Room-Temperature Time-Resolved Photoluminescence Studies of UV Emission from GaN/AlN Quantum Wells

Madalina Furis, Fei Chen, Alexander N. Cartwright

Department of Electrical Engineering, University at Buffalo, State University of New York, Buffalo NY, 14260

Hong Wu, William J. Schaff

Department of Electrical Engineering, Cornell University, Ithaca NY, 14853

ABSTRACT

Room temperature time-resolved photoluminescence (TRPL) studies of multiple quantum well (MQW) structures of the binaries GaN and AlN grown by molecular beam epitaxy are reported. The eventual application of these structures is for GaN intersubband IR light emitters. However, as an initial study, the structures are evaluated at UV to investigate materials parameters relevant to IR light emission. The nominally 0.9, 1.3 and 1.5 nm GaN quantum wells are clad by 6nm of AlN on top of a thick AlN buffer grown on sapphire. All samples consisted of 20 quantum wells. The observed peak energy of the emission spectrum is in excellent agreement with a model that includes the strong confinement present in these structures and the existence of the large built-in piezoelectric field and spontaneous polarization present inside the wells. Furthermore, consistent with screening of the in-well field as carriers are injected in the well, a clear blue shift of the emission is observed at short times after carrier injection. Subsequently, as the carriers recombine, the peak emission red-shifts and the screening of the field is reduced. Moreover, the observed lifetimes were energy dependent as should be expected from field dependent elongation of lifetimes due to spatial separation of the injected carriers. Specifically, the decay time at high energies can be fitted by a stretched exponential with a beta value of 0.8 which is consistent with carrier spatial separation. The lifetimes obtained from the fitting are of the order of 1ns, longer than the reported recombination lifetimes in similar GaN/AlGaIn MQW's. On the low energy side of the PL feature the intensity time decay becomes exponential with lifetimes ranging from 3 to 10ns. The strong UV emission at room temperature makes these structures promising for UV emitters.

INTRODUCTION

UV emitters characterized by wavelengths shorter than 350nm are essential for the development of optical storage and biological agent detection devices such as hand-held biosensors. The need for such emitters for biosensors is generated by the nature of the absorption and fluorescence spectra of organic molecules. For example, the fluorescing components in proteins are amino-acids such as phenylalanine, tryptophan and tyrosine. It is proposed that each biological agent is characterized by a distinct ratio between these components of emission determined by analyzing the fluorescence spectrum from proteins. The difficulty resides in exciting this fluorescence since all the amino acids exhibit an absorption edge below 350nm. At the same time, the development of UV lasers will increase the storage capacity of optical storage devices (such as CD's or DVD's) due to the much shorter wavelength and corresponding minimum achievable spot size.

Nitride semiconductors are one of the materials of choice in developing UV LED's and laser structures due to their large bandgaps (as high as 6.2eV in the case of AlN). Structures such as GaN/AlGaIn quantum wells with high aluminum content [1] exhibit emission at short wavelengths. However, the large lattice mismatch between the well and barrier materials results in the presence of growth defects and dislocations which, in turn, causes a decrease in the emission intensity, especially at room temperature where most devices operate. The photoluminescence intensity in this quantum wells decreases by a factor of 100 when the temperature is increased from 10 to 300K. Incorporating Al into the well material has the dual effect of reducing the lattice mismatch, which yields fewer growth defects, while pushing the emission deeper into the UV. Most recently, Chitnis et al. [2] have shown that such $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}$ heterostructures exhibit improved optical properties. Growth defects can also be avoided by using quaternary alloy AlGaInN heterostructures. Such layers, with different Al and In concentrations in the wells and barriers, can be lattice matched to the buffer. Recent time-resolved photoluminescence (TRPL) measurements on such structures [3] have shown that the emission efficiency at room temperature is greatly improved in comparison with GaN/AlGaIn structures. Despite this improvement, the PL decay is still dominated by non-radiative recombination at room temperature. In fact, both the ternary and quaternary well materials described above are plagued by point defects which are related to alloy fluctuation and compositional disorder. In addition to reduced efficiency, these defects result in broadening of the emission spectrum. Overall, while the reduced lattice mismatch in these structures provides some benefits, the use of ternary and quaternary well materials introduces other problems.

