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Evidence for resonant energy transfer in terbium-doped (Al,In)N films

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Abstract. Measurements of the characteristic luminescence green line family of Tb^{3+} embedded in magnetron sputtered and annealed $Al_xIn_{1-x}N$ films ($0 \le x \le 1$) indicate an intensity maximum at around the composition x_{Al} = 0.7 (band gap energy 4.1 eV). The results are described by resonant excitation via excitons bound to the Tb atoms starting from the RESI model (Lozykowski and Jadwisienczak, phys. stat. sol. (b) 244 (2007) 2109).

1. Introduction

One advantage of the Al-, In- and Ga-nitride system is the mutual miscibility of the three metal components, in general without noticeable alterations of the wurtzite crystal structure. This fact permits to produce a series of films with systematically changing band gaps by changing accordingly the composition, be it by direct deposition of crystalline material or of amorphous material with subsequent annealing. In this case one might suppose for a certain annealing temperature range a tendency to kinetically driven crystallization-induced ordering, e.g. [1]. Such a complication will not be a topic of this paper. Here we will be concerned with films the compositions of which vary from pure InN to AlN, ie. $Al_xIn_{1-x}N$ with $0 \le x \le 1$. The paper presents and discusses results on the luminescence properties of Tb^{3+} ions that are incorporated into the film by reactive sputter codeposition. After a brief outline of the experimental procedures, results on the luminescence properties, measured by optical excitation, will be reported in dependence of the band gap of the host material and of the annealing treatment. The considerations are restricted to the very important family of green luminescence lines $^5D_4 \rightarrow {}^4F_J$ which exhibit a prominent intensity maximum at a certain band gap energy. The results can be described on the basis of the model by Lozykowski and Jadwisienczak [2] who considered the luminescent decay at a rare-earth-structured isovalent (RESI) hole trap which is essentially a substitutional rare earth impurity. For the present purpose this model has to be extended by a resonance condition.

2. Experimental techniques

2.1. Film preparation

All $Al_xIn_{1-x}N$:Tb-films in the composition range $0 \le x_{Al} \le 1$ were deposited by reactive magnetron-sputtering on sapphire (0001)-, Si/SiO_x- and Si/SiN_x-substrates using an ATC 1500-F (AJA International) system. The films were co-sputtered using Al- (5N), In-(5N) and Tb-targets (3N4) in

pure nitrogen gas under a pressure of $p_{N2} = 7 \cdot 10^{-3}$ mbar[8]. The substrates had room-temperature. Nitrides with different Al-concentrations x_{Al} were obtained by correspondingly varying the sputtering-powers P_{Al} (100 - 300 W) and P_{In} (1 - 30 W). A constant Tb concentration in every layer was achieved by adjusting accordingly the Tb-power (3 and 6 W depending on the sputter time). The layers had a thickness of about 400 - 500 nm. All samples were annealed after deposition for 20 min at 660 °C under 8 bar nitrogen.

2.2. Film structure and composition

The Al contents x_{Al} of the samples were investigated by X-ray diffraction (XRD) in a D5000 (Siemens) (Cu-K_α-radiation, Bragg-Brentano-geometry). The spectra were recorded in the region 2Θ = 40 – 52° (Θ: diffraction, or Bragg, angle) to determine the shift with x_{Al} of the characteristic 102-peak of the hexagonal wurtzite phase. This shift is significant for the lattice parameter and can, by use of Vegard's law, be converted into the Al concentration. It is worth noting that cubic X-ray peaks could not be found, the films have wurtzite structure only.

The microstructure of the films has been investigated by cross-sectional transmission electron microscopy using a Philips CM 200 microscope (accelerating voltage 200 kV). The sample preparation utilized conventional techniques that consisted in gluing two samples together face-to-face, cutting this stack perpendicular into slices around 0.2 mm thick and grinding each slice to a thickness of around 50 µm. In a final step an ion miller was used to thin further until a hole appeared. The material near to the rim is transparent to the electron beam.

X-ray photoelectron spectroscopy (XPS) (Thetaprobe of Thermo-VG, Al-K_α-radiation) is utilized to quantify the metal elements and the content of oxygen which is the main impurity in the films. The pass-energy and the step-width were 100 eV and 0.1 eV, respectively. Concentration depth profiles have been obtained by sequential crater sputtering with an argon ion beam.

2.3. Optical measurements

2.3.1. Transmission. The optical transmission spectra of the AlInN-layers were observed with the dual-beam spectrometer Cary 5000 (Varian). The wavelength range 200 - 2500 nm was recorded with a step-width of 1 nm and an integration-time of 0.1 s. The absorption coefficient α can be calculated from the measured transmittance T and the determined layer thickness d via the formula $T = \exp(-\alpha d)$.

