

ELECTRONIC STRUCTURE AND PROPERTIES OF NITRIDE SEMICONDUCTOR COMPOUND ALLOYS

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Linear Combination of Atomic Orbitals (LCAO) electron band structure calculations are used to examine the influence of common defect structures that may arise as artifacts during the growth of InN. For 1.9 eV band-gap InN, the formation of indium rich non-stoichiometric InN leads to the creation of a lower band-gap material, due to the single substitution of indium atoms on nitrogen sites. Optical absorption at energies as low as 0.20 eV for non-stoichiometric InN is calculated, consistent with recent observations of the optical absorption spectrum. The role of oxygen alloying is also examined, and the ternary semiconductor $\text{InO}_y\text{N}_{1-y}$ with $y \sim 0.1$ is identified. It is also found that the presence of this concentration of O atoms in InN decreases the band-gap energy. Optical absorption as low as 1.19 eV can be evident, while exciton emissions are found to vary in energy over the range 0.84 – 1.01 eV. This work suggests that oxygen alloys play no role in causing any supposedly smaller band-gap of InN than the observed 1.9 eV.

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1. Introduction

The relatively recent observation of 0.7 eV photoluminescence for InN, and of absorption features near this energy, have been the subject of a number of recent papers [1, 2, 3]. It has been proposed that the low energy features indicate a 0.7 eV band-gap. However, the material had long been held to have a much higher band-gap of 1.9 eV. The large difference between these values is not presently understood. The Moss-Burstein effect does not explain the variation seen for material of low carrier concentration, and Vegard's law indicates that oxygen levels in the higher band-gap material are insufficient to account for the difference [4].

Sample inhomogeneity offers a strong possible explanation. The growth conditions are known to form non-stoichiometric indium nitride during the growth of nitride films. One now seeks to investigate the possibility that these low energy features arise as growth artifacts, due to an alloy formed by non-stoichiometric InN containing single In substitutions on N sites. The author also investigates the influence of oxygen incorporation in InN, since oxygen has been claimed to be responsible for the 1.9 eV band-gap [3]. Oxygen is a common contaminant of InN, and is also present at the interface with sapphire substrates. However, the role of oxygen is largely uninvestigated.

In this paper, the energy band-gaps of InN containing high concentrations of oxygen, and of non-stoichiometric InN:In, are calculated as functions of quasi-elementary cells in which the electron is localized. It is found that the existence of excitons in InN containing oxygen determines the photoluminescence spectra. Distinctive features of the optical absorption spectra of InN containing oxygen and of non-stoichiometric InN:In can be understood on the basis of localized electron states. The theoretical results are found to be in good agreement with experimental data.

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2. The ternary alloy $\text{InO}_y\text{N}_{1-y}$ and its binary constituents

Little is known about the behaviour of oxygen in InN. There is speculation, as yet unsubstantiated, that the oxygen alloy is responsible for the observed 1.9 eV band-gap of polycrystalline InN grown by RF sputtering [3]. Interestingly, there is strong evidence of oxide segregation in polycrystalline InN grown at low temperatures [5]; the alloyed species being most likely to occur in single crystal material grown at higher temperatures. Although it has been shown that ion milling techniques overestimate the oxygen content in InN, elastic recoil analysis has shown that polycrystalline InN grown by RF sputtering typically contains up to 10 atomic percent of oxygen [1]. The author therefore models $\text{InO}_y\text{N}_{1-y}$ only as an alloyed species, with oxygen at this concentration substituting on the nitrogen site. Segregated oxygen species in wurtzite InN containing oxygen are not considered. According to [6], oxygen occupies a nitrogen site, with the group VI atom on the group V site acting as a single donor. For this arrangement, a ternary semiconductor $\text{InO}_y\text{N}_{1-y}$ with $y \sim 0.1$ may be considered in terms of two binary constituents, the InN host lattice and InO distributed through the host. These conditions allow us to introduce a primitive cell of the binary constituent InO which must satisfy the following conditions: *a)* the O atom substitutes for an N atom, retaining the tetrahedral geometry of the crystal cell; *b)* the O atom has a valence of 6 and the In atom has valence of 3; *c)* the In-O bond is ionic-covalent. Using these conditions, the energy band-gap of tetrahedral InO is found, by the method described in [7], to be 2.15 eV. Charge transfer between the *s*- and *p*-orbitals of the O atom and the *s*- and *p*-orbitals of the In atom is found, by consideration of spin orbital splitting and the use of perturbation theory, to be significant - the valence charge of the In atom increases to 3.5 electrons and that of the O atom decreases to 5.5 electrons; a conclusion in accord with oxygen acting as a donor in InN [6]. A perturbation theory treatment of the sp^3 orbital interactions between O and In in the tetrahedral cell of InO shows that the energies of the electrons belonging to the *s*-orbitals and to the *p*-orbitals change, becoming: - for the In atom: $\epsilon_s = -8.40$ eV, $\epsilon_p = -2.29$ eV, and for the O atom: $\epsilon_s = -29.58$ eV, $\epsilon_p = -17.81$ eV. Finally, the tetrahedral covalent radii [8] of the In and O atoms in the tetrahedral InO cell yield a distance between the In and O atoms of 2.10 Å.

