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Energy band gap and optical properties of non-stoichiometric InN—theory and experiment

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Abstract

The influence of antisite defects in InN is analyzed theoretically using a Linear Combination of Atomic Orbitals approach. The procedure used is validated by confirming the band gaps of common binary alloy semiconductor materials. InN with N_{In} and In_N antisite defects are then analyzed and it is found that in the case of InN:N_{In}, the excess nitrogen acts as a donor species with its level resident in the conduction band. For InN:In_N, it is shown that when there is a significant density of the excess indium present as the antisite defect, tunnel optical absorption should occur in the infrared at 0.2 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 [1–3]. It has been proposed that the low-energy features indicate a 0.7 eV band gap. However, the material has frequently been observed, and over a long period of time, to have an optical absorption band gap close to 1.9 eV. The discrepancy is not presently understood.

Proponents of the narrower gap have invoked a massive Moss–Burstein shift and/or the presence of large quantities of oxygen impurity to explain the wider gap. However, the former provides no explanation of the wide gap in a material of low carrier concentration, while an elementary consideration of Vegard's law indicates that oxygen levels in the higher band gap material are insufficient to account for the difference [4]. On the other hand, there are plausible allocations of the strong 0.7 eV optical feature to point-defect-related energy banding at about one-third band gap. The consequential sample inhomogeneity offers a strong possible explanation for the formation of this band.

Growth conditions are known not to favor stoichiometric InN. The equilibrium phase diagram does not show a cusped solidus close to the stoichiometric ratio as is commonly found in both III–V and II–VI inter-metallic binary semiconductors. In practice, InN growth always uses kinetic techniques in which the energetics do not inhibit antisite substitutional defects. We here report an investigation into the possibility that the 0.7 eV features arise as artifacts associated with very high densities of such defects. The approach, appropriate to such a configuration, is to treat InN as an alloy of the ideal stoichiometric compound and a "defect binary" consisting of InN containing both single In substitutions on N sites and single N substitutions on In sites.

The theoretical approach chosen describes interactions between atomic orbitals belonging to the nearest neighboring atoms and is based on the Hartree–Fock model of electron interactions. The one-electron Schrödinger equation describing the interaction between neighboring orbitals is derived and forms the basis for calculations of the energy terms of the valence electrons of the atoms

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belonging to the solid state. These energy terms are then used for calculation of the linear combination of atomic orbitals (LCAO) electron band structure of selected binary semiconductors and in particular is validated through calculation of the energy band gaps of InP, InAs, InSb, GaN and AlN which are experimentally non-controversial. The method is then applied to the calculation of the energy band gap of InN, both in its stoichiometric form and as the non-stoichiometric compound having high densities of single antisite substitutions. The optical properties of the non-stoichiometric InN are discussed on the basis of the calculated electron band structure.

2. Determination of the valence electron energies of atoms belonging to a tetrahedral cell in the solid state

A system containing two neighboring atoms in a tetrahedral cell connected by an ionic–covalent bond is investigated in the region where the electronic density has a high variation. The ionic–covalent bond is based on two hybrid orbitals belonging to the neighboring atoms engaged in the bond. Each hybrid orbital contains atomic orbitals defined for the isolated atom. In this paper, the hybrid orbital and its interactions are constructed under the following considerations:

(i) Only the atomic orbitals having radii greater than half of the inter-atomic distance and occupied by electrons participate in the formation of the hybrid orbital. These atomic orbitals are called valence atomic orbitals.
(ii) The electronic charge of an atomic orbital participating in the hybrid orbital is attracted by the electronic charge participating in the hybrid orbital of the other atom engaged in the bond.
(iii) The positive charges of the nuclei are equal to their valences.