Unlike all other potential UV emitters materials mentioned in the previous paragraph, GaN/AlN heterostructures avoid the issues associated with point defects by utilizing only pure binary materials, which in addition exhibit the largest possible bandgap offset among the nitrides. Despite this attractive characteristic, the large lattice mismatch between GaN and AlN (2.6%) and the lack of thorough optical investigations on the barrier (AlN) material are clear impediments in the development of efficient UV emitters based on such heterostructures. In this work, we present the results of room-temperature time-resolved photoluminescence measurements on GaN/AlN multiple quantum well (MQW) heterostructures showing that, despite the large lattice mismatch, such structures exhibit good luminescent properties and, most importantly, the emission seems to be dominated by radiative recombination at room temperature.

EXPERIMENTAL DETAILS

The three GaN/AlN MQW samples were grown on a sapphire substrate by plasma-enhanced molecular beam epitaxy (MBE). They contain 20 GaN 0.9, 1.3, or 1.5nm wells separated by 6nm AlN barriers grown on the top of a thick AlN buffer layer. High-resolution x-ray characterization measurements have shown satellite peaks indicating a very good superlattice structure with fully relaxed barriers and strained wells [4].

The TRPL measurements were performed in the backscattering geometry using conventional optics. The excitation was provided by the frequency tripled 800nm output of a Coherent REGA9000 regenerative amplifier. The pump beam is characterized by a 200fs pulse width, a 250kHz repetition rate and an average power of 5mW at 266nm. The photoluminescence was spectrally resolved by a Chromex 250IS monochromator and detected by a Hamamatsu C4334 streak camera with a typical jitter of 50ps.

DISCUSSION

Normalized time-integrated photoluminescence spectra taken at room temperature from the samples under study are shown in figure 1(a). The energies corresponding to the photoluminescence peak vary as a function of well width and are in good agreement with a calculation of the e_1h_1 transition energy performed using the Numerov method [5,6]. This calculation takes into account the built-in electric field present in the wells and the barriers along the growth direction as a result of the piezoelectric and spontaneous polarization existing in both materials. The magnitude of the piezoelectric component depends on the strain induced by the lattice mismatch and the barrier and well widths. A detailed discussion of the built-in electric fields in nitride heterostructures along with the most recent update on the numerical values of the several physical constants used in our calculations can be found in reference [7]. For the case of the samples under study the electric field is equal to approximately -8MV/cm in the GaN wells and 1MV/cm in the AlN barriers. In the presence of such an electric field along the growth direction, the energy corresponding to the e_1h_1 transition in the quantum well is red-shifted with respect to the zero-field situation (due to the quantum confined Stark effect [8] and the band filling effects). The presence of the build-in electric field is thus confirmed by the blue-shift observed in the PL energy in figure 1(b). At such short times, the space charge field induced by the presence of spatially separated injected carriers in the quantum wells is partially screening the build-in electric field and the PL energy approaches the zero-field value. For the sample in figure 1(b) we estimated the blue shift due to screening effects to be approximately 44 meV (considering we inject approximately $6 \times 10^{12} \text{ cm}^{-2}$ carriers in each well). The difference between this number and the actual measured blue shift (140meV) is due to band filling effects. The Fermi energy is equal to 72meV for electrons and 14meV for holes. The total estimated blue shift is equal to the sum of the screening and band filling contributions ($\sim 130 \text{ meV}$) in good agreement with the experimental value. In addition to screening and band filling, another contribution in the blue shift may be due to the large changes in the recombination lifetimes due to well width fluctuations.

Figure 1. Time-integrated (a) and time-resolved (b) photoluminescence spectra from the samples under study at different delay times. The blue shift at short delay times is due to the partial field screening by the injected carriers and band filling effects.

As the time passes the carriers recombine and the screening effect disappears. The Fermi level is also moving toward the bottom of the first energy band and the emission energy decreases.

