Pergamon

Solid State Communications, Vol. 101, No. 9, pp. 643–646, 1997

0038–1098/97 $17.00+.00

PII: S0038-1098(96)00697-7

SIMILARITIES IN THE BANDEDGE AND DEEP-CENTRE PHOTOLUMINESCENCE MECHANISMS OF ZnO AND GaN

D.C. Reynolds,[a] D.C Look,[a] B. Jogai[a] and H. Morkoç[b]*

[a]University Research Center, Wright State University, Dayton, OH 45435, USA
[b]Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

(*Received* 26 *August* 1996; *accepted* 8 *November* 1996 *by A.H. MacDonald*)

Several of the optical transitions in ZnO and GaN appear to derive from a similar origin and have considerable overlap in the energy regions where they occur. In particular the donor–acceptor pair transitions and the well known "yellow band" in GaN and the analogous "green band" in ZnO show remarkable similarities. Because of these similarities it is likely that the respective transitions in the two materials are defect related and share common mechanisms. © 1997 Published by Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

The III–V nitrides have recently attracted much attention because of their large band gaps, high thermal conductivities and high melting points. Many of the problems encountered by researchers working with these materials is the lack of consistent high quality material. The highest quality GaN grown to date has been grown by molecular beam epitaxy (MBE) and by metal organic chemical vapour deposition (MOCVD) on a variety of substrates. The lattice mismatch as well as the stacking order mismatch between most of the currently used substrate materials and GaN is substantial. The substrate mismatch leads to strain induced defects and dislocations. Efforts are now being made to obtain closely lattice matched substrates that will minimize strain induced defects. One of the promising materials that provides a close lattice match to GaN is ZnO, which also has the wurtzite stacking order. In addition to having the same crystal structure and close lattice match, ZnO also exhibits optical properties similar to those observed in GaN. It is the purpose of this paper to delineate the similar optical properties and to point out where models used to explain a specific property in one material may be applicable in explaining a similar property in the other material. In particular the well known broad yellow band in GaN and a similar broad band, historically referred to as the green band, in ZnO appear to have similar origins.

A number of studies have been devoted to the origin of the yellow band in GaN. Controversy still exists, however, concerning the position of the electronic levels giving rise to the transition that produces the yellow band as well as the complex nature of the deep level. Ogino and Aoki [1] as well as Hofmann *et al.* [2] propose a model in which the transition between a shallow donor and a deep level gives rise to the yellow band. Alternatively Glaser *et al.* [3] propose a model in which the transition proceeds from a deep level to an effective mass acceptor. Here we show that the transition responsible for the green band in ZnO supports the model of [1] and [2] and can also nicely account for the very large width of the band. This sample explanation may also apply to the yellow band in GaN.

2. EXPERIMENTAL

The ZnO crystal used in this experiment was a platelet type crystal grown from the vapour phase. The

*On sabbatical leave at Wright Laboratory, Wright Patterson Air Force Base, OH 45435, under a University Resident Research Program funded by the Air Force Office of Scientific Research.

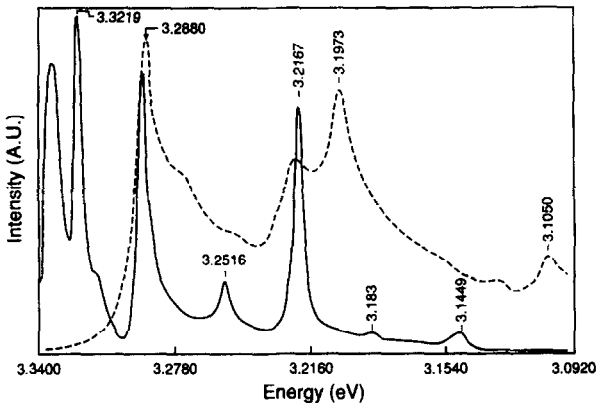

Fig. 1. Donor–acceptor pair transitions in GaN, dashed curve and in ZnO, solid curve. The zero phonon transitions along with their phonon replicas are identified in the text

