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EDGE EMISSION OF $Al_xGa_{1-x}N$

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The photoluminesence in the edge emission region of $Al_xGa_{1-x}N$ ($0 \leqq x \leqq 0.24$) has been studied. The compositional dependence of the band gap was studied and the bowing parameter was determined: $b = 0.98$ eV. With increasing x the edge emission peak broadens, explanation of the mechanism of which has been attempted.

1. INTRODUCTION

A GREAT DEAL of research is being carried out about the growth, electrical and optical properties of III–V ternary alloy semiconductors [1–5]. Good control of lattice constant, refractive index, desired band gap, the change of band gap from the direct to the indirect and vice versa have made the wide gap ternary solid solutions as promising materials for many optoelectronic applications. Such solid solutions are of particular interest where lattice matched heterostructures are required. However reports of growth and luminescence studies of wide gap semiconductors like AlGaN are scarce. Of particular importance is the photoluminescence (PL) study in the edge emission region of $Al_xGa_{1-x}N$ which, however, has not been reported so far.

It has already been reported [6] that a buffer layer of AlN having a thickness of about 500 Å on (0 0 0 1) sapphire substrates facilitates the growth of good quality crystalline GaN and $Al_xGa_{1-x}N$ with optically flat surfaces free from cracks, the X-ray rocking curve being relatively narrow. Such layers have been shown to be excellent in terms of morphological, crystalline and optical properties. If grown on GaN with a buffer layer of AlN between GaN and sapphire the surface morphology of the grown layers improves further and the narrowest X-ray rocking curve becomes narrower, the half width being within a few minutes [7]. Such a narrow half width has never been reported in $Al_xGa_{1-x}N$. In this paper the PL study of the edge emission region of $Al_xGa_{1-x}N$ with x up to 0.24, grown as stated above, are reported.

2. EXPERIMENTAL

Epitaxial layers of $Al_xGa_{1-x}N$ were grown on sapphire (0 0 0 1) substrates by MOVPE using AlN as a buffer layer [AlGaN/AlN/Al_2O_3]. Similar layers were also grown on GaN forming heterostructure [AlGaN/GaN/AlN/Al_2O_3]. TMG, TMA and NH_3 were used as source materials. The thickness of the epitaxial film was a few μm. Single crystals could be obtained up to $x = 0.4$ at substrate temperature of 1020°C. The amount of Al and other impurities in the sample were studied by XMA.

PL spectra were measured between 4.2 and 300 K. GaN has a band gap of 3.39 eV at room temperature [8]. The band gap of $Al_xGa_{1-x}N$ increases with increasing x, thereby the edge emission shifts more and more towards UV region until the band gap of AlN (6.2 eV) [9] is attained. The sample placed on a cold finger of a cryostat, was excited by a pulsed N_2 laser (Molectron model UV12) or a Xe–lamp (500 W). The emission spectra were processed by a spectrometer (SPEX 1704) and a box-car averager (PAR model 162). Because of the limitation of excitation sources, our attempts for the study of PL of the edge emission were limited for the samples up to $x = 0.24$.

3. RESULTS AND DISCUSSION

3.1 *General Emission Spectra*

The PL spectra of undoped samples at 4.2 K are shown in Fig. 1. The most dominant emission is due to the so called I_2 line of $Al_xGa_{1-x}N$. A clear hump or step like structure at 3.46 eV is due to the luminescence of I_2 line [9] of GaN under layer in the heterostructure samples [AlGaN/GaN/AlN/Al_2O_3]. In fact this was not observed in samples as of AlGaN/AlN/Al_2O_3. From the spectra the following noticeable points become obvious:

(i) The energy position of the main peak shows a shift towards higher energy side with increasing x. This shift corresponds with the change in the band gap.

(ii) Multiple peaks are observed in each sample. With increasing x the excitonic emission region broadens.

(iii) A new line I_U at the higher energy edge beyond I_2 was observed in almost all the samples.

The above features will be discussed below.