3. Determination of the valence electron energies of an In atom substituting for a N atom in the structure of non-stoichiometric InN

The system containing two neighbouring atoms in the tetrahedral cell, connected by an ionic-covalent bond, is the subject of investigation in the region where the electronic density has a high variation. The ionic-covalent bond is based on two hybrid orbitals belonging to the neighbouring atoms engaged in the bond. Each hybrid orbital contains atomic orbitals defined for the isolated atom. In this paper, the hybrid orbital is constructed under the following considerations:

- i)* Only atomic orbitals having radii greater than half of the inter-atomic distance and occupied by electrons participate in the forming of the hybrid orbital. These atomic orbitals are called valence atomic orbitals;
- ii)* Only part of the charge of the electron belonging to the valence atomic orbital is engaged in the forming of the hybrid orbital. (The other part interacts with both the core electrons and the nuclei.);
- iii)* The electronic charges of an atomic orbital participating in the hybrid orbital are attracted by the electronic charges participating in the hybrid orbital of the other atom engaged in the bond.

The hybrid orbital fulfilling the conditions given above is

$$C^\xi |h^\xi(\mathbf{r})\rangle = \sum_i A_i^\xi |\psi_i^\xi(\mathbf{r})\rangle, \quad (1)$$

where C^ξ is a coefficient connected with the orthogonal requirements, the coefficients A_i^ξ are connected with condition *ii)* above, the sum is over all atomic orbitals $|\psi_i^\xi(\mathbf{r})\rangle$ participating in the bond, and ξ designates the cationic (or anionic) types of the nuclei in the solid state (below, the other type of the nuclei - anionic (or cationic) is designated by η).

The corresponding one-particle Schrödinger equation for the electron function $\psi_{i,\zeta}(\mathbf{r})$ is derived on the basis of the Hartree-Fock method, together with Kohn-Sham corrections [9], and of conditions *ii*) and *iii*) above. It is:

$$\begin{aligned}
& \{ -(1/2) \nabla^2 + [V^\zeta(\mathbf{r}) + \mu_c^\zeta[n^\zeta(\mathbf{r})]] \} \psi_{i,\zeta}(\mathbf{r}) + \int [(\sum_j |\psi_{j,\zeta}(\mathbf{r}')|^2) / |\mathbf{r} - \mathbf{r}'|] d\mathbf{r}' \psi_{i,\zeta}(\mathbf{r}) \\
& - \int \{ [(\sum_j \psi_{j,\zeta}(\mathbf{r}') \psi_{j,\zeta}(\mathbf{r})) \psi_{i,\zeta}(\mathbf{r}')] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r}' \\
& - \int [(\sum_j |A_j^\zeta \psi_{j,\zeta}(\mathbf{r}')|^2) / |\mathbf{r} - \mathbf{r}'|] d\mathbf{r}' A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}) - [V^\zeta(\mathbf{r}) + \mu_c^\zeta[n^\zeta(\mathbf{r})]] A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}) \\
& + \int \{ [(\sum_j A_j^\zeta \psi_{j,\zeta}(\mathbf{r}') A_{j,\zeta} \psi_{j,\zeta}(\mathbf{r})) A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}')] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r}' \\
& + \int [(\sum_j |A_j^\eta \psi_{j,\eta}(\mathbf{r}')|^2) / |\mathbf{r} - \mathbf{r}'|] d\mathbf{r}' A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}) + [V^\eta(\mathbf{r}) + \mu_c^\eta[n^\eta(\mathbf{r})]] A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}) \\
& - \int \{ [(\sum_j A_j^\eta \psi_{j,\eta}(\mathbf{r}') A_{j,\eta} \psi_{j,\eta}(\mathbf{r})) A_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}')] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r}' \\
& = \varepsilon_{i,\zeta} \psi_{i,\zeta}(\mathbf{r}) + \varepsilon_{\text{add},i} \psi_{i,\zeta}(\mathbf{r}),
\end{aligned} \tag{2}$$

