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# Research on electronic structure and optical properties of Mg doped $Ga_{0.75}Al_{0.25}N$

Mingzhu Yang [a], Benkang Chang [a,*], Guanghui Hao [a], Feng Shi [b], Honggang Wang [a], Meishan Wang [c]

[a] Institute of Electronic Engineering and Optoelectronic Technology, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Key Laboratory of Low Light Level Technology of COSTIND, Xi'an 710065, China
[c] School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China

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ABSTRACT

In order to study the influence of Mg doping on the electronic structure and optical properties of wurtzite $Ga_{0.75}Al_{0.25}N$ and the hydrogen passivation of Mg-doped $Ga_{0.75}Al_{0.25}N$, models of $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$, $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$ and $Ga_{0.6875}(MgH)_{0.0625}Al_{0.25}N$ are built. Based on first principle calculation, the atomic structures, band structure, Mulliken population, and optical properties of the Mg doped and Mg–H co-doped crystals are obtained. Results show the formation energy of Mg–H complex is smaller than that of only Mg doping in the material. The Fermi levels of the two Mg doped crystals enter into the valence bands and Mg doping makes the crystals turn into p-type degeneracy semiconductors. Meanwhile, the Fermi level goes back to the gap between conduction band and valence band in the Mg–H co-doped model. The Mulliken charge of Mg atom decreases after adding the H atom, showing that hydrogen results in the passivation and weaker ionicity of the Mg impurity. After Mg doping, the first dielectric peak shifts to lower energy since the Al:3p and Ga:4p state in the conduction band move to the range of lower energy. The metal reflective region of the semiconductor also shift to lower energy range after My doping. Mg doping enhances the absorption coefficient at the range of 1.05–3.47 eV while weakens it at the range of the 10.00–20.00 eV.



## 1. Introduction

GaAlN based ultraviolet (UV) emitters and detectors have been used in large varieties of novels applications such as free space communications, medical diagnostics, biochemical agent detection, disinfection and sterilization [1]. GaAlN-based photocathodes possess negative electron affinity (NEA), low dark current, high response speed, and sharp cutoff frequency, so they are currently attracting extensive attention [2]. Many research groups have prepared GaAlN photocathodes with high quantum efficiency based on good preparation technologies [3,4], in which controllable doping is particularly essential. Various metal contacts were applied to p-type GaN and GaAlN, such as Au [5,6], Ni [5], Ti [5], and Mg [6], in which Mg is the favorable element for preparation of GaN and GaAlN photocathodes. There are strong experimental results given by Nakamura et al. [7] indicating that hydrogen plays a crucial role in the passivation of Mg acceptors in GaN. Van Vechten et al. [8] propose the incorporation (and subsequent removal) of hydrogen as a general method for improving p-type doping of wide band gap semiconductors. In the recent years, researches on Mg doped GaAlN photocathodes mainly concentrate on the doping process and photoemission property, but the influence of Mg doping on electronic structure and optical properties of GaAlN photocathodes is few, nor the research of hydrogen passivation mechanism in Mg-doped GaAlN.

In this paper, based on density function theory (DFT), the formation energy, atomic structure, electronic structure, and optical properties of Mg doped $Ga_{0.75}Al_{0.25}N$ are calculated. And the influence of hydrogen passivation in the Mg doped $Ga_{0.75}Al_{0.25}N$ is discussed. The work has profound guiding significance for experimental research of Mg doped GaAlN photocathodes.

## 2. Theoretical model and calculation method

Wurtzite GaN belongs to the P63mc(186) space group; symmetry is C6v-4, the lattice constant is $a = b = 0.3189$ nm, $c = 0.5185$ nm, and $\alpha = \beta = 90°$, $\gamma = 120°$ [9]. $Ga_{0.75}Al_{0.25}N$ models are obtained by substituting 25% Ga atoms for Al atoms based on GaN crystals. In the GaN($2 \times 2 \times 2$) supercell model shown in Fig. 1(a), there are 16 Ga atoms. So there are $C_{16}^2$ kinds of schemes for building $Ga_{0.75}Al_{0.25}N$ ($2 \times 2 \times 2$) supercell model. The model where Al atoms are located in the para-position of the adjacent two layer is energetically favorable [10], which is shown in Fig. 1(b). As the radius of Mg atom is similar to those of the Ga and Al atoms, so it was thought that the Ga and Al atoms can be

* Corresponding author. Tel.: +86 18066086052; fax: +86 025 84315177.
*E-mail address:* bkchang@mail.njust.edu.cn (B. Chang).

