

## Structure of Isolated Oxygen Impurity States in InN

Dimiter Alexandrov<sup>1</sup>, Scott Butcher<sup>2</sup>, Nikolaus Dietz<sup>3</sup>, and Hang Yu<sup>1</sup>

<sup>1</sup>Department of Electrical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, P7B5E1, Canada

<sup>2</sup>BluGlass Limited, 74 Asquith Street, SILVERWATER, NSW 2128, Australia

<sup>3</sup>Department of Physics and Astronomy, Georgia State University, 29 Peachtree Center Avenue, Atlanta, GA, 30302-4106

### ABSTRACT

The electron state structure of isolated interstitial O atoms in real InN (containing clusters of InN, clusters of InON and clusters of non-stoichiometric InN:In) is the subject of investigation in this paper. It is shown that for the interstitial O atoms the corresponding symmetry is equivalent to that of an O atom in vacuum if the dielectric permittivity of InN is considered, and therefore the hydrogen like impurity atom analysis can be applied for isolated interstitial O atoms hosted in a real InN lattice. It is found that: *i*) If the O atom is interstitially incorporated in a cluster of pure InN the impurity state has an energy of -5.11 eV, which acts as a donor level with ionization energy +0.06 eV, and also this state is a donor level with an ionization energy of -0.02 eV for a cluster of InON if this cluster occurs at a distance of less than 30 Angstroms; *ii*) The impurity state has energy -5.15 eV if the O atom is interstitially incorporated in a cluster of InON, which acts as a donor level with ionization energy +0.02 eV, and also this state is a donor level with ionization energy +0.10 eV for a cluster of InN if this cluster occurs on a distance less than 60 Angstroms from the O atom. *iii*) If the O atom is interstitially incorporated in cluster of non-stoichiometric InN:In the impurity state has energy -5.38 eV, which is in the valence band of this cluster. However this state acts as donor level for both cluster of InN and cluster of InON if they are on distance less than 59 Angstroms from the O atom. The donor ionization energy for the first cluster is +0.33 eV, and for the second cluster it is +0.25 eV.

### INTRODUCTION

Thin films of InN deposited on AlN or sapphire show interesting optical properties with respect to both the optical absorption edge and the maximum of the photo-luminescence spectrum. Both spectral quantities have been observed to show significantly narrower energy intervals, to as low as 0.7 eV, in comparison with the corresponding interval of 1.9 eV long established for InN. These specific features have been the subject of investigation in several papers [1 – 3, etc.]. Theoretical investigations of the optical features of InN have been carried out on the basis of InN electron band structure [4, 5, etc.]. Oxygen is a common contaminant in InN. There are two possible positions for oxygen atoms in the structure of InN: 1) The oxygen atom can be alloyed to form the ternary compound  $\text{InO}_y\text{N}_{1-y}$  where oxygen is substituting on the nitrogen site. 2) The oxygen atom can be an isolated interstitial atom in the InN matrix, or it can be a non-isolated interstitial atom in the same structure if the concentration of the non-alloyed O impurities is higher. The alloyed O atoms are known to change the electron band structure and this has been subject of the author's previous work [4, 5]. The electron state structures of isolated interstitial O atoms in real InN (containing clusters of InN, clusters of  $\text{InO}_y\text{N}_{1-y}$  and clusters of

non-stoichiometric InN:In) is the subject of investigation in this paper. The authors have applied the hydrogen like impurity atom analysis and they have investigated the behavior of interstitial O atom for following cases: *i*) Incorporation of O atom in a cluster of pure InN; *ii*) Incorporation of O atom in a cluster of  $\text{InO}_y\text{N}_{1-y}$ ; *iii*) Incorporation of O atom in cluster of non-stoichiometric InN:In (substitutions of In atoms on N sites). (As a matter of fact the clusters pure InN,  $\text{InO}_y\text{N}_{1-y}$  and non-stoichiometric InN:In form the structure of real InN.) The corresponding impurity levels are calculated and their positions in the electron band structure of real InN are shown.

