# Electron Band Structure of MnGaN

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## ABSTRACT

Investigation of the properties of $Mn_xGa_{1-x}N$ semiconductor alloy is performed on the basis of LCAO electron band structure of this semiconductor. The authors model this alloy on the basis of Mn substitutions on Ga sites and it is identified that the ternary semiconductor $Mn_xGa_{1-x}N$ has two tetrahedral binary constituents – GaN and MnN. It is found that the $sp^3$ hybrid orbital of the N atom attracts an electron from the 3*d* orbital of the Mn atom and thus the Mn-N bonding becomes of $sp^3$ type. In this way the total electron spin of the 3*d* orbital of the Mn atom becomes 3/2, which determines that the energy levels $^4F$, $^4D$, $^4P$ and $^4G$ belonging to this orbital to be occupied. LCAO electron band structure of wurtzite $Mn_xGa_{1-x}N$ for points $\Gamma^{\upsilon}_{c1}$ and $\Gamma^{\upsilon}_{v15}$ ($\upsilon$ = 1, 2, 3, 4, 5) is calculated by previously developed method and the positions of the levels $^4F$, $^4D$, $^4P$ and $^4G$ in this structure are determined. It is found dependence of the total electron spin of the Mn atom on the position of the Fermi level in the electron band diagram of $Mn_xGa_{1-x}N$. Also it is found that the total spin depends on electron inter-band transitions as well. The optical properties of the wurtzite $Mn_xGa_{1-x}N$ are determined as well.

## INTRODUCTION

The $Mn_xGa_{1-x}N$ semiconductor alloy is important for investigation due to expectations of unique properties. The alloys related to GaN show interesting optical properties such as both optical absorption and photo-luminescence spectra [1 – 6, etc.]. Especially it is valid for the semiconductor $In_xGa_{1-x}N$ that shows wide variation of the optical absorption edge due to existence of tunnel optical absorption and variation of the maximum of the PL spectrum due to excitons of the structure [7 – 9]. From other side the spin of the electrons belonging to 3*d* orbital of the Mn atom can be considered to be a precondition for magnetic properties of $Mn_xGa_{1-x}N$ with a possible application in the spintronics. It determines the scientific efforts for investigation of the impact of Mn atom, which substitutes on Ga site in the structure of $Mn_xGa_{1-x}N$ [10 – 14, etc.]. In this paper the authors present results of theoretical study of the properties of $Mn_xGa_{1-x}N$ based on its Linear Combination of Atomic Orbitals (LCAO) electron band structure. Investigation of the behavior of the 3*d* and 4*s* valence electrons of Mn atom substituting on Ga site in the structure of GaN crystal lattice is presented in terms of both creation of ion-covalent bonds and electron spin. Calculation of LCAO electron band structure of $Mn_xGa_{1-x}N$ is performed and the positions of the 3*d* electron levels of Mn atom are presented. Both the optical absorption edge and the maximum of the PL spectrum of $Mn_xGa_{1-x}N$ are determined. The total electron spin of the 3*d* orbital of the Mn atom is found and its dependence on the position of the

Fermi level is determined. The influence of the optical inter-band transitions on the total electron spin is discussed.

## RESULTS

The authors model the MnGaN alloy on Mn content. Segregated Mn species in wurtzite GaN containing Mn are not considered, only alloyed species with Mn substituting on the gallium site. For this arrangement a new ternary semiconductor $Mn_xGa_{1-x}N$ with $0 < x < 1$ is identified and it has two binary constituents – GaN (the existing binary crystal) and MnN that exists in the structure of $Mn_xGa_{1-x}N$. This condition allows the authors to introduce a primitive cell of binary constituent MnN satisfying the following conditions: a) Mn atom substitutes for a Ga atom saving the tetrahedral symmetry of the crystal cell; b) two of the valence electrons of isolated Mn atom occupy 4*s* orbital and other 5 valence electrons occupy $^6S$ level of the 3*d* orbital (according to Hund's rule the electron spin of the ground state $^6S$ is 5/2); c) the Mn-N bond is ion-covalent and it has tetrahedral symmetry. Using the conditions a), b) and c) the authors have found that the $2sp^3$ hybrid orbital of N atom attracts an electron from the $^6S$ level of the 3*d* orbital of neighboring Mn atom. The reason for this attraction is existence of polar energy between these neighboring orbitals that has value of -1.37 eV and it acts in direction to the $2sp^3$ hybrid orbital.

