowski and Jadwisieniczak [9] who considered, for the case of AlN, isovalent rare earth induced centres (RESI) formed by RE^{3+} -ions to which an exciton is bound. They discriminate three types of centres formed by a single, two nearby and three Tb ions ($\text{RESI}_{\text{I, II, III}}$). The exciton binding mechanism results from the difference in electronegativity (and possibly also in size) by which a hole is attracted, which in turn binds an electron due to coulomb interaction to form a bound exciton. The associated defect level can be located within the band gap, its energy position depending upon band gap, exciton energy and energy by which the hole is bound to the RE^{3+} -isovalent ion.

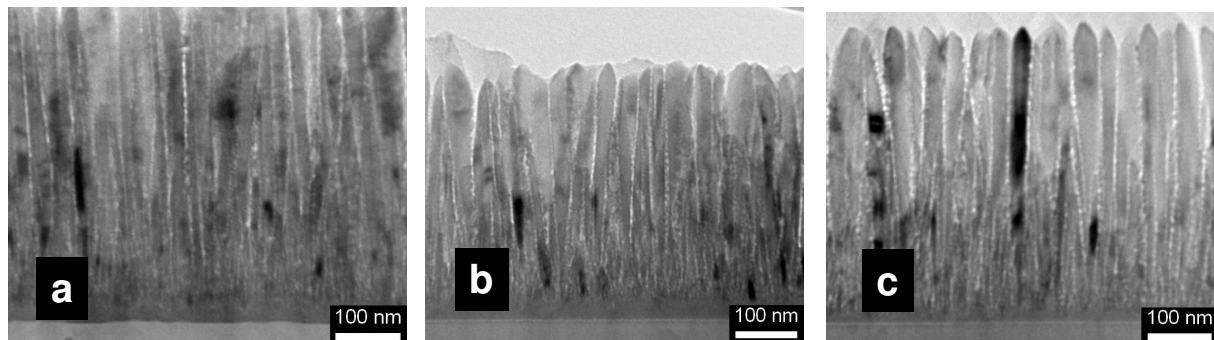


Figure 3. Microstructures of AlInN films with Al contents $x_{\text{Al}} = 0.61, 0.78$ and 0.82 in a, b and c, respectively. All samples have fibre structure, fibre grain diameter around 40 nm. The grain boundaries are decorated by white contrasts very probably due to preferential ion etching during sample preparation for the cross-sectional transmission electron microscopy.

Unfortunately these energy data are not known for the present material system (Al,In)N for whole the In concentration range since the necessary measurements could not yet be performed. Instead we proceed in modelling by analogy to the results of Nepal et al. who measured Tm induced RESI levels in the system $\text{Al}_x\text{Ga}_{1-x}\text{N}$ by thermal quenching experiments [10]. The evaluated data support the conclusions that with smaller band gap energy, E_g , the RESI levels move nearer to the conduction band edge in agreement with theoretical results [11], and that parallel to it also the binding energy, E_b , of the exciton to the Tb centre decreases. Haynes [12] has estimated this binding energy to relate to the trap position, E_{trap} , with reference to the conduction band edge as $E_b = 0.1 E_{\text{trap}}$. Based on these results the properties of the present system $\text{Al}_x\text{In}_{1-x}\text{N}$ can now be discussed at least in principle.

Figure 4 shows the band gap energy as evaluated for this system [5] with reference to the valence band edge as a function of the layer composition. In addition, energy levels of the Tb ion are introduced with the ground level coinciding with the valence band edge. The three Tb-RESI energy levels assigned by Lozykowski and Jadwisieniczak to the AlN matrix are introduced also (see the three dashes in the right ordinate) and the possible changes with reference to the valence band edge as a function of the In concentration are indicated (green dashed lines). The resonance condition in the transfer of the energy of the decaying exciton bound to the Tb luminescence centre is given in this plot when a dashed line (bound exciton energy) crosses a Tb level line. Two circles coloured violet mark crossings relevant to the present luminescence intensity measurements as a function of the band gap energy (composition). The crossing of the RESI_{III} defect energy line with the 5D_3 Tb level indicates the resonance that is correlated with the observed luminescence maximum at the band gap energy $E_g = 4.1$ eV ($x = 0.78$). The second circle at $E_g = 5.6$ eV ($x = 0.96$) denotes resonant interaction with the outer electron states $5d_i$ of the Tb ions. This interaction can tentatively be correlated with the intensity increase observed to be characteristic of the low In end of the $\text{Al}_x\text{In}_{1-x}\text{N}$ series. The rather broad shape of this intensity increase can then attributed to the comparably broad energy width of the $5d_i$ states that are as outer states very much dependent on the fluctuations in the atomic surroundings in the matrix. A third, empty circle at $E_g = 2.9$ eV ($x = 0.52$) indicates a further resonant interaction. The respective luminescence maximum is, however, not observed in our experiments, very possibly because of thermal quenching (distance of the trap to the conduction band less than, say, 0.4 eV). Luminescence measurements at low temperatures still need to be performed to clarify this aspect.

