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A computational study of magnetic exchange interactions of 3d and 4f electrons in Ti-Ce co-doped AlN

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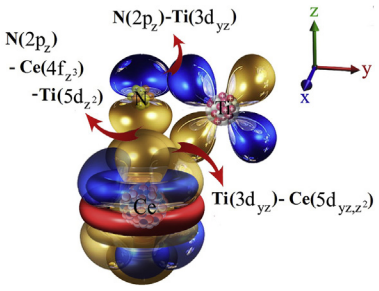
HIGHLIGHTS

- Double exchange interaction in Ti:AlN.
- Impurity induced narrowing of band gap.
- Superexchange interaction in Ce:AlN.
- 3d-4f exchange interaction between Ti-3d and Ce-4f states.
- High Curie temperature n-type ferromagnetic semiconductors.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the nature of 3d-4f exchange interactions in III-Nitride semiconductors, Ti-Ce co-doped AlN were studied using first principles calculations. The calculations were performed using supercell approach with varying dopant concentration and different inter-dopant separation. The configuration with dopant located as nearest neighbor distance and diluted concentration of 3.125% was found most stable. The results exhibited prominent evidence of 3d-4f-5d strong hybridization suggesting 3d-4f direct exchange interactions which may play valuable role to exploit the system as high Curie temperature ferromagnetic semiconductors for use in spintronics. Moreover, metal to metal charge transfer was also observed in the materials which may be exploited for their use in electrochemical applications. The 4f-5d and 3d-5d hybridizations were observed that predicts excellent luminescence phenomena in the materials. The presence of impurity related deep intermediate bands suggest applications of the materials in opto-electronic and spintronics devices.

1. Introduction

Diluted magnetic semiconductors (DMSs) based on transition metals (TM) and rare earth metals (RE) doped elements have a good control on both charge and spin of electron simultaneously. These materials are suitable for use in spintronics devices such as spin LEDs, spin FETs, magnetic tunnel junctions, spin based quantum dots, magnetic random access memory (MRAM) resonant tunneling diodes and magnetic memory storage devices. Dietl et al. theoretically predicted that DMS based on compound semiconductors can provide ferromagnetic materials having high Curie

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temperature [1,2]. It attracted rich scientific attention and researchers attempted to explore many new materials including GaAs, InAs, GaN, AlInN, AlN, ZnO, TiO_2, $SnAs_2$ etc to search for robust ferromagnetism [3–9].

TM and RE doped compound semiconductors have been widely studied due to their potential in devices. DMS based on III-Nitrides compound semiconductors, especially TM:AlN and TM:GaN, proved to be significant materials [9–15]. These materials, due to possibility of ferromagnetism well above room temperature and availability of existing technology base for their applications in devices, are promising materials for spintronics. Recently AlN, which is a one of widest direct band gap semiconductor (6.28 eV at room temperature), has earned focal research interest due to its numerous applications in thin film gas sensors, heat spreaders, heterojunction diodes, micro-electro-mechanical systems, UV light emitting diodes, opto-electronics and spintronics devices [11–16]. After its first synthesis in 1928, AlN is now available in excellent crystalline quality and is renowned due to its superb thermal conductivity, high elastic modulus and great temperature stability, good thermal conductivity and nontoxic nature [22]. From view point of AlN based DMSs, several theoretical and experimental efforts exhibiting Curie temperature above room temperature have been reported including Cr:AlN, Mg:AlN, Cu:AlN [6,14–22]. D. Kumar et al. reported ferromagnetism in $Al_{1-x}Cr_xN$ thin films prepared using reactive co-sputtering and observed Curie temperature above 900 K at 2.7% Cr concentration [19]. The first principles calculations performed for Cr, Mn and Fe doped AlN demonstrated ferromagnetism in the materials [20]. Recently experimental findings on Cu-doped AlN single crystal whiskers were found consistent with the first-principles calculations and suitable magnetic properties were observed [21]. However, no prominent evidence was found for ferromagnetism due to the substitutional doping of these dopants in the host matrix is yet to be established and usually the problem of dopant precipitation/clusters/secondary phases is faced. In some TM doped AlN high Curie temperature was observed due to the nanoscale clustering of magnetic atoms [23].

The attempts have been reported to dope AlN with whole series of 3d TMs and 4f REs by different groups. RE elements having unfilled 4f shell are interesting because of their screening effects but are comparatively less studied as impurities in AlN [24–30]. The electronic and optical properties studied using first principles calculations for Tm:AlN have been reported [26,30]. Dridi et al. reported electronic and magnetic properties of Eu doped cubic AlN [27]. Recently A. Dar et al. suggested Ce:AlN to be a resourceful DMS [31].