The charge transfer $\Delta Q$ from 3*d* orbital of the Mn atom to the $2sp^3$ hybrid orbital of the N atom is calculated by using the following expression, which comes from perturbation theory

$$\Delta Q = [2^{1/2} (-V_{sd\sigma} + 2*3^{1/2} V_{pd\sigma}) / 2]^2 / (\varepsilon_{2h} - \varepsilon_{3d})^2 \quad (1)$$

Where $\varepsilon_{2h}$ is the energy of the $2sp^3$ hybrid orbital, $\varepsilon_{3d}$ is the energy of the 3*d* orbital, and $V_{sd\sigma}$ and $V_{pd\sigma}$ are the matrix elements for interaction 2*s*-3*d* and σ-interaction 2*p*-3*d* respectively. It is found that the matrix element $V_{pd\pi}$ of π-interaction 2*p*-3*d* has negligible value if the interaction $2sp^3$-3*d* occurs in tetrahedral cell. (It has to be considered that 2*s* and 2*p* orbitals form the $2sp^3$ hybrid orbital.) It is found that the charge transfer is 0.83 electrons, which can be considered to be significant value determining in fact that one electron has been replaced from the 3*d* orbital of Mn atom to the neighboring $2sp^3$ hybrid orbital of the N atom. Two conclusions can be made on the basis of this result: *i)* the 3*d* orbital of Mn atom doesn't participate in Mn-N ion-covalent bond although this orbital provides an electron for this bond; and *ii)* the Mn-N ion-covalent bond is of $sp^3$ type and it takes place on the basis of two hybrid orbitals – $2sp^3$ of the N atom and $4sp^3$ of the Mn atom. For calculation purposes the authors have found the energy of the 4*p* orbital of Mn atom to be $\varepsilon_p$ = - 4.64 eV. (The Hartree-Fock method [15] has been used under consideration of Koiller-Falicov assumption [16], which has been applied in the case of 3*d*-4*p* interaction.)

LCAO electron band structure of wurtzite $Mn_xGa_{1-x}N$ for temperature 300K for points Γ are calculated by the previously developed method [7]. For the sake of simplicity the wurtzite $Mn_xGa_{1-x}N$ is 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 [7] that the electron energy in a primitive super-cell of the multinary crystal can be presented in the following way.

$$E(\mathbf{r}) = \sum_{\mathbf{q}} \boldsymbol{\delta}(\mathbf{r} - \mathbf{R}_{\mathbf{q}}) E(\mathbf{q}) \quad (2)$$

Where **r** is the radius-vector of the electron, E(**q**) is electron energy in the quasi-elementary cell **q** having radius-vector $\mathbf{R_q} = q_1\mathbf{a}_1 + q_2\mathbf{a}_2 + q_3\mathbf{a}_3$ ($\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the three basis vectors of the primitive super-cell), and $\boldsymbol{\delta}(\mathbf{r} - \mathbf{R_q})$ 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 both the optical absorption and the photoluminescence spectra for semiconductor compound alloys can respectively be taken as the 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 (determining corresponding sectors of the LCAO electron band structure – Fig.1) taken in the following order must be used for $Mn_xGa_{1-x}N$: *1*) pure GaN quasi-elementary cell surrounded by second neighboring Ga cations; *2*) mixed Mn-GaN quasi-elementary cell containing 1.5 atoms of Ga and 0.5 atoms of Mn surrounded by second neighboring Ga cations; *3*) mixed Mn-GaN quasi-elementary cell containing 1 atom of Ga and 1 atom of Mn surrounded by second neighboring Ga cations; *4*) mixed Mn-GaN quasi-elementary cell containing 0.5 atoms of Ga and 1.5 atoms of Mn surrounded by second neighboring Ga cations; *5*) pure MnN quasi-elementary cell surrounded by second neighboring Ga cations.