2.3.2. Luminescence. The photoluminescence measurements were taken by with a Fluorolog-3 (Horiba Jobin Yvon) in the spectral range 280 - 800 nm. The excitation light (Xenon-lamp) had a wavelength of 230 nm. The step-width and the integration-time were 1 nm and 1 s, resp. A 280 nm-edge filter was used to avoid signals from the excitation source.

3. Results and discussions

3.1. The band gap values of $Al_xIn_{1-x}N$ alloys

The band gap value, E_g, for each of our films has been obtained by an extrapolation to absorption coefficient $\alpha = 0$ of the linear part of the curve α^2 versus the photon energy $h\nu$, which plot describes the properties of a direct semiconductor. Figure 1 summarizes our band gap values as a function of the aluminum content x_{Al} and compares them to values obtained by other authors as collected by Yeh [2]. Our values follow the dependency of all other values quite nicely although admittedly at the high energy values of the scatter range. The bowing parameter is B = 3.99 eV almost the same as the one obtained by Yeh et al. [2] of B = 4.1 eV. Two remarks should be added. First, the measured energy gap of our AlN is slightly smaller than literature suggests, 5.94 eV instead of 6.2 eV [3]. This measured reduced value is certainly due to the fact that the used equipment was limited to 6 eV and Urbach states strongly influenced the extrapolation evaluation of the band gap energy. The second remark concerns the measured band gap energy of our InN films, whose value is found to be 1.81 eV instead of the nowadays accepted value of 0.6 to 0.8 eV [4,5]. This discrepancy needs detailed discussion which is beyond the scope of the present contribution. It should only be mentioned that the

considerable oxygen content of the present films can be presumed to cause increased effective band gap energy of InN due to the partial formation of oxidic compound structures [4] or of nanocrystals [5]. Yeh et al. [2] have considered the Burnstein-Moss shift as an alternative mechanism which we cannot ascertain for our samples as data on carrier densities are not available yet. All these aspects appear not important for the following as we will be concerned mainly with compositions around the middle of the covered range near to $x_{Al} = 0.7$ and the band gap energy associated with it.

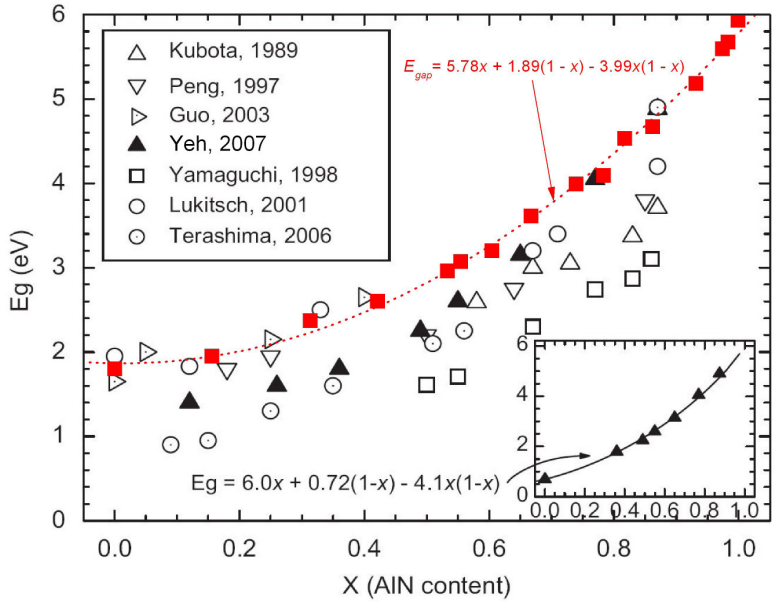

Figure 1. Energy gap values measured on the present AlInN films (filled squares) as a function of the aluminum content x_{Al}. The dotted interpolation curve through these values yields a bowing parameter of 3.99 eV (see inserted equation). Plot after Yeh et al. [2] where the data references (insert, top left) can also be found. Insert at bottom right shows Yeh's data and fitting equation.

3.2. Photoluminescence properties

Examples of the measured Tb luminescence spectra are shown in figure 2 for three AlInN specimens with band gap energies of 3.6, 4.1, and 5.2 eV. The respective interatomic transitions of the family $^5D_4 \rightarrow {}^7F_J$ are identified. One notices a strong dependence of the luminescence intensity on the band gap energy. This dependency is evident from figure 3 which shows the integrated intensity of this luminescence family as a function of the band gap. One observes a prominent intensity peak at a band gap of 4.1 eV. Below this peak there is practically no intensity at all, above -after a steep decay- the luminescence intensity slowly increases with band gap energy again. As the intensity of the maximum is increased by around a factor of 40 in the rather narrow band gap energy window of (4.1 ± 0.5) eV one can assume a resonant type of Tb excitation which will be the basis for the following interpretation.