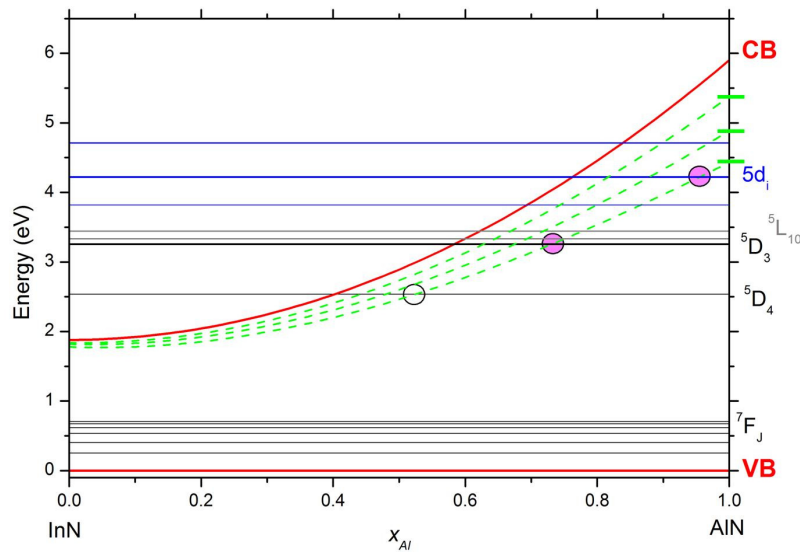


Figure 4. Model of the exciton-Tb resonant energy transfer. Shown are the Tb conduction band CB as a function of the aluminium content x_{Al} with reference to the valence band VB (red lines), the RESI levels of the three exciton states in AlN as treated in ref. 9 (green), and Tb atomic levels, some of them identified by term symbols. The green dashed curves denote the potential positions of the RESI centers with decreasing band gap. Resonant energy transfer can occur where the energetic position of the exciton trap coincides with an atomic Tb level, indicated by circles. For further discussion see text.

3.2. Terbium luminescence as a function of the Terbium concentration

Independent of the detailed mechanism described thus far of the excitation of the Tb ion luminescent centres, insight is helpful into the interaction between bound exciton and Tb luminescent centre. Essentially two different interaction mechanisms were discussed in the literature. Firstly the Förster mechanism which is based on the electrostatic interaction between two electrical dipoles [13], secondly the quantum mechanical exchange interaction [14], see also the summary [15]. Which of these is adequate to describe the present system can in principle be assessed by evaluating the luminescence intensity as a function of the Tb centre concentration. The probability, P_{dd} , for energy transfer according to the dipole-dipole interaction depends on the distance, R_{dd} , between the reacting centres as $P_{dd} \approx R_{dd}^{-6}$. The exchange interaction is characterized by a dependence $P \approx \exp(-R/L)$, which is a very short range interaction (L is the effective Bohr radius [15]). The average spatial distance between centres is just $R = 1/c^{1/3}$ (c is Tb centres per volume), thus $P_{dd} \approx c^{-2}$.