The LCAO electron band structure calculations for each quasi-elementary cell are performed by method given in [17]. The electron energy terms $\varepsilon_s$ and $\varepsilon_p$ for both N atom and Ga atom are taken from [18], and $\varepsilon_s$ for Mn atom is taken from [15]. The electron energy term $\varepsilon_p$ for Mn atom is determined above. The nearest-neighbor matrix elements are determined according to [17] and the inter atomic distance between Mn atom and N atom in the tetrahedral cell MnN is considered to be 2.08 Å. (This consideration is based on tetrahedral radii of both atoms N and Mn.) The calculated electron band structure is given in Fig.1 (not in scale).

The energy levels $\Gamma^{\upsilon}_{c1}$ and $\Gamma^{\upsilon}_{v15}$ are determined by taking the energy of the vacuum as being equal to zero. The energy difference $E^{\upsilon}_{g} = (\Gamma^{\upsilon}_{c1} - \Gamma^{\upsilon}_{v15})$ gives the energy band gap of sector $\upsilon$. The shifts of the boundaries of the energy band gaps in Fig.1, and the corresponding energy intervals are due to defects in the crystal lattice of $Mn_xGa_{1-x}N$ – i.e. the existence of two sorts of atoms on cationic sites. The nature of these shifts is different from the nature of the shifts of the boundaries of the energy band gap described in [19, 20].

In fact the Mn atom substituting on Ga site becomes $Mn^{3+}$ ion. The charge transfer between 3*d*-orbital of Mn atom and $2sp^3$- hybrid orbital of the N atom is almost one electron and as result the part of the valence electron cloud of Mn atom is replaced in direction to N atom, i.e. donor behavior can be expected from the alloyed Mn atoms. From other side only four electrons remain on 3*d* orbital of the Mn atom and according to Hund's rule the total electron spin becomes 3/2 rather than 5/2 and the corresponding states have, by the same rule, higher energy. There are four such states of varying orbital angular momentum designated by $^4G$, $^4P$, $^4D$ and $^4F$ that have energies -7.36 eV, -6.99eV, -6.37 eV and -4.74eV respectively. (The energy of the ground state $^6S$ is -10.24 eV.) All energy states are shown in Fig.1 as well. These energy states are not engaged in the ion-covalent bonds and they act as impurity states. Normally these states

are occupied by electrons. However these occupancies depend on the position of the Fermi level. It is most of all valid for levels $^4D$ and $^4F$ that are in the energy band gap. The levels $^4G$ and $^4P$ are in the valence band and their ionization energies are less than zero. It means a partial empty valence band can cause electron transitions from these levels. All of the above facts determine that the total electron spin depends on both the position of the Fermi level and the inter-band electron transitions in the semiconductor $Mn_xGa_{1-x}N$.

