EXTRORDINARY PHOTOLUMINESCENCE CHANGES OBSERVED IN InGaN/GaN QUANTUM WELLS INTERPRETED

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ABSTRACT

$In_XGa_{1-X}N/GaN$ heterostructures and quantum wells (QWs) are particularly important in the application of III – V nitride materials for light emitting diodes (LEDs) and laser diodes because their optical properties suit the active region of blue - green light emitting devices. The photoluminescence (PL) emission from $In_XGa_{1-X}N/GaN$ quantum well structures has recently been reported [1, 2] where, for successive annealing operations, the PL peak suffers a primary red shift, followed by a blue shift. As stated by workers, the explanation of such phenomena is complicated. This paper is intended towards a proper explanation of the observed experimental results through suitable quantum mechanical models.

INTRODUCTION

Nitride based semiconductors are being intensively studied due to the interest in ultraviolet-blue-green light emitting devices. The ternary compound semiconductor InGaN has a direct band gap from 1.95 to 3.4 eV at room temperature and extremely large heterojunction band offset which makes the material highly successful and promising for light emission around the blue -green region [3]. Despite the high dislocation density in GaN and InGaN grown on sapphire, surprisingly high light emission efficiency has been achieved in $In_XGa_{1-X}N/GaN$ based light emitting devices [4,5,6]. Most of the GaN based light emitting devices are grown by metalorganic chemical vapor deposition (MOCVD). The high compositional fluctuation of In content have been observed as shown in Fig. 1 [7]. During the epitaxial growth of InGaN/GaN structures and during the fabrication of devices, InGaN layers undergo several periods of high temperature thermal annealing. The intermixing and redistribution of the Indium composition, strain and band structures of the QW may be changed after these thermal treatments, leading to changes of the optical properties [2,8]. These have usually been studied by photoluminescence (PL), since PL has emerged as a powerful tool for studying the optical properties and interdiffusion of nanostructures [9,10].

Recently very interesting PL results of annealing of $In_XGa_{1-X}N/GaN$ QWs of 3 nm and 4 nm widths have been reported by Yi – Yin Chung *etal* [1]. The QWs have been subjected to thermal anneals of 800º, 850º and 900ºC for 30 minutes. It is interesting to note that initially the PL peaks instead of shifting towards the usual blue, shifts towards red and on further annealing at high temperatures the peak shifts towards blue. The effect is

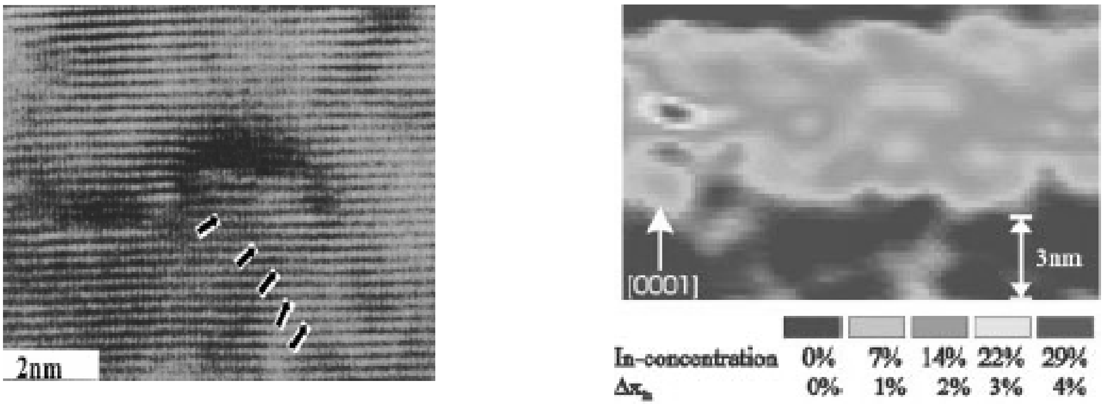

Fig.1: HRTEM images of MOCVD grown $In_XGa_{1-X}N/GaN$ quantum wells on sapphire showing inhomogeneity of growth.

more pronounced in the 3 nm QW as compared to the 4 nm well. For $In_XGa_{1-X}N$/GaN QWs, the PL peak shifts are reported to be monotonic on the blue side [11]. The respective decrease and increase of the energy of the PL peak have been attributed to changes in the inherent strain, changes in the piezoelectric components, localization of carriers in the QWs and to the interdiffusion of In and Ga in and out of the QWs.