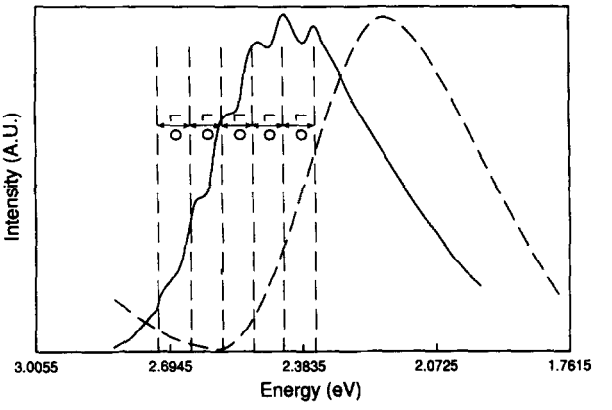

Fig. 2. The yellow emission band, dashed curve, observed in GaN and the green emission band, solid curve, observed in ZnO. The structured peaks occurring on the high energy side of the green band are separated in energy by that of the longitudinal optical phonon in ZnO

growth technique has been previously described [4]. The GaN sample that was used was grown by MBE on a sapphire substrate. Hall and electrical conductivity measurements were used to characterize the electrical parameters of the samples. The photoluminescence (PL) was excited with a He–Cd laser. The measurements were made at 2 K with the sample immersed in liquid He. The spectra were analyzed with a high-resolution 4 m spectrometer equipped with an RCA C31034A photomultiplier tube for detection.

3. EXPERIMENTAL RESULTS

Representative photoluminescence (PL) spectra from GaN exhibit free– and bound–exciton transitions near the absorption edge. At somewhat lower energies a series of donor–acceptor-pair lines are observed (zero phonon line at 3.2880 eV) where the zero phonon lines is followed at lower energies by phonon assisted transitions. These transitions are shown in Fig. 1, dashed curve. The transition at 3.2880 eV results from the recombination of a shallow donor and a Si acceptor. It is recognized that Si is an amphoteric impurity in GaN and normally produces donor states. The transitions at 3.1973 eV and 3.1050 eV are phonon assisted transitions. The transition at 3.2167 eV results from the recombination of the shallow donor with the Mg acceptor. This transition is close to the first phonon transition associated with the Si acceptor. The assignment of the Si and Mg acceptor transitions is based on the published binding energies of these acceptors as well as the knowledge that the MBE reactor probably contained residual Mg, resulting from previous Mg doping.

The transitions observed in ZnO, shown in Fig. 1, solid curve, are remarkably similar to the established donor–acceptor pair transitions in GaN. The donor–acceptor pair bands have been previously identified in ZnO [5, 6]. The first donor–acceptor transition occurs at 3.3219 eV with phonon replicas at 3.2516 eV and 3.183 eV. The second transition occurs at 3.2880 eV with phonon replicas at 3.2167 eV and 3.1449 eV. The phonon replicas in the two spectra are separated by the longitudinal optical phonon energies associated with the respective materials. While the identity of the donors and acceptors in ZnO is unknown, the similarity of the band gaps of ZnO and GaN together with the appearance of the pair transitions in the same energy region would indicate that the donor and acceptor binding energies are not greatly different in these two materials.

At somewhat lower energies than the donor–acceptor-pair transitions (2.2–2.3 eV) the well-known yellow band is observed in GaN as shown in Fig. 2, dashed curve. This band is seen in high conductivity MBE material (N deficient) and disappears in semi-insulating material (N rich). A similar band, historically called the green-band, has been observed in ZnO and is also shown in Fig. 2, solid curve. It has been shown in ZnO that the relative intensities of the phonon assisted peaks and the green band depend markedly on the electrical conductivity of the samples, the intensities of the two peaks becoming nearly equal at high conductivities [5, 6]. It has also been shown that the conductivity of ZnO is affected strongly by excess Zn, with the conductivity increasing rapidly with increasing Zn concentration [7]. Similar studies show that the conductivity of GaN decreases with increasing N concentration [7]. These similarities suggest that the green-band in ZnO and the yellow-band in GaN may be associated with a related defect mechanism.