where $V^\zeta(\mathbf{r})$ and $V^\eta(\mathbf{r})$ are the static potentials on the cationic (anionic) site and on the anionic (cationic) site respectively, $\mu_c^\zeta[n^\zeta(\mathbf{r})]$ and $\mu_c^\eta[n^\eta(\mathbf{r})]$ are the correlation contributions to the chemical potentials of uniform gases of densities $n^\zeta(\mathbf{r})$ and $n^\eta(\mathbf{r})$ on the cationic (anionic) site and on the anionic (cationic) site respectively, and $\varepsilon_{\text{add},i}$ is the additional energy involved in the system due to the influence of the bond.

In the Schrödinger equation given above, the first second and third terms represent the interactions of the electron with the static and chemical potentials of the atom, with the other electrons in the atom, and interchanged interactions respectively [9]. The fourth fifth and sixth terms represent the lost parts of the same interactions, due to the removal of part of the electrical charge in the bond. The seventh, eighth and ninth terms represent the added part of the same interactions, due to the contributions of the neighbouring atom engaged in the bond.

If we want to use the energy term $\varepsilon_{i,\zeta}$ in the LCAO calculations of the electron band structure, we have to treat the atom on the cationic (anionic) site as isolated in respect of $\varepsilon_{i,\zeta}$ – i.e. its total electron energy must be equal to the energy of the isolated atom. Considering this condition and using the procedure described in [9], the following equation is found ($j \neq i$):

$$\begin{aligned}
& -(1/2) \iint \{ [(\sum_j |A_j^\zeta \psi_{j,\zeta}(\mathbf{r}')|^2) |\psi_{i,\zeta}(\mathbf{r})|^2] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r} d\mathbf{r}' \\
& + (1/2) \iint \{ [(\sum_j A_j^\zeta \psi_{j,\zeta}(\mathbf{r}') A_{j,\zeta} \psi_{j,\zeta}(\mathbf{r})) \psi_{i,\zeta}(\mathbf{r}') \psi_{i,\zeta}(\mathbf{r})] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r} d\mathbf{r}' \\
& + \int |\psi_{i,\zeta}(\mathbf{r})|^2 \{ \varepsilon_c^\zeta[n^\zeta(\mathbf{r})] - \mu^\zeta[n^\zeta(\mathbf{r})] \} d\mathbf{r} \\
& + (1/2) \iint \{ [(\sum_j |A_j^\eta \psi_{j,\eta}(\mathbf{r}')|^2) |\psi_{i,\zeta}(\mathbf{r})|^2] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r} d\mathbf{r}' \\
& - (1/2) \iint \{ [(\sum_j A_j^\eta \psi_{j,\eta}(\mathbf{r}') A_{j,\eta} \psi_{j,\eta}(\mathbf{r})) \psi_{i,\zeta}(\mathbf{r}') \psi_{i,\zeta}(\mathbf{r})] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r} d\mathbf{r}' \\
& - \int |\psi_{i,\zeta}(\mathbf{r})|^2 \{ \varepsilon_c^\eta[n^\eta(\mathbf{r})] - \mu^\eta[n^\eta(\mathbf{r})] \} d\mathbf{r} \\
& = 0,
\end{aligned} \tag{3}$$

where $\varepsilon_c^\zeta[n^\zeta(\mathbf{r})]$ and $\varepsilon_c^\eta[n^\eta(\mathbf{r})]$ are the correlation energies satisfying the following equalities: $\mu^\zeta[n^\zeta(\mathbf{r})] = d(n^\zeta \varepsilon_c^\zeta)/dn^\zeta$ and $\mu^\eta[n^\eta(\mathbf{r})] = d(n^\eta \varepsilon_c^\eta)/dn^\eta$.