An explanation of this unusual phenomenon is quite complicated since the band offset ratios are not quite established and strain changes band offset ratios [12], moreover it involves alloy clustering, interdiffusion etc. In this paper we try to explain the experimental observations.

RED AND BLUE SHIFT OF THE PHOTOLUMINESCENCE SPECTRA ON ANNEALING

Fig. 2 shows the changes of the PL peak as reported [1]. The 3 nm and 4 nm wide QW samples were grown on sapphire substrates by MOCVD and the as grown samples were thermally annealed in a quartz tube furnace at 800°, 850°, 900°C in nitrogen for 30 minutes. Initially the PL peak energy decreases, when the temperature is increased i.e. the effective diffusion length increases, the PL peak energy increases. The high resolution transmission electron microscopic (HRTEM) images of the QWs indicates that the fluctuations in the well width are very wide and at places they are even less than 20 Å. A large variation of In content from about 20% to greater than to 54% has been reported by the authors before annealing. After annealing a homogenization of In content and the well width is shown along with some out diffusion.

During progressive annealing procedures, the QWs gradually increases in width and due to the decrease of In in the QW the band gap of the $In_XGa_{1-X}N$ increases as shown in fig. 3. As reported [11] for the annealing of $In_XGa_{1-X}N$/GaN QWs the PL peaks have a monotonic blueshift on annealing. The observed strange red shift followed by blueshifts of the PL peaks of $In_XGa_{1-X}N$/GaN on annealing are not very well explained.

RESULTS AND EXPLANATIONS

The phenomena of annealing, i.e. red shift followed by a blue, can be explained by considering a QW of 20°A width and In composition greater than equal to 80% which correspond to an E_g around 2 eV [13], the band gap energy of GaN being 3.4 eV. Table. 1 [2] shows the band offset ratios obtained through different experiments. From our knowledge of band offset calculation [12] with strain, we have assumed the band offset ratios to be 50:50. The effective masses are assumed [3] to be $0.2m_0$ for electrons and $1.2m_0$ for holes. The band gap E_g of $In_xGa_{(1-x)}N$ has been calculated from [3] the equation:

$$E_g(x) = xE_{g,InN} + (1 - x) E_{g,GaN} - bx(1 - x) \qquad (1)$$

where x is the mole fraction of Indium $E_g(x)$ represents the band gap energy of $In_xGa_{(1-x)}N$, $E_{g,InN}$ and $E_{g,GaN}$ represent the band gap energies of the compounds InN and GaN respectively, and b is the bowing parameter. In our calculations $E_{g,InN}$ was 2 eV, $E_{g,GaN}$ was 3.4 eV, and b was 1.00 eV. The variation of the band gap with the In concentration starting from GaN to InN is shown in fig. 4.

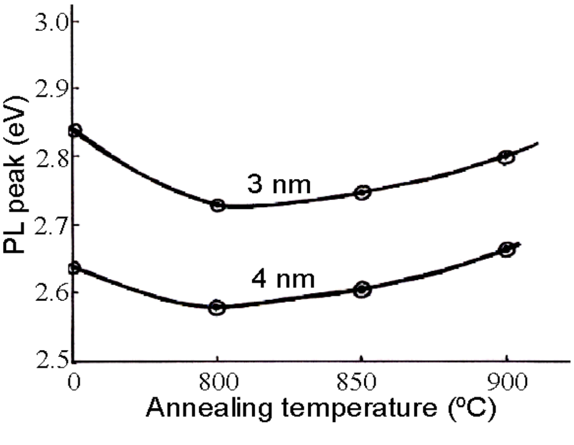

Fig.2: Variation of PL peak with annealing temperature.