## RESULTS

Linear Combination of Atomic Orbitals (LCAO) electron band structures of both wurtzite  $\text{InO}_y\text{N}_{1-y}$  and wurtzite non-stoichiometric InN:In for points  $\Gamma$  are calculated by the previously developed method [6]. For the sake of simplicity both the wurtzite  $\text{InO}_y\text{N}_{1-y}$  and the wurtzite non-stoichiometric InN:In are called multinary crystal. A multinary crystal is considered to be a periodical crystal having a large primitive super-cell, containing a finite number of quasi-elementary cells. It is found [6] that the electron energy in a primitive super-cell of the multinary crystal can be presented in the following way.

$$E(\mathbf{r}) = \sum_{\mathbf{q}} \delta(\mathbf{r} - \mathbf{R}_{\mathbf{q}}) E(\mathbf{q}) \quad (1)$$

Where  $\mathbf{r}$  is the radius-vector of the electron,  $E(\mathbf{q})$  is electron energy in the quasi-elementary cell  $\mathbf{q}$  having radius-vector  $\mathbf{R}_{\mathbf{q}} = q_1\mathbf{a}_1 + q_2\mathbf{a}_2 + q_3\mathbf{a}_3$  ( $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  are the three basis vectors of the primitive super-cell), and  $\delta(\mathbf{r} - \mathbf{R}_{\mathbf{q}})$  is a delta-function. The electron band structure of the multinary crystal can be determined on the basis of the interactions within the primitive super-cell, which determine the corresponding sub-bands. As a matter of fact the electron band structure of the multinary crystal determined in this way contains the same sub-bands as those determined for the primitive super-cell of the same multinary crystal without consideration of the localizations of the interactions. However here the sub-bands are localized in the corresponding quasi-elementary cells.

Detailed investigation shows that for the purpose of inter-band electron transitions for semiconductor compound alloys it can be taken parts of the LCAO electron band structures corresponding to configurations of the quasi-elementary cells giving deepest energy pockets for the electrons in the conduction band, deepest energy pockets for the holes in the valence band, and that these energy pockets are on shortest distances. In order for these three conditions to be satisfied configurations of five different types of wurtzite quasi-elementary cells taken in the following order must be used: *i*) for  $\text{InO}_y\text{N}_{1-y}$  (energy separations shown in Fig.1): 1) InO quasi-elementary cell surrounded by second neighboring O anions; 2) InO quasi-elementary cell having second neighboring anions O and N; 3) mixed InN-O quasi-elementary cell containing two atoms of In, one atom of O and one N atom, having second neighboring anions O and N; 4) InN quasi-elementary cell having second neighboring anions O and N; 5) InN quasi-elementary cell surrounded by second neighboring N anions. *ii*) for non-stoichiometric InN:In (energy separation shown in Fig. 2): 1) pure InIn quasi-elementary cell surrounded by second neighboring N anions; 2) mixed InN-In quasi-elementary cell containing 3.5 atoms of In and 0.5 atoms of N, having second neighboring N anions; 3) mixed InN-In quasi-elementary cell containing 3 atoms of In and 1 atom of N, having second neighboring N anions; 4) mixed InN-In quasi-elementary cell

containing 2.5 atoms of In and 1.5 atoms of N, having second neighboring N anions; 5) pure InN quasi-elementary cell surrounded by second neighboring N anions.

The LCAO electron band structure calculations for each quasi-elementary cell are performed by method given in [7]. The electron energy terms  $\varepsilon_s$  and  $\varepsilon_p$  for both N atom and In atom are taken from [8], and the same energy terms for O atom substituting on N site in the structure of InN are determined in [4]. The nearest-neighbor matrix elements are determined according to [7] and the required inter atomic distances are calculated on the basis of tetrahedral radii of atoms In, N and O. The calculated electron band structures (not in scale) are given in Fig.2 for non-stoichiometric InN:In and in Fig.1 for  $\text{InO}_y\text{N}_{1-y}$ . The energy levels  $\Gamma^{\nu}_{cl}$  and  $\Gamma^{\nu}_{vl5}$  are determined by taking the energy of the vacuum as being equal to zero. The energy difference  $E^{\nu}_g = (\Gamma^{\nu}_{cl} - \Gamma^{\nu}_{vl5})$  gives the energy band gap of sector  $\nu$ . The shifts of the boundaries of the energy band gaps in Fig.1 and in Fig.2, and the corresponding energy intervals are due to defects in the crystal lattices of both  $\text{InO}_y\text{N}_{1-y}$  and InN:In – i.e. the existence of two sorts of atoms on anionic sites. The nature of these shifts is different from the nature of the shifts of the boundaries of the energy band gap described in [9, 10].