The presence of electric fields in quantum well heterostructures results in the spatial separation of the electrons and holes confined in the wells. The carriers accumulate at opposite sides of the quantum well and the electrons and holes wavefunction overlap decreases considerably, as well as the emission efficiency. Our calculations show that, despite the high built-in electric fields, for a thin GaN/AlN well the carriers wavefunctions remain confined in the well due to the large bandgap offset (1.9eV) between the GaN wells and AlN barriers.

The photoluminescence decay times at several energies across the photoluminescence feature are plotted in figure 2(a). On the high energy side of the PL spectrum the decay is non-exponential and characterized by short decay times (shorter than 1ns). On the low energy side the decay becomes exponential and characterized by longer lifetimes (7ns). This behavior is characteristic for nitride heterostructures and has been observed in GaN/AlGaN [9,10] as well as InGaN/GaN[11,12,13] quantum well heterostructures. A calculation [14] of the PL decay times which takes into account the dynamic screening of the built-in electric fields by the injected carriers shows that the lifetime increase on the low energy side of the PL feature and the non-exponential character of the decay can be the result of the presence of built-in electric fields. The field-dependent elongation of carrier lifetimes is a result of the reduction of the wavefunction overlap in the presence of the built-in electric field.

The long lifetime values measured on the low energy side of the PL feature at room temperature indicate the recombination is dominated by radiative processes (non-radiative recombination happens on a much faster scale-hundreds of picoseconds). This demonstrates that the GaN/AlN structures are promising not only for the development of LED's, but possibly for achieving population inversion and lasing.

In order to further investigate the possible origins of the non-exponential PL intensity decay, we fitted the decay data with a stretched exponential:

Figure 2. (a) Photoluminescence intensity decay at different energies across the PL feature and (b) Stretched exponential fitting to the decay data on the high energy side of the photoluminescence spectrum.

$$I = I_0 \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \quad (1)$$

The parameter β varies between 0 and 1 and provides information on the recombination mechanism. This type of PL decay has been explored in InGaN/GaN heterostructures [15] and a direct connection has been established between the values of the β parameter and the nature of carrier localization. According to this interpretation, the non-exponential character of the decay is due to the presence of potential fluctuations (e.g. In –rich regions in the case of InGaN/GaN MQWs) where the carriers are localized before recombining. Since the characteristics of such potential fluctuations are not the same across the sample, we expect considerable differences between the wavefunction overlap of carriers trapped in different potential fluctuations. The nature of localization centers in GaN/AlN structures is not known at the present, however, we can always assume the existence of potential fluctuations associated with interface roughness or growth defects. The non-exponential behavior and the carrier lifetimes dependence on energy can also be due to the presence of such regions where carriers are localized before recombination. The stretched exponential decay model is based on the assumption that there is a possibility for the carriers to move from one potential fluctuation to another through a hopping mechanism. As a result the carrier lifetimes must depend on the hopping distance and the number of potential fluctuations the carrier encounters before recombination. This type of mechanism is described quantitatively by the magnitude of the β parameter, namely β values smaller than 0.5 correspond to the hopping mechanism described, whereas for β values between 0.6-0.9, the carrier lifetimes are elongated by the built-in electric field and the subsequent spatial separation of carriers [16].

Figure 2(b) summarizes the results of a stretched exponential fitting to the decay data on the high-energy side of the photoluminescence feature. The β parameter equals 0.8, indicating no hopping mechanism takes place and the non-exponential character is determined only by the built-in electric fields and possible carrier localization. The effective lifetimes are very short because the high-energy side of the PL reflects the recombination of hot carriers which relax very quickly to the bottom of the conduction band.