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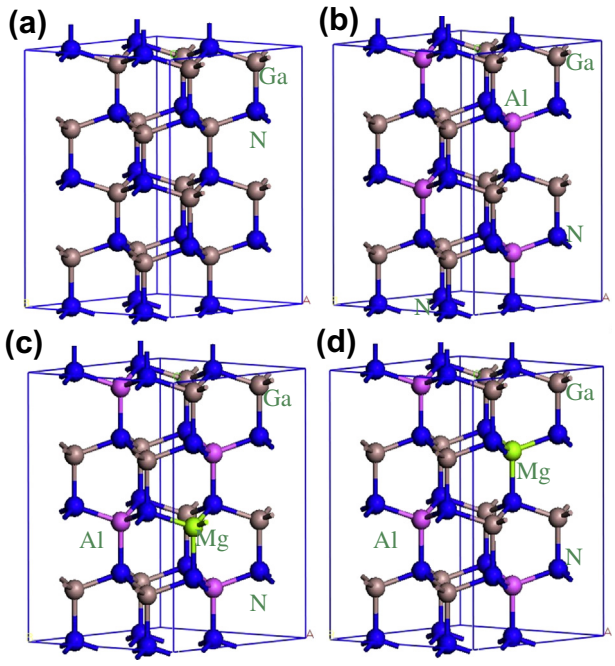


**Fig. 1.** Computational models (a) GaN($2 \times 2 \times 2$), (b) $Ga_{0.75}Al_{0.25}N(2 \times 2 \times 2)$, (c) $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$ and (d) $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$.

replaced by Mg atoms, and the Mg atoms exist in $Ga_{0.75}Al_{0.25}N$ crystals as substitutional dopants. The Mg doping models were obtained based on $Ga_{0.75}Al_{0.25}N$ ($2 \times 2 \times 2$) supercell. The $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$ crystal is obtained by substituting Ga atom with Mg atom, and the $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$ crystal is obtained by substituting Al atom with Mg atom. For the two Mg-doped models, the positions of Mg atoms are chosen based on the principle of lowering total energy. The models of $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$ and $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$ are shown in Fig. 1(c and d). There are 11 Ga atoms, 4 Al atoms, 1 Mg atom, and 16 N atoms in the model of $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$, and there are 12 Ga atoms, 3 Al atoms, 1 Mg atom, and 16 N atoms in the model of $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$.

As the radius of H atom is very little, it exists in GaAlN as interstitial impurity. Hydrogen can occupy for high-symmetry sites surrounding the Ga(Mg) atom, two bond centering sites (BC) and two anti bonding sites (AB), as shown in Fig. 2. In this work, four

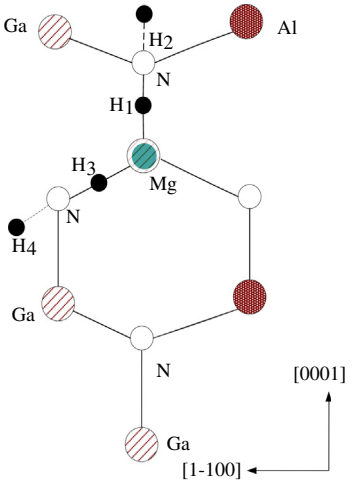


**Fig. 2.** Possible hydrogen sites surrounding Ga(Mg) atom in the (11–20) plane of wurtzite $Ga_{0.75}Al_{0.25}N$(BC//:$H_1$, BC⊥:$H_3$, AB//:$H_2$, AB⊥:$H_4$).

models of $Ga_{0.6875}(MgH)_{0.625}Al_{0.25}N$ corresponding to four different positons of H atom are built. For every model, there are 11 Ga atoms, 4 Al atoms, 1 Mg atom, 1 H atom, and 16 N atoms.

