Improving optical properties of wurtzite GaN with C and Fe co-doping: A DFT+U study

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Abstract

Density Functional Theory with Hubbard U parameter (DFT + U) was used to study the impact of C (6.25%) and Fe (12.5%) mono- and co-doping on wurtzite GaN, which modified the structural, electrical, magnetic, and optical properties. Under conditions of abundant N, the doping effect led to an increase in thermodynamic formability. For all the dopant combinations, a reduction in the bandgap was seen. GaN becomes a ferrimagnetic material because of co-doping. The performance of the C and Fe co-doped GaN was the best due to the redshift of the absorption edge, which resulted in the improved absorption of near ultraviolet (UV) and visible-infrared (VIS-IR) photonic energies for both monodoping and co-doping structures. The doping caused an increase in the refractive index and dielectric constant. For C and Fe co-doped GaN, the maximum static dielectric constant and refractive index were 19.58 and 4.45, respectively. The findings of this work therefore point to the possible use of C, Fe mono- and co-doped GaN in UV, IR optoelectronic and photonic devices.

1. Introduction

Gallium Nitride is an III-V wide direct bandgap semiconductor. Due to its high strength of bonds, large bandgap, high thermal conductivity, high heat capacity, chemical stability, energy efficiency, and cost-effectiveness, it is widely used in high power and frequency devices [1], optoelectronic devices [2], spintronics [3], solar cells [4], LEDs [5], heterojunction field-effect transistors (HFETs) [6], photonic crystals [7], biological sensors [8] and spin lasers [9]. GaN semiconductor devices have been a prominent technology in terms of UV photodetection. UV photodetectors (UV PDs) convert UV optical signals into electronic signals. GaN being a wide bandgap semiconductor (∼ 3.44 eV) can operate at room temperature, minimizing the heat loss with the capacity to filter the visible range energy which is highly expected for UV PDs [10]. Again, day by day the requirement for UV lasers with much shorter wavelengths is increasing and the use of wide bandgap semiconductor is becoming very essential [11, 12]. Researchers are studying the potential uses of GaN for both wurtzite and zinc blende phases experimentally and theoretically. Due to the thermodynamic stability of wurtzite GaN [13, 14], our research interest grew more to widen the optoelectronic applications of the wurtzite phase by the means of doping.

Dopants play a significant role in tuning the electronic, magnetic, and optical properties of semiconductor and magnetic devices. For example, a recent study shows that rare-earth element doping in GaN provides superior conductivity for various solar cell and optoelectronic uses [15]. Moreover, doping with Rh and Pt also enabled GaN semiconductor to act as a potential catalyst in photocatalysis reaction of CO₂ [16]. So, the strategies for effective doping in semiconductor devices to obtain desired properties have been a sought-after topic among researchers for the past decades till today. Co-doping has been a functional strategy in semiconductor physics as it increases dopant stability and carrier mobility [17]. It also tailors the electronic structure [18], induces magnetic properties [19], and provides better photoelectrochemical activity [20] than mono-doped materials. Recently transition metals are doped in GaN to sense industrial toxic gases [21]. Transition metals are also doped in wide bandgap semiconductors to seek room
temperature ferromagnetism along with superior optoelectronic properties [22–25]. Much research is done with wide bandgap dilute magnetic semiconductors for spintronic applications. In addition, Abdalla et al [26] mentioned in their study the prospect of carbon co-doping with transition metals to obtain room-temperature ferromagnetic properties. Enhanced optoelectronic property along with stable magnetism was obtained when carbon was co-doped with various transition metals [27–32]. Mounkachi et al [29] performed a first principle study by co-doping GaN with C and Fe to study the electronic and magnetic properties. Their results significantly vary from ours. Along with assessing electronic and magnetic property, we intended to focus more on the optical properties for C and Fe co-doping which was not studied yet to date. So, we performed DFT + U calculation by the CASTEP code to investigate the co-doping and monodoping effect of carbon and iron on the structural, electronic, magnetic, and optical properties.

This paper is organized into three sections. Section I provides the introduction of our research study, section II elucidates the computational methodology and section III encompasses the results and discussions of the structural, electronic, magnetic, and optical properties for potential applications in optoelectronics.