3.2 *Compositional dependence of band gap*

With increasing x, the energy position of the main peak shows a shift toward high energy side and this shift

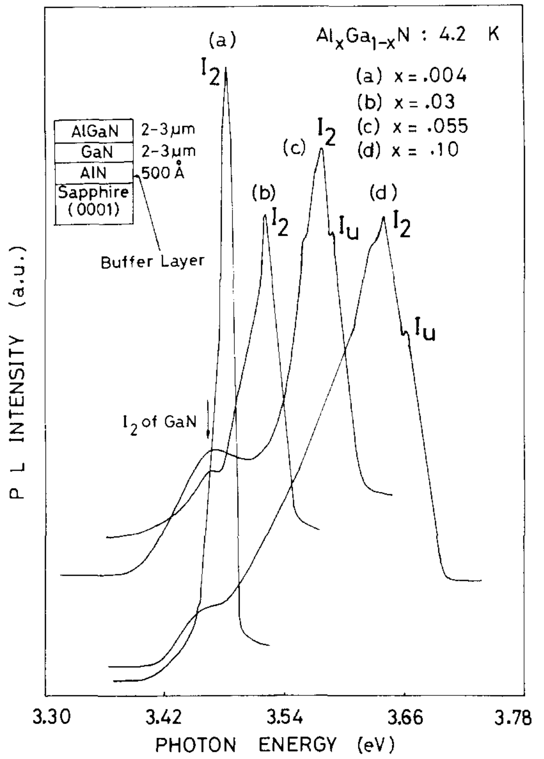

Fig. 1. Photoluminescence spectra of $Al_xGa_{1-x}N$ grown on GaN for $0.004 \leqq x \leqq 0.10$ at 4.2 K. I_U is the new line that could not be assigned properly and I_2 is the donor-bound exciton line. The structure at 3.46 eV is due to the emission of I_2 line of GaN under layer [9].

corresponds well with the change in band gap. Figure 2 shows the plot of the energy position of the main peak vs x up to $x = 0.24$. From the figure it is clear that the compositional dependence of the most dominant emission, assumed mainly due to I_2 line, follows the following parabolic curve

$$h\nu_{I_2} = 3.47 + 1.75x + 0.98x^2 \text{ (eV)}. \quad (1)$$

The origin of all the excitons which exhibit the most dominant emission for different values of x may not necessarily be the same. However, if it so happens that all these dominant emissions are due to the bound excitons of the same or similar origin, this curve of the compositional dependence of $h\nu_{I_2}$ can be considered to be the compositional dependence of the band gap without much error. Consequently, it can be inferred that the compositional dependence of the band gap bows downwards, and the bowing parameter is $b = 0.98$ eV (equation 1).

The compositional dependence of the band gap in the same samples has also been studied from the absorption measurement [7]. From the plot of the absorption coefficient vs x at room temperature it has been found that the curve bows downwards, the bowing parameter being $b = 1 \pm 0.3$ eV; which is consistent with the present result. The compositional dependence of the band gap of $Al_xGa_{1-x}N$, thus derived from PL as well as from absorption measurement contrasts with that of the samples grown by low pressure MOVPE [10] according to which the band gap varies linearly with x. If the x dependence of the band gap be linear then the intercept of the straight line should correspond to the band gap of GaN. But the intercept of the data of [10] gives 3.7 eV which is much higher than the well known band gap of GaN (3.39 eV). Furthermore, the present result disagrees with that of samples grown by MBE [11] according to which the bowing parameter as in equation (1) is $b = -0.866$ eV which is a negative value and contradicts to our positive value of $b = 0.98$ eV.

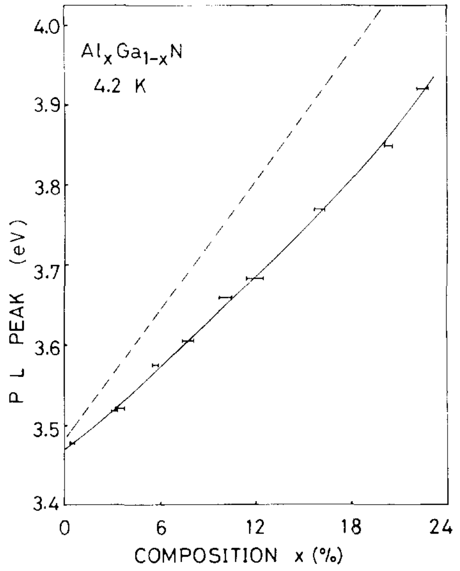

Fig. 2. Compositional dependence of the most dominant peak i.e. I_2 line of $Al_xGa_{1-x}N$ at 4.2 K is a measure of the compositional dependence of the direct energy gap E_g. The figure shows that the curve bows downwards, bowing parameter being $b = 0.98$ (see text). The linear change of band gap with increasing x is shown by the dotted line, from which the amount of bowing corresponding to some particular value of x can be estimated.