All calculations were performed with the quantum mechanics program of CASTEP [11] based on density function theory (DFT). The *Broyden Fletcher Goldfarb Shanno* (BFGS) algorithm was used to optimize the structures of the crystal models. The final sets of energies were computed with an energy cutoff of 500 eV after a series of convergence test. The convergence was set to energy change below $2 \times 10^{-6}$ eV/atom, force less than 0.005 eV/nm, the convergence tolerance of a single atomic energy below $1 \times 10^{-5}$ eV/atom, stress less than 0.05GPa, and change in displacement less than 0.0001 nm. The calculations were carried out with a plane-wave pseudo potential method based on DFT combined with the generalized gradient approximation (GGA) [12,13]. In this calculation, the GGA was parameterized by Perdew, Burke, and Ernzerhof (PBE) [12,13]. The integral in the Brillouin zone was sampled with the Monkhorst–Pack [14] scheme and special $k$ points of high symmetry. The number of k points is $9 \times 9 \times 9$ in the calculation. All calculations were carried in reciprocal space with Ga:$3d^{10}4s^24p^1$, Al:$3s^23p^1$, N:$2s^22p^3$ and Mg:$2p^63s^2$ as the valence electrons. The underestimation for the band gap by GGA was corrected by scissor approximation technique (SAT) [15,16], which amounts to a rigid shift to the conduction band states so that the experimentally reported gap is well reproduced and the accuracy of the optical properties was improved.

## 3. Results and discussion

### 3.1. Formation energies

The formation energy $E_{formation}$ determines the concentration $c$ of the impurity in the semiconductor through the expression [17]:

$$c = N_{sites} \exp(-E_{formation}/k_B T) \tag{1}$$

where $N_{sites}$ is the number of sites in the lattice(per unit volume) in which the impurity can be incorporated, $k$ represents Boltzmann's constant, and $T$ is the temperature. Eq. (1) in principle holds only in the thermodynamic equilibrium. However, growth of a semiconductor is obviously a nonequilibrium process. Furthermore, even in nonequilibrium conditions the formation energy of an impurity is a useful concept, since configurations with high formation energies will obviously be difficult to incorporate. The higher the formation energy is, the lower the concentration of the impurity is. The formation energies of $Mg_{Ga,}$ $Mg_{Al}$, H, and Mg–H complex are defined as [17]:

$$E_{form}[Mg_{Ga}] = E_{tot}[Ga_{0.6875}Mg_{0.0625}Al_{0.25}N] - E_{tot}[Ga_{0.75}Al_{0.25}N] - \mu_{Mg} + \mu_{Ga} + qE_f \tag{2}$$

$$E_{form}[Mg_{Al}] = E_{tot}[Ga_{0.75}Mg_{0.0625}Al_{0.1875}N] - E_{tot}[Ga_{0.75}Al_{0.25}N] - \mu_{Mg} + \mu_{Al} + qE_f \tag{3}$$

$$E_{form}[H] = E_{tot}[Ga_{0.75}Al_{0.1875}N(H)] - E_{tot}[Ga_{0.75}Al_{0.25}N] - \mu_H + qE_f \tag{4}$$

$$E_{form}[(Mg-H)_{Ga}] = E_{tot}[Ga_{0.6875}(Mg-H)_{0.0625}Al_{0.25}N] - E_{tot}[Ga_{0.75}Al_{0.25}N] - \mu_H - \mu_{Mg} + \mu_{Ga} + qE_f \tag{5}$$

where $E_{tot}[Ga_{0.75}Al_{0.25}N]$, $E_{tot}[Ga_{0.6875}Mg_{0.0625}Al_{0.25}N]$, and $E_{tot}[Ga_{0.75}Mg_{0.0625}Al_{0.1875}N]$ represent the total energies of $Ga_{0.75}Al_{0.25}N$, $Ga_{0.6875}Mg_{0.0625}Al_{0.25}N$, and $Ga_{0.75}Mg_{0.0625}Al_{0.1875}N$ respectively. $\mu_{Ga}$, $\mu_{Al}$ and $\mu_{Mg}$ are the chemical potentials of Ga, Al, and Mg respectively, $q$ represents the charge state of the Mg acceptor, and $E_f$ represents Fermi level. When the Fermi level is set as 0 eV,