The stoichiometry considerations discussed above

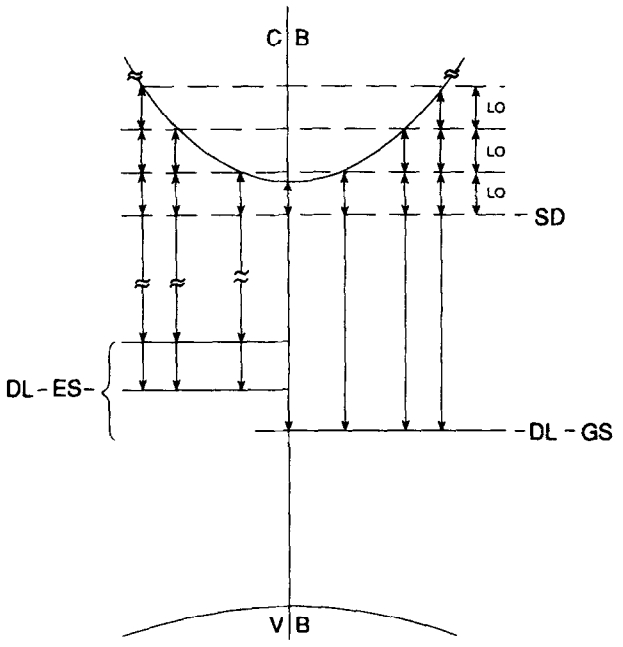

Fig. 3. Model to explain the green-band emission in ZnO. Band model in K-space shows the conduction band, the shallow donor level (SD), the deep level ground state (DL-GS) and the deep level excited states (DL-ES). The longitudinal optical phonons are designated as (LO). The energies of the above states are all related to the valence band

suggest certain point defects as viable candidates for the yellow band in GaN and the green band in ZnO. That is, in Ga-rich GaN, we would expect high quantities of the N vacancy V_N, Ga interstitial Ga_i, and/or the Ga antisite Ga_N. In Zn-rich ZnO, the analogous defects would be V_O, Zn_i and Zn_O. Recent theoretical calculations [8] in GaN predict shallow donor states for V_N and Ga_i but mid-gap unfilled levels for Ga_N. The latter defect could presumably act as a double donor or double acceptor since the neutral state contains two electrons in a four-fold degenerate level. Thus, from this point of view, it is possible that the yellow band in GaN involves Ga_N and the green band in ZnO involves Zn_O.

Experiments by Ogino and Aoki [1] and by Hofmann *et al.* [2] suggest that the yellow band in GaN results from the recombination between a shallow donour and a deep level. The complex nature of the deep level is unclear. Ogino and Aoki [1] propose a complex consisting of a Ga vacancy and a C on a N site (CN). Hofmann *et al.* [2] propose that the deep level may be a double donour though an acceptor cannot be ruled out. Suski *et al.* [9] suggest that the deep level is an antisite (N_{Ga}). A recent paper by Neugebauer and Van de Walle [10] report that their calculations show that the complex consisting of a Ga vacancy and CN as well as the N_{Ga} are thermodynamically unstable. They propose that the deep level is a Ga vacancy or related complex. It is clear that a consensus has not been reached on the makeup of the deep level.