The 3d-4f exchange interactions are weaker than 3d-3d due to strongly localized nature of 4f orbitals in RE atoms. These weak exchange interactions are however important for magnetic materials. Campbell was the first to propose a model for explaining 3d-4f interactions and afterwards Brooks developed it by explaining how 4f localized electrons polarize 5d states which interact with 3d orbitals [33]. 3d-4f compound and alloys are very important for realizing permanent magnets but rare investigations have been made on study of simultaneous doping of 3d and 4f ions. Few latest researches relevant to 3d-4f co-doped semiconductors are Mn-Nd co-doped ZnO [32], Eu-Co co-doped ZnO [34], Mn-C co doped GaN [35] and Cr-Nd co-doped GaN [36] however no such study has yet been reported for AlN. The study of 3d-4f exchange interactions may not only shed light to understand underlying mechanism of ferromagnetism but also explore further potentials of AlN. In order to carry out the task, we doped AlN with Ti-Ce pair having $3d^1$-$4f^1$ configuration and carried out systematic first principles calculations.

2. Computational detail

The calculations presented herein are based on density functional theory implemented in ADF-BAND package which employs linear combination of atomic orbitals. Thermodynamically stable wurtzite structure for AlN was considered for the calculations [12] and the studied configurations include 32 and 64 atoms supercells in which Al atoms were substitutionally replaced by Ti and Ce dopants. The respective substitution of the dopants provides impurity concentration of 6.25% and 3.125% in the matrix. Ti or Ce atoms as substitutional dopant in AlN supercell are symbolized as Ti_{Al} and Ce_{Al} respectively [4]. Monkhorst Pack Mesh of $2 \times 2 \times 2$ was used. The configurations studied consisted of 32-atoms supercells AlN in the form of pure AlN having unit cell formula of $Al_{16}N_{16}$, Ti doped AlN denoted by unit cell formulae of $Al_{15}Ti_1N_{16}$ and $Al_{14}Ti_2N_{16}$, Ce doped AlN with unit cell formula of $Al_{15}Ce_1N_{16}$ and Ti-Ce co-doped AlN representing by unit cell formula of $Al_{14}Ti_1Ce_1N_{16}$. For study of low doping concentration of 3.125%, a $2 \times 2 \times 4$ supercell of 64 atoms was simulated with unit cell formula $Al_{30}Ti_1Ce_1N_{32}$. To explore the effect of dopant location on exchange interaction, we studied two types of configurations with variable Ti_{Al}-Ce_{Al} separation; first at nearest neighboring position with $d_{Ti\text{-}Ce}$ ~2.9 Å and second at next neighboring position with $d_{Ti\text{-}Ce}$ ~ 5.6 Å. TZ2P basis sets were used and all calculations were performed with GGA-PBE exchange functional [37–39]. To overcome inevitable limitation of GGA functional, Hubbard correction U parameter was also employed (4.4 eV for Ti and 5.4 eV for Ce) to improve 3d-4f exchange interactions in TMs and REs co-doped compound [40–42]. The calculations were self consistent with all configurations fully relaxed starting from experimental lattice constants a = 3.11 Å and c = 4.98 Å [43,44] and the energy convergence criteria was 10^{-5} eV. The frozen core approximation was used and Al [$3s^2$ $3p^1$], N [$2s^2 2p^3$], Ti [$4s^2 3$ d^2] and Ce [$4f^1 5d^1 6s^2$] were treated as valence electronic configurations.

3. Results and discussion

This study involves detailed calculations of pure AlN, Ce:AlN, Ti:AlN and Ti-Ce:AlN in FM, AFM configurations at varying inter-dopant separation and varying dopant concentration using GGA and GGA + U. However the findings related to Ti-Ce:AlN are described in the following sections.

3.1. Structural of the materials

WZ-AlN co-doped with Ti and Ce in the form of unit cell $Al_{14}Ti_1Ce_1N_{16}$ was studied using GGA and GGA + U. Ti and Ce are substitutionally doped at the cationic Al-sites with separation $d_{Ti\text{-}Ce}$ equal to 2.923 Å (nearest neighbor distance) and 5.697 Å (next nearest neighbor distance) as shown in Fig. 1. The dopants located at Al-sites caused elongation of lattice parameters c and a to 5.245 Å and 3.131 Å (for nearest neighbor) and 5.180 Å and 3.128 Å (for next nearest neighbor) respectively.

The solubility and stability of the dopant in host matrix is predicted using formation energy of the doped material. The calculated value of formation energy for Ti-Ce codoped AlN with dopants at nearest neighboring positions ($E_f = -237.73$ eV) is smaller than that of dopants at next neighboring positions ($E_f = -230.68$ eV) which indicates the comparative stability of this configuration. It agrees with recent study exhibiting the dopants sited at nearest neighboring positions as preferred and stable configuration [35].

3.2. Electronic properties

The substitutional dopants related to TM and RE metals appear