The corresponding Schrödinger equation for the electron function of the hybrid orbital $\psi_i(\mathbf{r})$ $(i = a, c)$ is derived on the basis of the Hartree–Fock method, and conditions (i), (ii) and (iii) given above. It is

$$\left[-(1/2)\nabla^2 + U_i(\mathbf{r}) + \int \psi_i(\mathbf{r}')^*\psi_i(\mathbf{r}')/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' + \int \psi_j(\mathbf{r}')^*\psi_j(\mathbf{r}')/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' - \varepsilon_{\mathrm{cor}}\right]\psi_i(\mathbf{r}) - \int \psi_j(\mathbf{r}')^*\psi_i(\mathbf{r}')\psi_j(\mathbf{r})/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}' = \varepsilon_i'\psi_i(\mathbf{r}), \quad (1)$$

where $U_i(\mathbf{r})$ is the Coulomb potential of the ion occupying the i site, $\varepsilon_{\mathrm{cor}}$ the correlation energy, and ε_i' the electron energy term of the hybrid orbital engaged in the bond. The first integral is connected with the Coulomb repulsive potential of two electrons on the same ion site, the second integral is the corresponding potential of one electron on each site, and the third integral is the exchange potential. All of these integrals are two-center Coulomb integrals. The solution of Eq. (1) is connected with determination of the values of the following two-center Coulomb integrals:

$$V_i = \int \psi_i(\mathbf{r}')^*\psi_i(\mathbf{r})^*\psi_i(\mathbf{r}')\psi_i(\mathbf{r})/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\,d\mathbf{r}, \quad (2)$$

$$J_{ij}' = \int \psi_j(\mathbf{r}')^*\psi_i(\mathbf{r})^*\psi_j(\mathbf{r}')\psi_i(\mathbf{r})/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\,d\mathbf{r}, \quad (3)$$

$$K_{ij}' = \int \psi_j(\mathbf{r}')^*\psi_i(\mathbf{r})^*\psi_j(\mathbf{r})\psi_i(\mathbf{r}')/(1/|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}'\,d\mathbf{r}. \quad (4)$$

The main disadvantage of the energies represented in Eqs. (3) and (4) is that they do not take account of the overlap matrix element S. Considering S, we find

$$J_{ij} = J_{ij}'(1-2S^2)/(1-S^2), \quad (5)$$

$$K_{ij} = K_{ij}'(1-2S^2)/(1-S^2). \quad (6)$$

The first, second and the third terms of Eq. (1) determine the Hamiltonian of the isolated atom i $(i = a, c)$. The terms corresponding to Eqs. (5) and (6) are connected with the influence of valence electrons of the neighboring atom j $(j = c, a)$. Using Ref. [5], we find the numerical value of J_{ij}' to be given by

$$J_{ij}' \sim (V_a + V_c)/2. \quad (7)$$

The influence of the correlation energy on the energy ε_i' is represented by the term

$$\varepsilon_{\mathrm{cor}} \int \psi_i(\mathbf{r})^*\psi_i(\mathbf{r})\,d\mathbf{r} = \varepsilon_{\mathrm{cor}}N, \quad (8)$$

where N is the number of the covalent electrons in the region of interaction of two hybrid orbitals belonging to neighboring atoms.

3. Energy band gaps of InN, InP, InAs, InSb, GaN and AlN

The correlation energy $\varepsilon_{\mathrm{cor}}$ is determined by using Ref. [5] and the matrix element V_4 is determined as follows. According to Ref. [6], V_4 appears due to the interaction between two hybrid orbitals belonging to neighboring atoms. This matrix element is responsible [7] for the curves of the sub-bands corresponding to the top of the valence band and to the bottom of the conduction band. For the purposes of this paper, we consider V_4 not to contain terms resulting from the interaction between antibonding and bonding states, i.e., it is valid to write

$$V_4 = V_{4,\,\mathrm{bond}} + V_{4,\,\mathrm{a\text{-}bond}}, \quad (9)$$

where $V_{4,\mathrm{bond}}$ and $V_{4,\mathrm{bond}}$ correspond to interactions between the bonding and antibonding states, respectively. The determination of V_4 is made for InN, InP, InAs, InSb, GaN and AlN according to the following scheme:

(i) values of $V_{4,\mathrm{bond}}$ are taken from Ref. [6];
(ii) values of $V_{4,\mathrm{a\text{-}bond}}$ are calculated according to the rule