For the case of ZnO a typical green-band obtained from a platelet type crystal a 2 K is shown in Fig. 2, solid curve. A modulated structure is observed on the high energy side of the band. The modulated structure can be explained from the model shown in Fig. 3. The PL emission results from the recombination between the shallow donor level and the deep level. Hot electrons in the conduction band are pumped up by the HeCd excitation source. Peaks in the PL emission band occur whenever the energy of the PL peak coincides with the sum of the energies of the donor level plus an integral multiple of a principal optical phonon-energy. At adjacent energy values an equilibrium number of electrons will arrive at the donor level and thus take part in the recombination with the deep level. The deep level will also have accompanying excited states due to interaction with local vibrational modes as well as lattice modes. It would be expected that the dominant transition would occur between the shallow donor and the ground state of the deep level. Transitions will also occur between the shallow donor and the excited states of the deep level, with reduced oscillator strengths. This model agrees with the model proposed by Ogino and Aoki [1] and by Hofmann *et al.* [2] for GaN and has the added advantage that it can explain the width of the emission band. The width of the yellow band in GaN and the green band in ZnO is extremely broad and would not be explained by the width of the impurity levels. The phonon involved in the green-band in ZnO is the longitudinal optical phonon, which has an energy of 0.072 eV, corresponding to the energy separation of the PL peaks on the high energy side of the green-band. It is noted in Fig. 2 that the modulated structure does not occur on the low energy side of the green band. This would be expected since the phonons that are involved in cascading hot electrons from the conduction band to the donor level are not involved with the low energy emission. This emission is accounted for by recombination of donor electrons with excited states of the deep level. The microscopic nature of the deep level is uncertain; it may be a complex centre whose excited states consist of both local vibrational modes and lattice modes. These excited states are so distributed that they do not produce a resolvable modulated structure on the low energy side of the green band.

If one now assumes that there is a relationship between the green-band in ZnO and the yellow-band in GaN, then a similar model would apply to the latter. This would support the model of Ogino and Aoki and Hofmann *et al.* [2] and would also explain the very large

width of the yellow band. The modulated structure observed for the green band in ZnO could not be accounted for by the alternative model, proposed by Glaser *et al.* [3], to explain the yellow band in GaN. In the Glaser model the electrons transfer from a shallow donor to the deep state in a non-radiative process followed by radiative decay from the deep state to a shallow acceptor.

In conclusion we have shown that some of the optical transitions in ZnO are similar to transitions observed in GaN. It would therefore seem reasonable that the models for the similar transitions would be applicable to both materials. This being the case the green-band model proposed here for ZnO could also account for the often observed yellow-band in GaN.

Acknowledgements—The authors would like to thank T.A. Cooper for electrical measurements and C. Huang and C.W. Litton for technical support. The work of D.C.R., D.C.L. and B. Jogai was performed at the Avionics Directorate, Wright Laboratory, Wright Patterson Air Force Base under USAF Contract No. F33615-91-C-1765. The work at the University of Illinois was funded by ONR under the group monitored by Y.S. Park and M. Yoder. H.M. thanks Dr. G. Witt of AFOSR for his support.

REFERENCES

1. Ogino, T. and Aoki, M., *Jpn. J. Appl. Phys.*, **19,** 1980, 2395.
2. Hofmann, D.M., Kovalev, D., Steude, G, Meyer, B.K., Hoffmann, A., Eckey, L., Heitz, R., Detchprom, T., Amano, H. and Akasaki, I., *Phys. Rev.*, **B52,** 1995, 16702.
3. Glaser, E.R., Kennedy, T.A., Doverspike, K., Rowland, L.B., Gaskill, D.K., Freitas, J.A., Jr., Asif Khan, M., Olson, D.T., Kuznia, J.M. and Wickenden, D.K., *Phys. Rev.*, **51,** 1995, 13326.
4. Park, Y.S. and Reynolds, D.C., *J. Appl. Phys.*, **38,** 1967, 756.
5. Heiland, G., Mollno, E. and Stockmann, F., in Solid State Physics (Edited by F. Seitz and D. Turnbull), Academic Press, Inc., New York, 1959, Vol. 8.
6. Andress, B., *Z. Physik*, **170,** 1962, 1.
7. Look, D.C., Reynolds, D.C., Kim, W., Oktas, O., Botchkarev, A., Salvador, A. and Morkoç, H., *Appl. Phys. Lett.* (to be published).
8. Boguslawski, P., Briggs, E.L. and Bernholc, J., *Phys. Rev.*, **B51,** 1995, 17255.
9. Suski, T., Berlin, P., Teisseyre, H., Leszcynsky, M., Grzegory, I., Jun, J., Bockowski, M., Porowski, S. and Moustakas, T.D., *Appl. Phys. Lett.*, **67,** 1995, 2188.
10. Neugebauer, J. and Van de Walle, C.G., *Appl. Phys. Lett.*, **69,** 1996, 503.