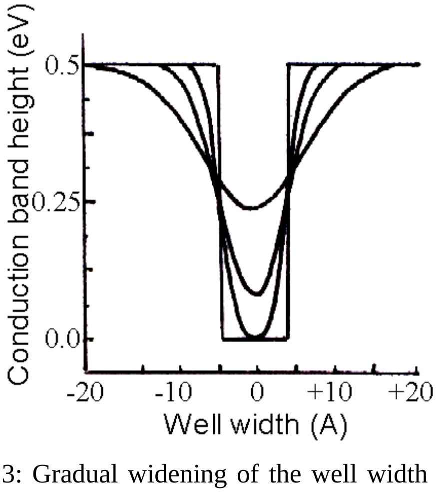

Fig.3: Gradual widening of the well width along with increasing band gap

Table 1: Band offset parameter obtained in different studies

Band offset parameter	**Technique**
38:62	Optical pumping
30:70	X-ray photoemission Spectroscopy
62:38	Photoluminescence
68:32	Calculation
83:17	Calculation

It is interesting to note that the change of the band gap for unit change in the In concentration around the InN end is very much smaller than the change of band gap around GaN for the same change in the In concentration. These seem to play a major role in understanding the mentioned phenomenon. The height of the QW of $In_XGa_{1-X}N$ with GaN is sufficient to accommodate the second electron and hole sub bands with parameters mentioned. The electron and hole levels were calculated from the equation [14]:

$$E_n = \frac{2P^2}{(P+1)^2}\left[\left(\frac{n\pi}{2}\right)^2 - \frac{1}{3(P+1)^3}\left(\frac{n\pi}{2}\right)^4 - \frac{27P-8}{180(P+1)^6}\left(\frac{n\pi}{2}\right)^6\right] \qquad (2)$$

for a well of finite height, where P is the *well-strength parameter*. The nature of out difussion of In were estimated from Fick's Law of diffusion [14].

$$C(z) = \frac{C_0}{2}\left[\operatorname{erf}\left(\frac{h-z}{L_D}\right) + \operatorname{erf}\left(\frac{h+z}{L_D}\right)\right] \qquad (3)$$

where C_0 is the initial In concentration, 2h is the well thickness, z is the distance in the growth direction with z = 0 at well center and $L_D = 2\sqrt{(Dt)}$ is the diffusion length, where t is the anneal time and D is the diffusion coefficient.

The results obtained are shown in Fig. 4. The bandgap energy of $In_xGa_{(1-x)}N$ is plotted against varying mole-fraction (x).When the QW is annealed the molefraction (x) of In inside the well changes, as the well broadens. The sum of the energies of the second electron level e_2 and the second hole level h_2 has been plotted in Fig. 4. with change of In mole fraction (x) on the same scale. The resultant PL peak energy is shown in the same figure.

With decrease in the In molefraction, the PL peak initially shows a decrease in energy. On further decrease of the In molefraction the PL peak energy moves through an inflexion towards high energies. The resultant curve of the PL peak of fig. 4 can be compared with the experimental curves of fig. 2. They are very much similar in nature.

Because of the large bowing parameter of the bandgap energy change with (x), the slopes at different points of the curve are widely different as has been marked out in the figure.The decrease of ($e_{2} + h_2$)with (x) maintains an almost constant slope which would have been parabolic had it been plotted against the well width. During the early phases of annealing i.e. for the initial decreases of the Indium molefraction (x), the slope S3 =0.25 is much smaller than the slope S5 = 0.52. This means that initially the decrease of ($e_{2} + h_2$) is much larger than the increase in the bandgap energy of $In_XGa_{1-X}N$. The resultant PL peak energy, which is a combination of both, decreases during the initial phases of annealing. As the phenomenon of interdiffusion proceeds the slope

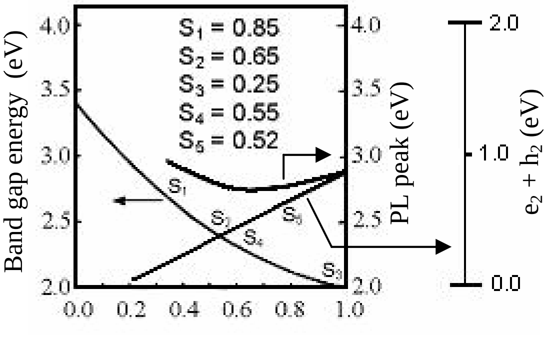

Fig. 4: Variation of band gap, sum of the energy levels with band gap and the resultant PL peak with In concentration (x).

of the bandgap energy curve increases and the PL peak starts increasing once the molefraction (x) falls below the inflexion, around (x) =0.6.The nature of the resultant change in the PL peak energy is of the same nature as reported from experiments. A red shift followed by a blue shift on annealing shows the changes of the PL peak as reported [1].