For sp^3 orbital bonds, there are eight equations of type (3) that form a system. Solution of this system gives the coefficients A_j^ζ and A_j^η . They are for every atomic orbital participating in the

ionic-covalent bond. In the case of an In-In bond, the system of these equations is simpler, due to the equivalence in the parameters of both atoms engaged in the interactions. In this case, the system is solved for Slater's type of atomic orbitals of the In atom, considering that the distance between the two In atoms is equal to twice the In tetrahedral radius (i.e. the distance is 2.88 Å). It is found that $A_s = 0.728$ and $A_p = 0.831$.

4. Energy band-gaps of non-stoichiometric InN:In and of InN containing oxygen

The energy band-gaps of wurtzite crystals of the pseudo-binary compounds non-stoichiometric InN:In and $\text{InO}_y\text{N}_{1-y}$ at Γ points ($\mathbf{k}=0$) are calculated by the method developed in [10]. The crystal is treated as periodic, with a large primitive super-cell containing a defined, finite number of quasi-elementary cells. The electron energy in a primitive super-cell can be written [10] as:

$$E(\mathbf{r}) = \sum_{\mathbf{q}} \delta(\mathbf{r} - \mathbf{R}_{\mathbf{q}}) E(\mathbf{q}), \quad (4)$$

where $\mathbf{r}$ is the radius-vector of the electron, $E(\mathbf{q})$ is the electron energy in the quasi-elementary cell $\mathbf{q}$ having a 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 pseudo-binary crystal is calculated via the interactions within the primitive super-cell, which determine the corresponding sub-bands. The electronic band structure determined in this way contains the same sub-bands as those determined for the primitive super-cell, with interaction localization ignored. However, the sub-bands are here localized in the corresponding quasi-elementary cells. The electronic band structures of non-stoichiometric InN:In and $\text{InO}_y\text{N}_{1-y}$ determined in this way are a continuous sequence of electronic band sub-structures, and each of them is calculated for the corresponding quasi-elementary cell.

It is necessary to use localized electron wave functions for the calculation of the electron band sub-structure of a quasi-elementary cell. In this paper, linear combinations of atomic orbitals (LCAO) are used as the functional basis of the computations, and the electronic band sub-structures at points Γ are calculated using the LCAO method ([11], page 61). The tetrahedral cell of the wurtzite pseudo-binary crystal is introduced to represent interactions between the nearest neighbour orbitals.

The orbitals corresponding to both the s - and the p -state of the valence electrons of the atoms are used in the calculations. Non-zero matrix elements are only those that represent interactions between the nearest neighbour orbitals and the second neighbour orbitals. Valence electron states engaged in the interactions comprise one s - and three p -states (p_x , p_y and p_z) per atom, so the corresponding LCAO Hamiltonian matrix of the tetrahedral cell contains 16 rows and 16 columns. The matrix elements $H_{\alpha\alpha}$ for $\alpha = 1, 2, 3, \dots, 8$ represent the orbital energy terms when the corresponding atom is in the crystal, so that:

$$H_{\alpha\alpha} = C_{\alpha} \varepsilon_{\alpha} \quad (5)$$

The energy terms ε_l ($l = s, p$) represent the energies of the s - and p -states of the isolated atoms. Their values are taken from [12] and from the parameters of the InO tetrahedral cell given above. The real coefficients C_l , for $\text{InO}_y\text{N}_{1-y}$, as provided in Table 1, are obtained by fitting at the wurtzite binary compositional limits (InN and InO for $\text{InO}_y\text{N}_{1-y}$). They describe well the corresponding energy bandwidths, and are in good agreement with the experimental results. The real coefficients C_{α} for In on N sites in non-stoichiometric InN:In are obtained from the data obtained in section 3, and by using the expressions $C_{\alpha} = A_{\alpha}^2$ (A_{α} are found as numerical values for the s - and p -states of the In atom on a N site). The real coefficients C_{α} for In in stoichiometric InN are taken from [10].