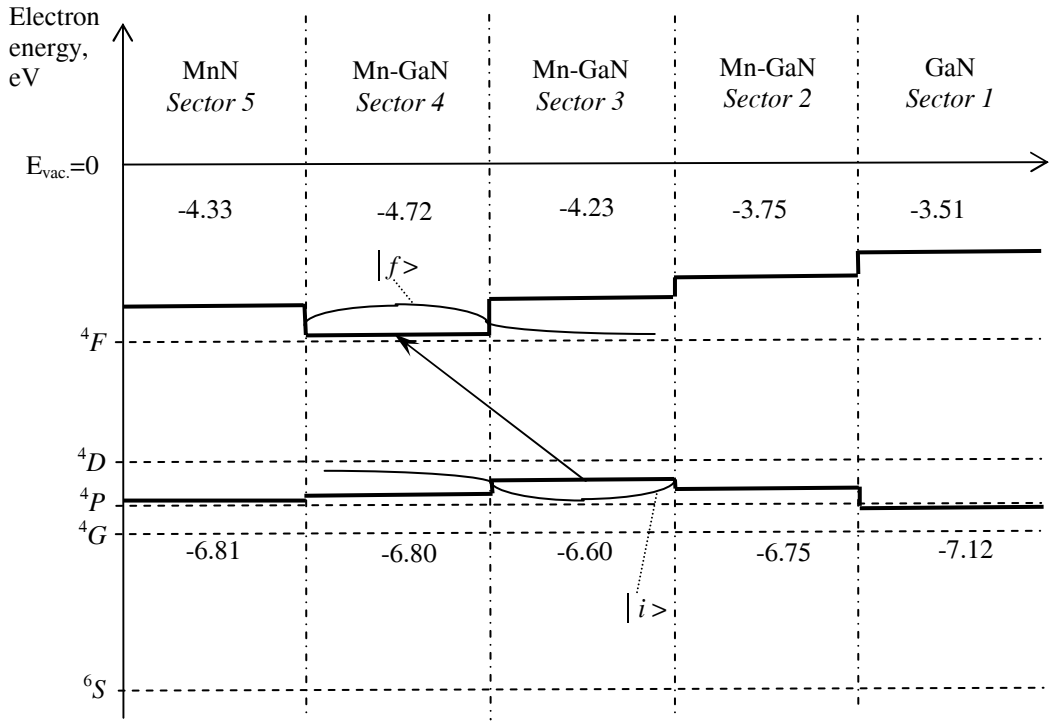


Fig. 1

## DISCUSSION

The tunnel optical absorption is investigated in details in [8, 9]. The basis of this phenomenon is the overlapping between the electron wave function $|i>$ of the initial electron state and the electron wave function $|f>$ of the final electron state in term of optical transition. Part of the graphics of Fig.1 provides the electron wave functions of the initial state $|i>$ and of the final state $|f>$ for $Mn_xGa_{1-x}N$ (it is important to be noted that the state $|i>$ is an electron state). Investigation of the calculated electron band structure (Fig.1) shows the following features: *a)* Tunnel optical absorption ($\Gamma^3_{v15} \rightarrow \Gamma^4_{c1}$) determines optical absorption edge for photon energies ~1.88 eV (shown in Fig.1). The experimentally observed optical absorption edge is ~1.50 eV in the samples of $Mn_xGa_{1-x}N$ without silicon impurities; *b)* Maxima of the PL spectra can be observed for energies 2.08 eV and 2.37 eV that are close to the experimental value of 2.20

eV, and ~2.48 eV, which is close to the experimental value of 2.70 eV. The exact value of the PL peak depends on the technological circumstances of the ratio Mn:Ga forming mixed quasi-elementary cells in the structure of $Mn_xGa_{1-x}N$.

As it was mentioned above the states $^4G$, $^4P$, $^4D$ and $^4F$ behave as impurity states and normally they are occupied. From other side the electrons occupying these states form the total spin. The states $^4D$ and $^4F$ are in the energy band gap and their occupancy is sensitive on the position of the Fermi level. It means the total spin is subject of change if the Fermi level crosses the states $^4D$ and $^4F$. The same phenomenon can be observed for states $^4G$ and $^4P$ if the layer of $Mn_xGa_{1-x}N$ contains high concentration of acceptor impurities and the Fermi level penetrates into the valence band. However the most important influence of states $^4G$ and $^4P$ can be expected if optical phenomena are considered. In fact both states can provide electrons for the valence band if the last one is partial empty. The electron transitions from states $^4G$ and $^4P$ into the valence band of $Mn_xGa_{1-x}N$ change the total spin. The occupancy of the valence band is connected with optical transitions between this band and the conduction band. It means both phenomena – optical absorption and photo-luminescence – are directly related to the total electron spin.

## CONCLUSIONS

The obtained results show presence of electron impurity states of the Mn atom in the valence band and in the energy band gap of $Mn_xGa_{1-x}N$. These energy states form the total spin. However from other side their occupancy in term of electrons depends on position of the Fermi level and on optical inter-band transitions. It means it could be expected that the magnetic properties of layers of $Mn_xGa_{1-x}N$ depend on the carrier concentrations and on optical phenomena in these layers. The obtained results can be used for further investigation of the properties of $Mn_xGa_{1-x}N$ and for design of spintronic devices.

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