CONCLUSIONS

In conclusion we have shown that, despite the large lattice mismatch, MBE grown GaN/AlN quantum wells exhibit room temperature photoluminescence associated with the radiative recombination of electrons and holes in the GaN wells. The PL peak position is in good agreement with a calculation that takes into account the piezoelectric and spontaneous polarizations existing inside the wells and barriers. A blue shift of the emission is observed at short times, due to the in-well field screening by the carriers injected in the well. The photoluminescence intensity decay varies across the PL feature and can be fitted with a stretched exponential. The values of the β exponent are greater than 0.5 indicating the non-exponential character of the PL decay can be attributed to the built-in electric field and carrier localization. The carrier lifetimes vary as a function of energy. Most importantly, the radiative recombination is the dominant carrier relaxation mechanism at room-temperature making such structures very promising for lasing applications.

ACKNOWLEDGEMENTS

This work was supported in part by ANC's NSF CAREER Grant #9733720, ONR YIP Grant #N00014-00-1-0508, a Defense University Research Initiative on Nanotechnology Grant #F496200110358 through the Air Force Office of Scientific Research, and WJS's NSF Grant #ECS-0123453 and by DARPA through WJS's Army Research Office Grant #DAAD19-02-0199.

REFERENCES

1. J. C. Harris, T. Someya, K. Hoshino, S. Kako, and Y. Arakawa, *phys. stat. sol. (a)* **180**, 339 (2000).
2. A. Chitnis, R. Pachipulusu, V. Mandavilli, M. Shatalov, E. Kuokstis, J. P. Zhang, V. Adivarahan, S. Wu, G. Simin, and M. Asif Khan, *Appl. Phys. Lett.* **81**, 2938 (2002).
3. Mee-Yi Ryu, C. Q. Chen, E. Kuokstis, J. W. Yang, G. Simin, and M. Asif Khan, *Appl. Phys. Lett.* **80**, 3943 (2002).
4. H. Wu, W. J. Schaff, M. Furis, A. N. Cartwright, K. A. Mkhoyan, J. Silcox, W. Henderson, W. A. Doolittle, and A. V. Osinsky (submitted to MRS Conference Proceedings)
5. J. M. Blatt, *J. Comp. Phys.* **1**, 382 (1967).
6. B. R. Johnson, *J. Chem. Phys.* **67**, 4086 (1977).
7. O. Ambacher, J. Majewski, C. Miskys, A. Link, M. Hermann, M. Eickhoff, M. Stutzmann, F. Bernardini, V. Fiorentini, V. Tilak, B. Schaff, and L. F. Eastman, *J. Phys.: Condens Matter* **14**, 3399 (2002).
8. G. Bastard, "Effect of Static External Electric and Magnetic Fields on the Energy Levels of Quasi Bi-dimensional Electron Gases", *Wave Mechanics Applied to Semiconductor Heterostructures*, Halsted Press (John Wiley & Sons, 1988) pp. 303-308.
9. P. Lefebvre, B. Gil, H. Mathieu, N. Grandjean, M. Leroux, J. Massies, and P. Bigenwald, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G3.69 (1999).
10. N. Grandjean, B. Damilano, J. Massies, G. Neu, M. Teissere, I. Grzegory, S. Porowski, M. Gallart, P. Lefebvre, B. Gil, and M. Albrecht, *J. Appl. Phys.* **88**, 183 (2000).
11. T. Kuroda, A. Tackeuchi, and T. Sota, *Appl. Phys. Lett.* **76**, 3753 (2000).
12. T. Kuroda and A. Tackeuchi, *J. Appl. Phys.* **92**, 3071 (2002).
13. A. N. Cartwright, P. M. Sweeney, T. Prunty, D. P. Bour, and M. Kneissl, *MRS Internet J. Nitride Semicond. Res.* **4**, 12 (1999).
14. D. Alderighi, A. Vinattieri, J. Kudrna, M. Colocci, A. Reale, G. Kokolakis, A. Di Carlo, P. Lugli, F. Semond, N. Grandjean, and J. Massies, *phys. stat. sol. (a)* **188**, 851 (2001).
15. M. Pophristic, F. H. Long, C. Tran, I. T. Ferguson, and R. F. Karliceck, Jr., *J. Appl. Phys.* **86**, 1114 (1999).
16. L. Pavesi, *J. Appl. Phys.* **80**, 216 (1996).