The matrix element $H_{\alpha\beta}$ ($\alpha \neq \beta$) represents the interaction between atomic orbitals belonging to different atoms. The matrix elements $H_{\alpha\beta}$ for ($\alpha = 1, 2, \dots, 8$ & $\beta = 1, 2, \dots, 8$ & $\alpha \neq \beta$) represent the

interactions between the orbitals of the atoms that are nearest-neighbours, and are calculated using the procedure given in ([11], page 48). The matrix elements $H_{\alpha\beta}$ for both ($\alpha = 9, 10, \dots, 16$ & $\beta = 1, 2, \dots, 8$) and ($\alpha = 1, 2, \dots, 8$ & $\beta = 9, 10, \dots, 16$) represent the interactions between the atomic orbitals of the atoms and the atomic orbitals of their second neighbours, and are determined by using the muffin-tin orbital method [13, 14]. The distances between atoms (second neighbours) engaged in the interactions, their tetrahedral covalent radii, and the distribution of the valence electrons in the tetrahedral cell are used as the basis of the calculations. The results of these calculations for $\text{InO}_y\text{N}_{1-y}$ are summarized in Table 2. The same matrix element for non-stoichiometric $\text{InN}:\text{In}$ are considered to be zero, due to the longer distances between second neighbours in this alloy. The matrix elements $H_{\alpha\beta}$ for ($\alpha = 9, 10, \dots, 16$ and $\beta = 9, 10, \dots, 16$) are taken to be zero. The LCAO Hamiltonian matrix of the quasi-elementary cell is determined by all cases of the matrix elements $H_{\alpha\beta}$ discussed above.

Table 1. Coefficients C_α .

For In in InN	$C_s=0.68$	$C_p=0.21$
For In on a N site in InN	$C_s=0.53$	$C_p=0.69$
For In bound to O in $\text{InO}_y\text{N}_{1-y}$	$C_s=0.72$	$C_p=0.23$
For O in $\text{InO}_y\text{N}_{1-y}$	$C_s=0.77$	$C_p=0.21$
For N in $\text{InO}_y\text{N}_{1-y}$	$C_s=0.68$	$C_p=0.35$
For In bound to N in $\text{InO}_y\text{N}_{1-y}$	$C_s=0.68$	$C_p=0.21$

Table 2. Matrix elements of the interactions between the second neighbour orbitals.

For $\text{InO}_y\text{N}_{1-y}$	$V_{ss\sigma}$	$V_{sp\sigma}$	$V_{pp\sigma}$	$V_{pp\pi}$
In-In interaction if both atoms are bound to N	- 0.2817 eV	0 eV	0.0165 eV	- 0.0082 eV
In-In interaction if both atoms are bound to O	- 0.2357 eV	0 eV	0.0165 eV	- 0.0082 eV
N-N interaction	- 0.0364 eV	0 eV	0.0010 eV	- 0.0005 eV
O-O interaction	- 0.0706 eV	0 eV	0.0015 eV	- 0.0008 eV
In-N interaction	- 0.1258 eV	0.0302 eV	0.0149 eV	- 0.0075 eV
In-O interaction	- 0.1368 eV	0.0276 eV	0.0072 eV	- 0.0036 eV
N-O interaction	- 0.0355 eV	0 eV	0.0023 eV	- 0.0012 eV

It is found that both the optical absorption and the photoluminescence spectra for non-stoichiometric $\text{InN}:\text{In}$ and $\text{InO}_y\text{N}_{1-y}$ can respectively be taken as the parts of the LCAO electron band structures corresponding to those configurations of the quasi-elementary cells which yield the deepest energy pockets for electrons in the conduction band and for holes in the valence band, and

that these energy pockets correspond to the shortest distances. In order for these three conditions to be satisfied, configurations of five different types of wurtzite quasi-elementary cell, taken in the following order, must be used:

i) for non-stoichiometric InN:In (energy separation shown in Fig. 1): 1) the In-In quasi-elementary cell; 2) the mixed In-In-N quasi-elementary cell (one half atoms of N and seven half atoms of In); 3) the mixed In-In-N quasi-elementary cell containing one atom of N and three atoms of In; 4) the In-In-N mixed quasi-elementary cell containing 1.5 atoms of N and 2.5 atoms of In; 5) InN quasi-elementary;

ii) for $\text{InO}_y\text{N}_{1-y}$ (energy separations shown in Fig. 2): 1) the InO quasi-elementary cell surrounded by second neighbour O anions; 2) the InO quasi-elementary cell having second neighbour anions O and N; 3) the mixed In-ON quasi-elementary cell containing two atoms of In, one atom of O and one N atom, having second neighbour anions O and N; 4) the InN quasi-elementary cell having second neighbour anions O and N; 5) the InN quasi-elementary cell surrounded by second neighbour N anions.