The plot of $h\nu_{I_2}$ vs x from the PL spectrum of the edge emission region corresponds to that of x at which $h\nu_{I_2}$ is dominant. In fact, the value of x determined by XMA is a volume average of the Al content present in the region of the sample measured. The X-ray analyses showed that there is a compositional fluctuation in the sample and there may be a region with less Al content [7]. The amount of fluctuation of composition vaired from sample to sample within few percent of x, the maximum being 8 to 10 percent of x among the samples investigated. As for example, in case of sample corresponding to the spectrum (b) of Fig. 1 where $x = 0.03$, the value of x varied from 0.0265 to 0.033. Thus if the

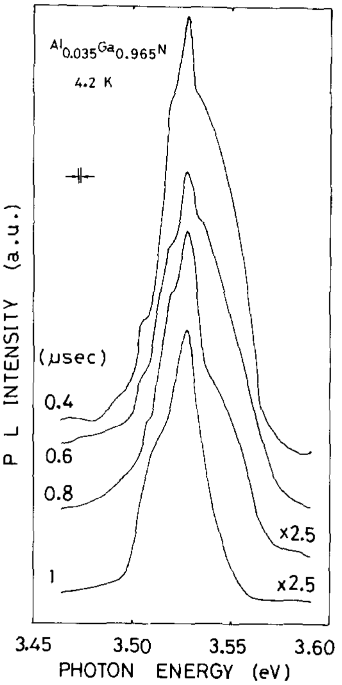

Fig. 3. Time resolved spectra of the edge emission of $Al_{0.035}Ga_{0.965}N$ at 4.2 K. The spectrum suffers narrowing with the increase of delay time.

plot of the curve corresponding to the average value of x is considered then the bowing characteristic is likely to be more toward downwards thereby the bowing parameter is expected to be slightly larger than 0.98 eV.

3.3 *Multiple peaks and broadening phenomena*

Multiple peaks each of which contributes in exhibiting broad excitonic emission region were observed in each sample. These peaks were observed with almost similar intensity in all the samples. A possibility of residual impurities (donors and/or acceptors) incorporated unintentionally during growth can not be excluded straight away. However, comparing the PL spectrum corresponding to the impurities present (eg. In, K, Sn, Si etc.) in the sample, detected by XMA, we could not assign the suitable explanation for the origin of such emission peaks. The amount of impurities was different from sample to sample.

Fluctuation of Al content in the samples were investigated and it has been found from XMA that such fluctuation exists in all the samples. The amount of fluctuation was found to increase with increasing x. The broadening phenomena were investigated in a good number of samples and are considered to be mainly due to the fluctuation of the composition. Such a fluctuation of the composition of the alloy causes a non uniformity in band gap. Hence many excitons corresponding to closely valued band gaps are present independently and take part in the emission process simultaneously, thereby the overall emission region broadens. The gradual rise of the lower energy edge and the sharp fall of the higher energy edge of the excitonic emission region resemble well that of the data obtained from the X-ray measurement [7]. Therefore, the fluctuation in the Al content in the samples is considered to be the dominant cause of the multiple and/or broad emission spectra. Now, a question arises: whether these excitons form discrete levels or a continuous band?

In order to clarify this point time resolved spectra were measured. Typical traces for a sample with less Al content ($Al_{0.035}Ga_{0.965}N$) are shown in Fig. 3. The half width of this emission region is 22 meV. It is clear that as the delay time increases the overall spectrum suffers narrowing. Narrowing phenomena observed in several samples showed that the higher energy edge dies down faster than the lower energy edge. The decay characteristics of the main peak of this sample showed the existence of more than two components: the faster one has time constant of 0.14 μs and the slower components about 4 μs. We found that increasing x yields shorter life of the excitonic emission. These facts suggest that the emission of exciton corresponding to the largest band gap due to the greatest Al content decays first. Some of the excitons may relax with the phonon emission to its nearby lower excitonic levels (due to slightly lower value of Al content) within the life time it possesses. The exciton at this new level may again relax to the neighbouring level immediately lower to it. Any way we can expect the emission at lower energy at this stage as observed experimentally. It may be inferred that all the excitons form discrete levels and contribute simultaneously in exhibiting a broad emission region. Similar phenomena of the excitonic emission region with increasing compositional fluctuation has been observed in the study of PL of GaAs–AlAs superlattice by Masumoto *et al.* [12].