The LCAO electron band structure of pure InN is taken from sectors 5 of both Fig.1 and Fig.2.

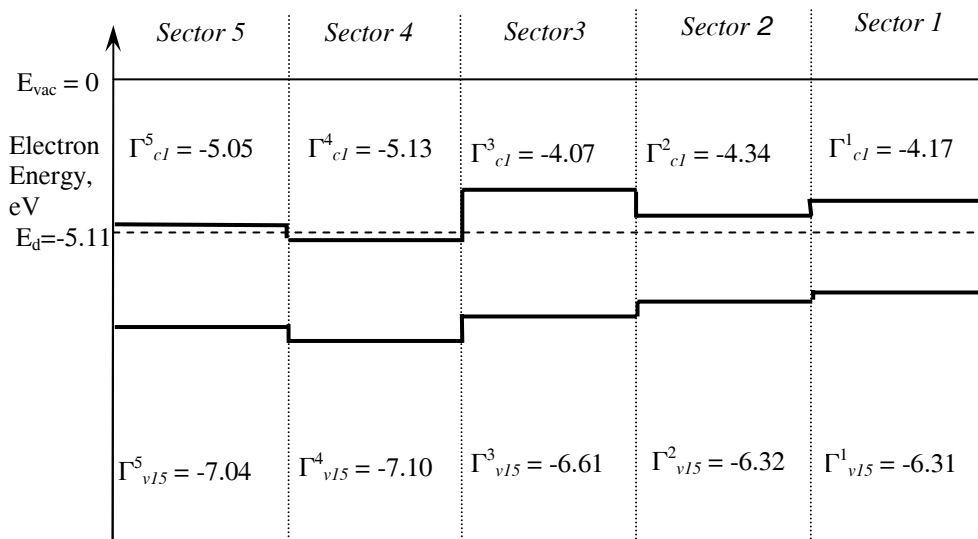


Fig.1. Cluster of  $\text{InO}_y\text{N}_{1-y}$  and donor level  $E_d = -5.11$  eV

The electronic structure of isolated oxygen impurity states can be found under consideration that the valence electrons of an incorporated interstitial O atom is not engaged in forming of ion-covalent bonds in InN, in  $\text{InO}_y\text{N}_{1-y}$  and in InN:In. Therefore a relatively long distance influence of the valence states in the above clusters can be expected and the hydrogen like impurity atom analysis [11] can be applied for isolated interstitial O atoms hosted in a real InN lattice. It means that the Schrodinger equation for a hydrogen atom, but with effective electron mass  $m$  and dielectric constant  $\kappa$  having values for clusters InN,  $\text{InO}_y\text{N}_{1-y}$  and InN:In, can be used.

$$[-\hbar^2 \Delta / (2m) - e^2 / (\kappa r)] F(\mathbf{r}) = E F(\mathbf{r}) \quad (2)$$

Where  $F(\mathbf{r})$  is ground-state wave function of the form

$$F(\mathbf{r}) = (\pi a^3)^{-1/2} e^{-r/a} \quad (3)$$

Where  $a$  is an effective Bohr radius, which determines localization radius of the wave function and

$$a = \hbar^2 \kappa / (m e^2) \quad (4)$$

The solution of (2) gives isolated electron states of the impurity atom

$$E_n = - e^4 m / (2 n^2 \kappa^2 \hbar^2) \quad (5)$$

Where  $n$  is integer number greater than zero. For determination of the isolated electron states it is considered  $n = 1$ .