Each type of quasi-elementary cell forms sector ν of the corresponding electron band structure ($\nu = 1, 2, 3, 4, 5$). In terms of both the optical absorption and the photoluminescence, the energy band-gaps of non-stoichiometric InN:In and of $\text{InO}_y\text{N}_{1-y}$ have to be determined as energy differences between Γ_{cl}^ν (the bottom of the conduction band of sector ν) and Γ_{v15}^ν (the top of the valence band of sector ν). The results of the calculations are given in Fig. 1 for non-stoichiometric InN:In and in Fig. 2 for $\text{InO}_y\text{N}_{1-y}$. The energy levels Γ_{cl}^ν and Γ_{v15}^ν are measured from a zero vacuum level. The energy difference $E_g^\nu = (\Gamma_{cl}^\nu - \Gamma_{v15}^\nu)$ gives the energy band-gap of sector ν . The shifts of the boundaries of the energy band-gaps in Figs. 1 and 2, and the corresponding energy intervals, are due to defects in the crystal lattices of non-stoichiometric InN:In and of $\text{InO}_y\text{N}_{1-y}$ respectively – i.e. the existence of two sorts of atom on cationic or anion sites. The nature of these shifts is different from the nature of the shifts of the boundaries of the energy band-gap, described in [15, 16].

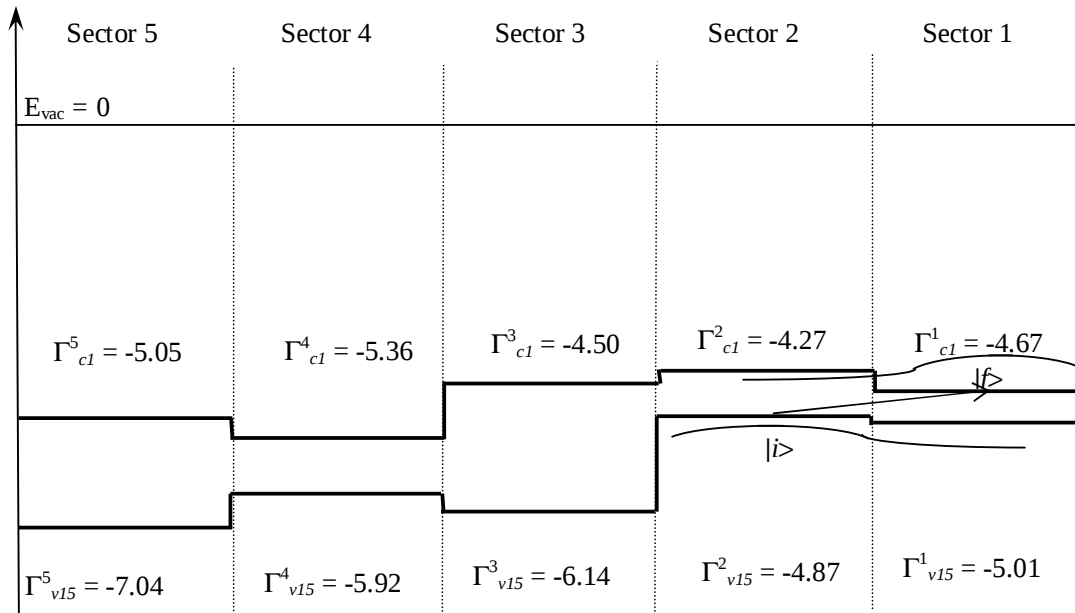


Fig. 1. Energy band-gap of non-stoichiometric InN:In.