CONCLUSIONS

The growth of $In_XGa_{1-X}N/GaN$ heterostructures and QWs is a difficult task particularly because lattice matched substrates are not available. The optical properties of the material and device are subjected to change after high temperature thermal annealing because of intermixing and redistribution of the Indium composition, strain and band structures of the QW. The high compositional fluctuation of In content and the wide variation of the thickness of QWs have been observed because of alloy disorder, clustering and fluctuation of the well width. These play important roles in the final device. The inhomogeneity is reduced to a certain extent on annealing.

In this paper we have explained the observed unusual changes of the PL peaks of $In_XGa_{1-X}N/GaN$ QWs on annealing. Initially the PL peak energy is lowered and as annealing proceeds the PL peak moves to higher energies. On annealing, the electron and hole levels decrease in energy as the effective well width increases. At the same time as the Indium out diffuses the bandgap of the well material increases. These two opposing phenomena contest and determine the final PL peak position. Initially the former is larger than the latter which produces a red shift of the PL peak, as annealing progresses and the In mole fraction drops, the latter becomes greater than the former and the PL peak undergoes a blueshift.

REFERENCES

[1] Yi-Yin Chung, Yen-Sheng Lin, Shih-Wei Feng, Yung-Chen Cheng, En-Chiang Lin, C. C. Yang, Kung-Jen Ma, Cheng Hsu, Hui-Wen Chuang, Cheng-Ta Kuo, and Jian-Shihn Tsang, J. Appl. Phys. 93, 9693 (2003).

[2] Chii-Chang Chen, Kun-Long Hsieh, Gou-Chung Chi, Chang-Cheng Chuo, Jen-Inn Chyi, and Chin-An Chang, J. Appl. Phys. 89, 5465 (2001).

[3] Shuji Nakamura etal, J. Appl. Phys. 74 (6), 3911 (1993).

[4] H. W. Shim, R. J. Choi, S. M. Jeong, Le Van Vinh, C.-H. Hong, E.-K. Suh, H. J. Lee, Y.-W. Kim and Y. G. Hwang, Appl. Phys. Lett. 81, 3552 (2002).

[5] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, Appl. Phys. Lett. 69, 4056 (1996).

[6] I. Akasaki, S. Sota, H. Sakai, T. Tanaka, M. Koike, and H. Amano, Electron. Lett. 32, 1105 (1996).

[7] D. Gerthsen, B. Neubauer, A. Rosenauer, T. Stephan, H. Kalt, O. Scho¨n and M. Heuken, Appl. Phys. Lett. 79 2552 (2001).

[8] E. Oh, B. Kim, H. Park, and Y. Park, Appl. Phys. Lett. 73, 1883 (1998).

[9] B.Allen , D. Biswas, J. M. Pastor, L. Gonzalez and J. M. Garcia, Phys. Stat. Sol.(a) 190, 3, 763 (2000).

[10] J. M. Pastor, D. Biswas, B. Allen, J. Bosch, L. Gonzalez and J. M. Garcia, Phys. Stat. Sol.(a), 190., 3, 599 (2002)

[11] Sang-Wan Ryu, In Kim, Byung-Doo Choe, and Weon Guk Jeong, Appl. Phys. Lett. 67, 1417 (1995).

[12] D. Biswas etal, Physical Review B, 40, 1058 (1989).

[13] Chii-Chang Chen etal, Appl. Phys. Lett. 77 (23), 3758 (2000).

[14] David L. Aronstein and C. R. Stroud, Jr., Am. J. Phys. 68, 943 (2000).

[15] W. P. Gillin, D. J. Dunstan, K. P. Homewood, L. K. Howard, and B. J. Sealy, J. Appl. Phys. 73 3782 (1993).