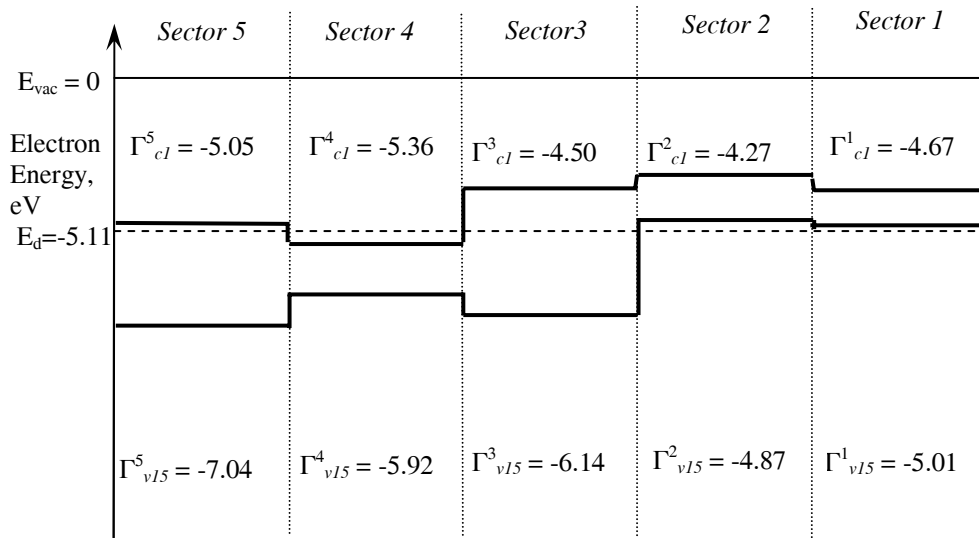


Fig.2 Cluster of non-stoichiometric InN:In and donor level  $E_d = -5.11$  eV

## DISCUSSION

The authors have used (4) and (5) for determination of localization radii and of electron energy states respectively of interstitially incorporated O atoms in clusters InN,  $\text{InO}_y\text{N}_{1-y}$  and InN:In. The values of  $\kappa$  are taken from [12], and  $m$  are taken from [4 – 6]. The following results have been obtained (relative to zero energy at the vacuum level):

*i)* If the O atom is interstitially incorporated in a cluster of pure InN the impurity state has an energy of -5.11 eV, which acts as a donor level with ionization energy +0.06 eV. Also this state is a donor level (Fig.1) with an ionization energy of -0.02 eV for a cluster of

$\text{InO}_y\text{N}_{1-y}$  if this cluster occurs at a distance of less than 30 Angstroms from the O atom, however if there is a cluster of  $\text{InN}:\text{In}$  in the same range this level goes into the valence band of this cluster (Fig.2) and it can form “electron bridge” between this band and the conduction band.

*ii)* The impurity state has energy  $-5.15$  eV if the O atom is interstitially incorporated in a cluster of  $\text{InO}_y\text{N}_{1-y}$ , which acts as a donor level with ionization energy  $+0.02$  eV. Also this state is a donor level with ionization energy of  $+0.10$  eV for a cluster of  $\text{InN}$  (Fig.3) if this cluster occurs on a distance less than 60 Angstroms from the O atom. This level has the same behavior as this in *i)* about cluster of  $\text{InN}:\text{In}$  only here the range is 60 Angstroms.