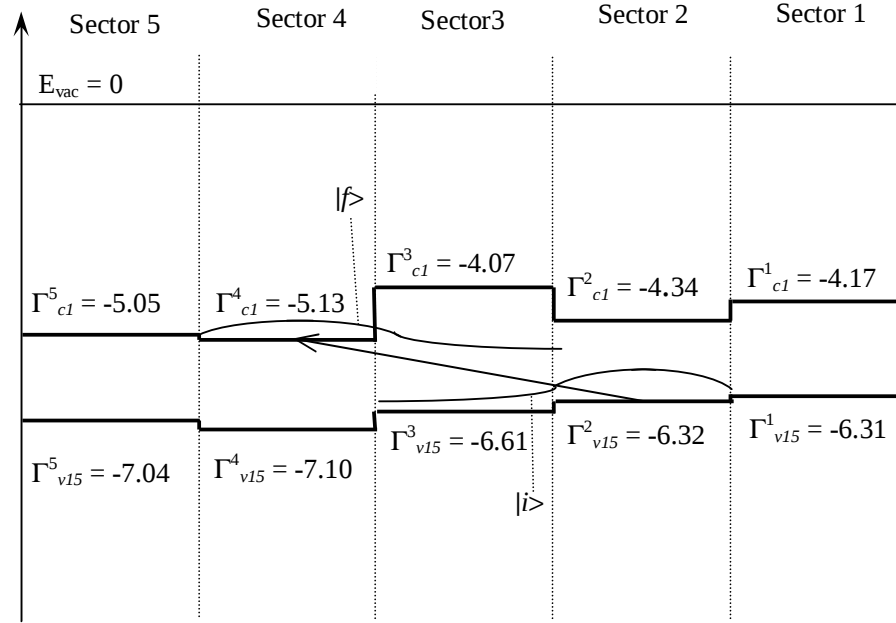


Fig. 2. Energy band-gap of InN containing oxygen.

5. Excitons in InN containing oxygen, and tunnel optical absorption in InN:In and InO_yN_{1-y}

The exciton ground state in InO_yN_{1-y} is formed by an electron occupying state Γ_{c1}^2 and a hole occupying state Γ_{v15}^1 (see Fig. 2). Using the method given in [10, 17], the hydrogen-like energy level E_n for the ground state ($n = 1$) is found to depend on the ratio between neighbouring O anions and neighbouring N anions surrounding the quasi-elementary cells of sector 2 of Fig. 2. It varies over the interval 0.84 – 1.01 eV. E_n determines the optical transitions connected with photon radiation due to annihilations between the electrons and the holes belonging to the exciton $\Gamma_{c1}^2 \leftrightarrow \Gamma_{v15}^1$ in InO_yN_{1-y}. The photo-luminescence rates depend on the number of excitons in the corresponding primitive super-cells. These are determined by experimental growth conditions and so have a strongly qualitative nature that cannot be expanded upon within the limits of this paper.

The tunnel optical absorption is introduced and explained in [17]. This phenomenon is responsible for the low energy optical absorption edge observed in samples of InN. According to both [17] and Fig. 1, tunnel optical absorption for InN:In appears between states Γ_{c1}^1 and Γ_{v15}^2 and it determines the energy band-gap $E_g = \Gamma_{c1}^1 - \Gamma_{v15}^2 = 0.2$ eV and the energy band-gap $E_g = \Gamma_{c1}^4 - \Gamma_{v15}^2 = \sim 1.19$ eV for InO_yN_{1-y} (Fig. 2). The energy range for InO_yN_{1-y} is close to the optical absorption edge for the Ioffe sample W431 [17], as shown in Fig. 3. Cornell samples follow a completely different relationship, as shown elsewhere [1]. At present, there are no reliable experimental data giving the optical absorption as a function of non-stoichiometry in InN. However, many experimentalists report an optical absorption edge in samples of InN below 0.6 eV, and the investigation of the optical properties of non-stoichiometric InN is in progress.

6. Conclusions

Transition energies in non-stoichiometric InN:In and in systems of InN containing oxygen have been characterised, and the energy band-gaps have been determined. They have been found to result in absorption properties in the same range as the recently-observed emission properties of MBE grown InN. It has further been shown that oxygen alloyed with InN (with the O substituting on

N sites as InO) has a lower band-gap for material with an oxygen content of the magnitude reported for RF sputtered InN. Thus, oxygen incorporated as an alloy species cannot be responsible for the 1.9 eV band-gap of the sputtered material.

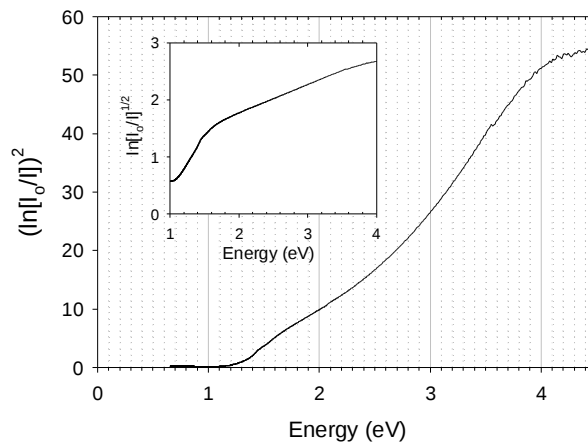


Fig. 3. The optical absorption edge in a sample of InN.

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