One possibility to evaluate the type of energy transfer consists of using the phenomenon of concentration quenching due to cross-relaxation [15]. It is known for Tb [16] that the transition $^5D_3 \rightarrow ^5D_4$ is similar in energy to the transition $^7F_6 \rightarrow ^7F_0$. The respective decay of one Tb ion in the 5D_3 excited state can consequently excite a second Tb ion from the ground state to a higher 7F state, provided this ion is sufficiently near in vicinity, see figure 5. This cross-relaxation diminishes the population of the 5D_4 level and thus the green luminescence. Figure 6 displays the presently available experimental results. Specifically the measured green intensities I_{5D4} are plotted as inverse values as a function of the Tb concentration. In order to compensate possible fluctuations in the excitation of the 5D_3 level and thus its population, this inverse value is multiplied by the intensity of the transitions $^5D_3 \rightarrow ^7F_J$. A clear decay of the I_{5D3}/I_{5D4} -values with increasing Tb concentration is evident. Further,

the experimental values are approximated with two curves representing the two energy transition models described above. The fit of both the Förster and the exchange model curves to the experimental data is rather good. However, this does not permit us to give a preference for one of the two energy transfer mechanisms. The scatter of the presently available data points is too large, and the investigated Tb concentration range is too small.

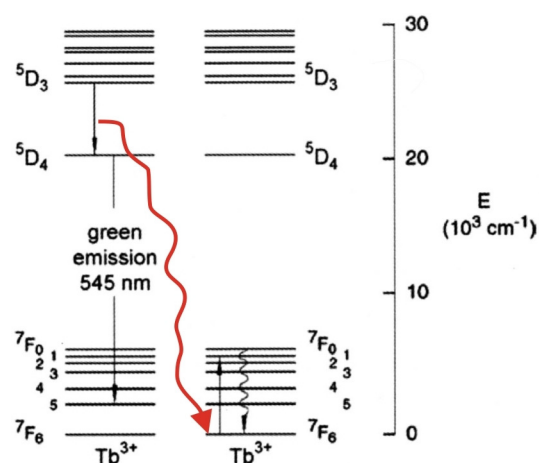


Figure 5. The process of cross-relaxation. Atomic level scheme for two adjacent Tb ions. The energy liberated by the decay of the excited state 5D_3 to 5D_4 is resonantly transferred to the adjacent Tb ion and excites a higher level 7F_J state. Sketch after [17].

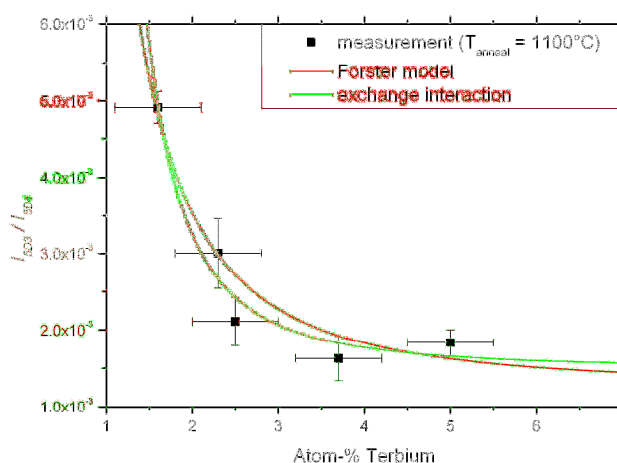


Figure 6. Luminescence intensity as a function of Tb concentration. As quantity for the intensity is used the integrated blue intensity of the 5D_3 family divided by the integrated green intensity of the 5D_4 family. The red and green curves indicate fit curves according to the dipole-dipole and the exchange mechanisms, respectively.

4. Conclusions

Our first results on luminescence of terbium ions embedded in films of AlInN in various compositions between AlN and InN indicate the advantage of a material system that covers a whole range of band gap energies. The advantage of the group-III-nitrides, AlN, InN and GaN, for the investigation of luminescence properties of rare earth ions is evident. These three compounds are principally miscible, only care has to be taken during deposition to avoid kinetically driven segregation during film deposition, eg. [18]. All the materials can grow with the same, wurtzite structure and are then all direct semiconductors avoiding cumbersome and straggling considerations that are necessary when optical properties of rare earths in matrices with different chemistry and lattice types are to be discussed. The results presented here have indicated that a resonance effect in the energy transfer mechanism can enhance the luminescence intensity very much by appropriately adjusting the band gap of the matrix. Unfortunately the results obtained thus far on the variation of the luminescence intensity with Tb concentration are not sufficient to discriminate whether the Förster or the exchange interaction are dominant in the energy transfer from the matrix into the Terbium luminescence centre.

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