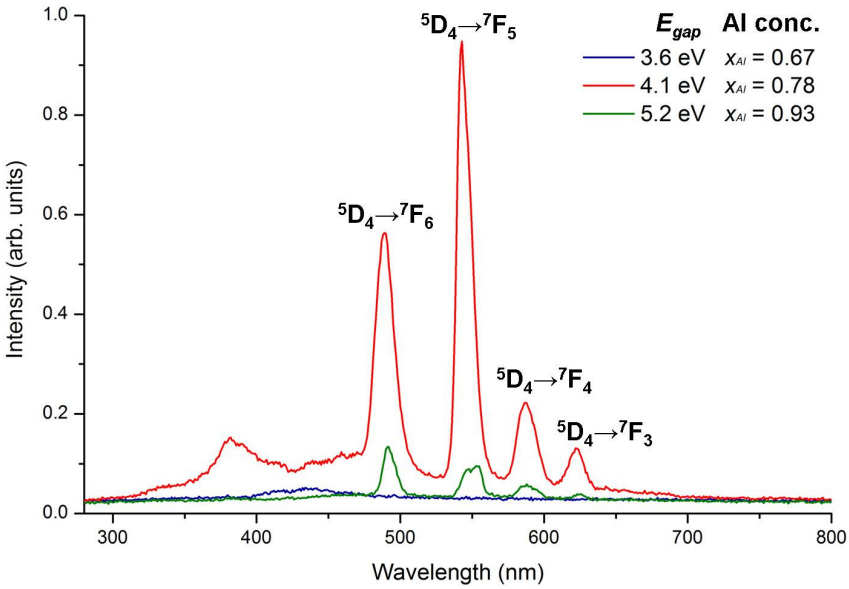

Figure 2. Luminescence spectra obtained from three AlInN films after annealing at 660°C for 20 min and 8 atmospheres nitrogen, band gap energies of 3.6, 4.1, and 5.2 eV. The Tb concentration is around 1 at.%.

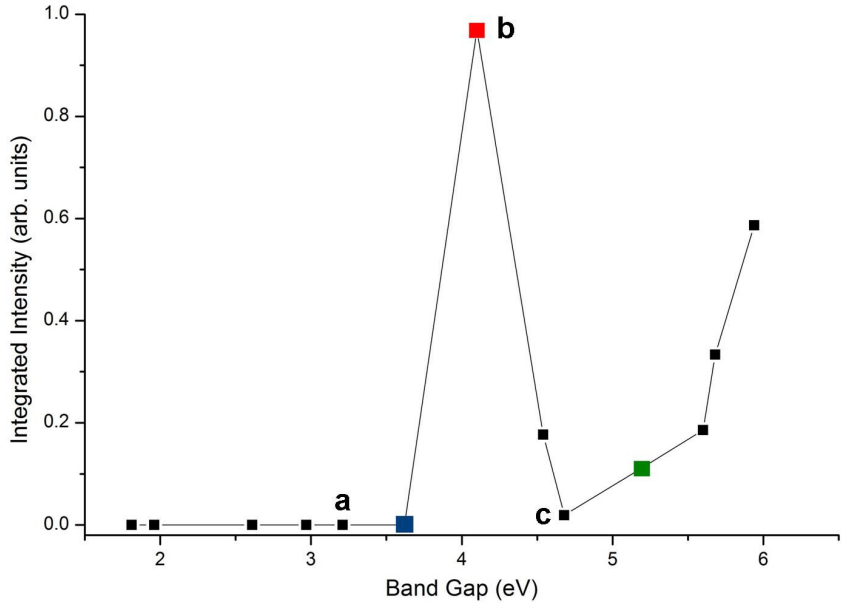

Figure 3. Integrated luminescence intensity of the line family $^5D_4 \rightarrow ^7F_J$ as a function of the band gap energy, adjusted in the AlInN films by varying the Al fraction. The films have been annealed at 660°C for 20 minutes at a nitrogen pressure of 8 atmospheres before measurements. The colored data points refer to the corresponding spectra shown with same color in figure 2. The letters a, b, c refer to those films whose structure images are shown in figure 4.