3.4 *Behaviour of the new line I_U*

A typical PL spectra of the edge emission of $Al_{0.12}Ga_{0.88}N$ at various temperatures are shown in Fig. 4. The figure shows the appearance of a peak I_U at 3.715 eV (4.2 K) followed by I_2 at 3.68 eV (4.2 K). The other peaks to follow after I_2 are at 3.651 eV and 3.619 eV. The shoulder at 3.462 eV is due to the luminescence of I_2 line of GaN under the AlGaN. Appearance of such a peak like I_U at higher energy edge beyond I_2 is similar to that of I_L of $Zn_xCd_{1-x}S$ [13], CdS_xSe_{1-x} [14, 15, 16] and $GaAs_{1-x}P_x$ [17]. In those papers the I_L line is attributed to the localized excitonic states (LES) which is caused by the potential fluctuations becaues of compositional fluctuations. We found that the difference in energy levels between I_U and I_2 lines increase with increasing x in a fashion similar to that between I_L and I_2 lines in $GaAs_{1-x}P_x$ [17] and in $Zn_xCd_{1-x}S$ [13]. Therefore, the peak I_U may correspond with that assigned to the localized excitonic states I_L.

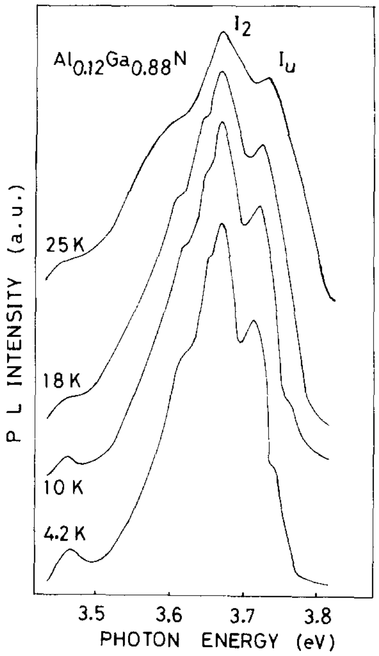

Fig. 4. Temperature dependence of the luminescence spectra (I_2 and I_U lines) of $Al_{0.12}Ga_{0.88}N$. The change of band gap within the range of temperature studied (4.2–25 K) is not appreciable enough to account for the identification of the peak shift of I_2 line, however, I_U shifts toward higher energy with increasing temperature.

The temperature dependence of I_U (Fig. 4) shows the gradual high energy shift with rising temperature. Similar phenomena were also reported by Suslina *et al.* in case of $Zn_xCd_{1-x}S$ [13]. They explained the mechanism as follows: with the rise of temperature the exciton is transferred to the high energy LES with the absorption of acoustic phonons, resulting in an increase of the possibility of emission at high energies. This transfer involves the probability regarding how many excitons are taking part in the migration process and this is decided by the ratio of the density of excitons in these states under consideration. We can not agree to their arguments. If all the excitons are transferred from one energy state to another state then a peak shift can occur. However, at thermal equilibrium the occurrence of a total transfer to high energy states is usually unlikely. Therefore, the narrowing/broadening of high/low energy edge by rising the temperature is a probable outcome as reported by Cohen and Sturge in analysing the localized excitonic states in CdS_xSe_{1-x} [15]. Thus the temperature dependence of I_U can not be suitably explained in the light of LES. Hence the origin of I_U could not be clearly assigned. In case of CdS_xSe_{1-x} and $GaAs_{1-x}P_x$, however, no comments are reported on temperature dependence of I_L.

4. CONCLUSION

The study of PL of the edge emission region of $Al_xGa_{1-x}N$ has been done upto $x = 0.24$. The compositional dependence of the band gap was studied and it has been observed that the band gap bows downwards with increasing x, the bowing parameter being $b = 0.98$ eV. A new line I_U has been observed the origin of which could not be assigned. Multiple peaks other than I_U line, which were observed in almost all the samples, could not be assigned for species of the impurity in the sample. With increasing x the edge emission region broadens, fluctuation of the Al content in the samples has been assumed to be the main cause of such a broadening phenomena.

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