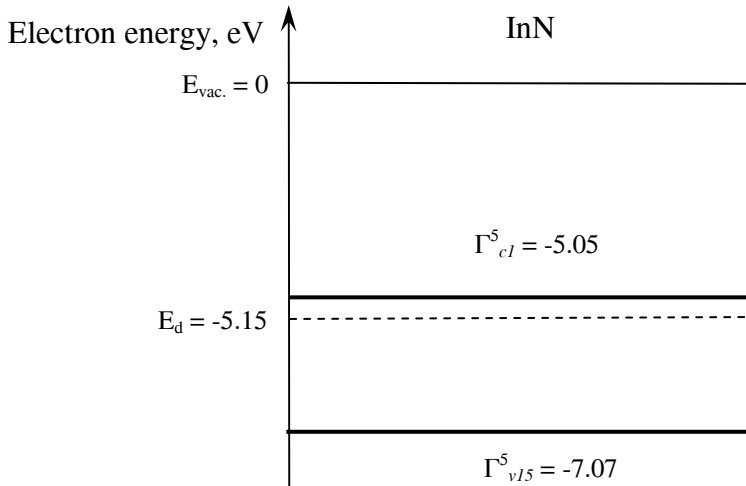


Fig.3. Cluster of  $\text{InN}$  and donor level  $E_d = -5.15$  eV

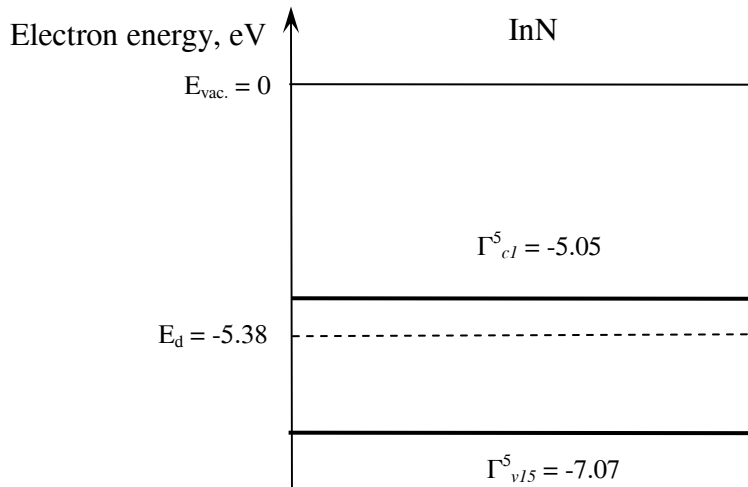


Fig.4. Cluster of  $\text{InN}$  and donor level  $E_d = -5.38$  eV

*iii)* If the O atom is interstitially incorporated in cluster of non-stoichiometric  $\text{InN}:\text{In}$  the impurity state has energy  $-5.38$  eV, which is in the valence band of this cluster. However this

state acts as donor level for both cluster of InN (Fig.4) and cluster of  $\text{InO}_y\text{N}_{1-y}$  if they are on distance less than 59 Angstroms from the O atom. The donor ionization energy for the first cluster is +0.33 eV, and for the second cluster it is +0.25 eV.

## CONCLUSIONS

The obtained results explain the influence of the electron impurity states of O atom interstitially incorporated in the structure of real InN. In fact the results confirm the donor behavior of the O atom in InN, which has been observed experimentally earlier. Because the oxygen is a common contaminant in InN this semiconductor normally has n-type conductivity which is well known. The oxygen levels can act as “electron bridges” between the valence band and the conduction band of real InN. The obtained results can be used for further investigation of the properties of InN and related alloys.

## ACKNOWLEDGMENTS

This work is supported by Discovery Grant to D. Alexandrov from the Natural Sciences and Engineering Research Council of Canada (NSERC).

## REFERENCES

1. K.S.A. Butcher, M. Wintrebert-Fouquet, Motlan, S. K. Shrestha, H. Timmers, K. E. Prince and T. L. Tansley, Proceeding of 2002 MRS Fall Meeting, Boston, MA, USA (2002).
2. J. Wu *et al.*, *Appl. Phys. Lett.*, **80**, 3967 (2002)
3. V. Yu. Davydov *et al.*, *Phys. Stat. Sol. (b)*, **234**, 787 (2002)
4. D. Alexandrov, K.S.A. Butcher, M. Wintrebert-Fouquet, *J. of Crys. Gr.*, **269**, 77 (2004)
5. D. Alexandrov, S. Butcher, T. Tansley, *Phys. Stat. Sol. (b)*, **203**, 25 (2006)
6. D. Alexandrov, *J. of Crys. Gr.*, **246**, 325 (2002)
7. W. A. Harrison, *Electronic Structure and the Properties of Solids*, Dover Publ. Inc, (1989)
8. F. Herman, B. Skillman, *Atomic Structure Calculations*, Prentice Hall (1963)
9. H. Fritzsche, *J. of Non-Crystalline Solids*, **6**, 49 (1971)
10. A. Efros, B. Shklovskii, “*Electronic Properties of Doped Semiconductors*”, Springer-Verlag, Berlin – Heidelberg (1984)
11. L. D. Landau, E. M. Lifshitz, “*Quantum Mechanics (Non-Relativistic Theory)*”, 2<sup>nd</sup> revised edition, Pergamon Press, Oxford (1965)
12. D. Alexandrov, S. Butcher, T. Tansley, Proceeding of International Conference on Optical and Optoelectronic Properties of Materials and Applications, ICOOPMA2006, 17 July – 21 July 2006, Darwin, Australia (2006)