3.3. Microstructure of the films

Figure 4 shows cross-sectional micrographs of the microstructure of the films most interesting in the present context having band gap energies at and around the luminescence intensity peak, at gap energies of 3.2, 4.1, and 4.54 eV. All three films exhibit practically the same structural elements. At first sight, the films have fiber like grains with grain diameters of, say, 50 nm. There is a typical development of the structure from the substrate interface to the surface, one first finds a thin practically amorphous layer, then a layer with very tiny crystallites from which the fiber structure emanates with a grain diameter that slowly grows towards the surface. Care has been taken to also make sure by diffraction analysis that phases different from wurtzite are absent, also no precipitates have been detected. In this respect one can assume that the structure of the films, albeit different in the Al content (x_{Al} = 0.61, 0.78, 0.82 in figure 4 a, b, and c, resp.), is comparable and we might focus here on the dependency of the luminescence on the gap energy only.

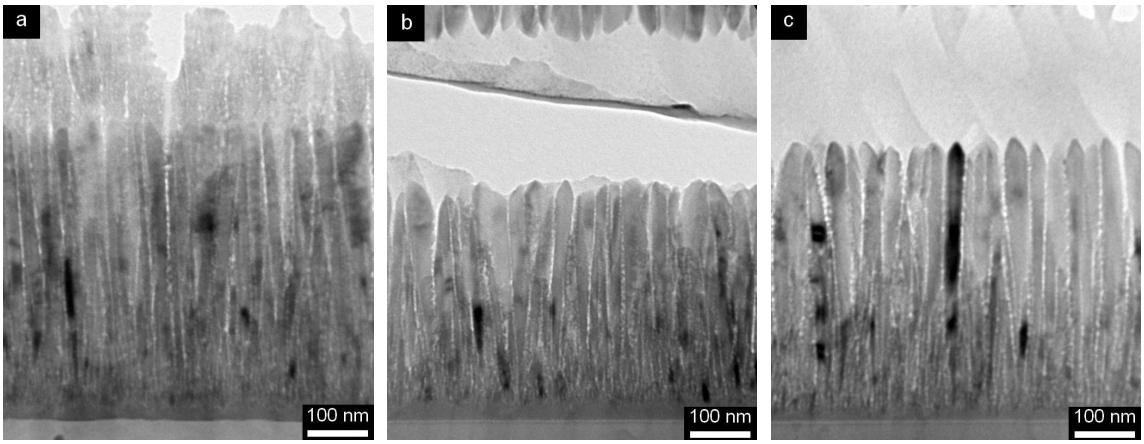

Figure 4. Microstructure of AlInN films observed by cross-sectional transmission electron microscopy. Al content x_{Al} = 0.61, 0.78, 0.82 in figure a, b, and c, resp. The upper bright part in figure a is an (inert) AlN cover layer initially used to prevent loss of nitrogen from AlInN during the anneal at 660°C. The bright partly dotted contrasts along the vertical grain boundaries are due to preferential ion beam etching at grain boundaries.

4. Tb-luminescence in view of resonant energy transfer

Our approach to explain the formation of a maximum in the Tb luminescence at band gap energy 4.1 eV starts from aspects formulated in the model of the rare earth structured isovalent (RESI) trap proposed by Lozykwski and Jadwisienczak [6]. This model considers a Tb impurity as an isovalent ion Tb^{3+} substitutionally incorporated on the metal site, in the present case the In or Al site. Tb thus has the same nominal charge as the matrix metal atom, but (as all rare earth atoms) has a smaller electronegativity. Also, because of its diameter larger than the matrix atoms, it causes a strain field and a deformation potential. In consequence Tb forms a trap state within the bandgap near to the valence band edge. This Tb (like also other lanthanides) isovalent state is different from the one of atoms of the main group, such as for example Sc, as it possesses internal low lying empty states that are shielded from the matrix making corresponding optical transitions insensitive to the surroundings.

The important aspect of such a trap is that it can bind a hole which by charge reasons attracts an additional electron to form a bound exciton. This exciton, on decay, can transfer its energy to the Tb ion. In the end this Tb excitation can lead to the emission of a luminescence photon with an energy characteristic of, for example, one line of the investigated luminescence family. There are many additional aspects with this RESI mechanism, such as temperature dependence of the luminescence, energy back transfer, cross-relaxation, which are considered in some detail in [6]. Here we are concerned with the luminescence at constant room temperature as a function of the band gap of the

AlInN matrix. Thus one needs to consider the characteristic entities of the excitation process as a function of the band gap energy, especially the position of the state of the bound exciton in the band gap, the energy of the exciton, and its binding energy to the trap.

In principle the approach of Lozykowski and Jadwisienczak [6] can be applied for discussion of our observations. Unfortunately the positions of the levels of the bound excitons in the band gap are not known as there are no measurements available, such as the thermal quenching behaviour of the Tb luminescence in AlInN (except AlN, see [6] and figure 5, levels introduced for AlN), from which one can derive the energy positions. The dependence of this level as a function of the band gap, i.e. of the In content, can thus be considered by analogy only. Such considerations are usually based on Haynes findings [7] that the binding energy E_{bind} (essentially the Coulomb interaction energy between hole and electron of the exciton) to the center is one tenth of the ionization energy E_{ion}. The binding energy is thermally supplied in the thermal quenching by which process the bound exciton is destroyed.

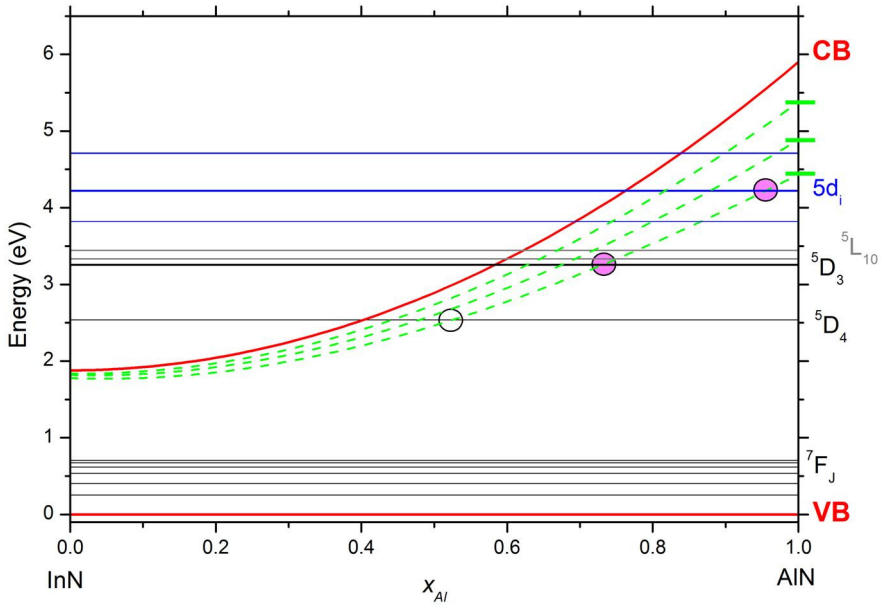

Figure 5. Modelling the resonant exciton-Tb energy transfer. Shown are the Tb conduction band CB as a function of the aluminium content x_{Al} with reference to the valence band VB (red curves), the RESI levels of the three exciton states in AlN as treated in ref. 6 (green), and Tb atomic levels for AlN. 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.

On the other hand, the ionization energy can be considered equivalent to the formation energy of the center, which describes the depth of the center. The depth decreases with decreasing band gap [8] (and consequently does the binding energy). This relationship is sketched in figure 5 for the AlInN. Plotted is the conduction band edge CB with reference to the valence band edge VB (red) as a function of the Al content. The levels of the three bound exciton traps (RESI centers consisting of one single, or two and three adjacent Tb atoms), as calculated and experimentally derived [6] for Tb in AlN, are introduced. From these levels tentative bands for the respective positions in films with ever smaller Al content are drawn (see [9] for a grasp of validity). Experimentally, our luminescence results do not give evidence for more than one center type. Figure 5 contains also a schematic of the atomic Tb levels in such a way that the energy scale also holds (Tb ground state coincides with upper edge of the valence band). Decay of a bound exciton liberates the energy between the bound exciton level and the valence band edge. In case, the exciton level happens to lie on a Tb level we have the resonant case

and a high energy transfer rate. It is evident that such a condition is met at around a band gap energy of 4.1 eV where the maximum of the emission $^5D_4 \rightarrow {}^7F_J$ occurs. Obviously the level $^5D_4$ is populated by the highly excited level $^5D_3$ from where the luminescent transitions to the ^7F_J levels occur.

It is interesting to look for other indications of the resonance model. Figure 3 indicates that the luminescence intensity steadily increases towards the composition AlN. According to figure 5 the bound exciton levels correspond to the $5d_i$ states which then can be occupied by resonant energy transfer. Also, the direct excitation of the level $^5D_4$ should, according to the resonance condition, occur at a band gap of around 2.5 to 3 eV (x_{Al} = 0.4 to 0.5), see figure 5. No luminescence intensity is observed from this level, figure 3. One explanation could be thermal quenching, because the bound exciton level is already rather near to the conduction band edge. Respective investigations are under way.

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