2. Computational method

In this work, calculations were performed using Cambridge Serial Total Energy Package (CASTEP) [33] code with DFT-based plane-wave pseudopotential [34, 35]. The structure optimization and property calculation were performed using generalized gradient approximation (GGA) with Perdew- Burke-Erenzerhof (PBE) function to deal with the exchange-correlation of electrons [36]. Vanderbilt-type ultrasoft pseudopotential was used to
account for the interaction between ions and electrons [37]. The GGA + U approach with the spin-polarized method was applied for both geometry optimization and property calculations since the GGA approach significantly produces incorrect results compared to experiments [38]. The Hubbard U parameter for N p-orbital and Fe d-orbital was 5 eV and 4.6 eV [39] respectively. For the computation of both geometry and property, plane wave kinetic energy cut off was 460 eV. 4 × 4 × 2 and 7 × 7 × 4 k point grids were chosen for relaxation and property calculation respectively according to the Monkhorst–Pack scheme [40]. The SCF tolerance was 5 × 10^{-5} eV/atom. The relaxation for lattice constants and position of atoms were terminated according to the Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS) when maximum energy change, the maximum force of the atom, maximum stress, and maximum displacement reached 1 × 10^{-5} eV atom^{-1}, 0.03 eV Å^{-1}, 0.05 GPa, and 0.001 Å respectively.

A supercell of 2 × 2 × 2 configuration is built containing 32 atoms which are adequate for substitutional doping. The structures are shown in figure 1. For mono-doped Ga_{16}C_{1}N_{15} (figure 1(a)) and Ga_{14}Fe_{2}N_{16} (figure 1(b)), one C atom replaced one N atom (6.25% doping concentration) and two Fe atoms replaced two Ga atoms (12.5% doping concentration) respectively. The co-doped structure, Ga_{14}C_{1}Fe_{2}N_{15} (shown in figure 1(c)) is built replacing one N atom with one C atom and two Ga atoms with two Fe atoms to obtain 6.25% C concentration and 12.5% Fe concentration. Five configurations were chosen wherein each configuration parallel and anti-parallel spin alignments were calculated representing the ferromagnetic and antiferromagnetic states of the co-doped structure respectively. The energy difference between ferromagnetic and antiferromagnetic states is calculated. If the energy difference is positive and more than 30 meV, then the antiferromagnetic structure is stable at room temperature (by mean-field approximation) [41]. In our study, the stable structure of Ga_{14}C_{1}Fe_{2}N_{15} is configuration 1 with the anti-parallel spin arrangement of the Fe atoms. The mean-field approximation to obtain the stable magnetic structure by calculating the energy differences and the

| Material                  | Mulliken charge | Mulliken charge | Mulliken charge | Mulliken charge |
|---------------------------|-----------------|-----------------|-----------------|-----------------|
| GaN                       | 1.15            | −1.15           | —               | —               |
| C doped GaN               | 1.03 (−1.11)    | −0.99           | —               | —               |
| Fe doped GaN              | 1.14 (−1.07)    | —               | 0.81            | 0.81            |
| C-Fe co-doped GaN         | 1.09 (−1.06)    | −0.92           | 0.71            | 0.82            |

Table 2. Mulliken charge of the compounds.

| Configuration | Fe-Fe distance (Å) | ΔE = E_{FM} − E_{AFM} (meV) |
|---------------|--------------------|-------------------------------|
| 1             | 3.216              | 360.9                         |
| 2             | 3.211              | 182.2                         |
| 3             | 4.545              | −2.1                          |
| 4             | 5.240              | 29.2                          |
| 5             | 6.148              | 5.49                          |

Table 3. Fe-Fe distance in Angstrom (Å) and Energy differences between parallel and anti-parallel spin arrangement for 5 configurations of the C-Fe co-doped GaN supercell.

Table 4. Formation energies (E_{f}) for the compounds under Ga and N-rich conditions.

| E_{f} (formation energy) | Ga-rich (eV) | N-rich (eV) |
|--------------------------|--------------|-------------|
| C doped GaN              | 2.67         | −2.32       |
| Fe doped GaN             | 5.56         | −1.51       |
| C-Fe co-doped GaN        | 7.82         | −1.23       |
Figure 2. (a) Band Structure of C-doped GaN, (b) DOS of C-doped GaN, (c) Band Structure of Fe-doped GaN, (d) DOS of Fe-doped GaN.

Figure 3. (a) Band Structure of C and Fe co-doped GaN, (b) DOS of C and Fe co-doped GaN.
use of Hubbard U to obtain accurate band gaps were not conducted by Mounkachi et al [29] due to which our results differed from theirs.

For mono-doped Ga$_{16}$C$_1$N$_{15}$ only the two Fe atoms at the nearest position with anti-parallel spin are considered the stable configuration. The configuration is consistent with another DFT study where it shows that stable antiferromagnetic is obtained when two Fe atoms are at the closest distance [26].

3. Results and discussions

3.1. Structural properties

The ground state of GaN is a wurtzite structure. It belongs to the space group $P6_{3}mmc$. The optimized lattice constants of undoped GaN were calculated to be $a = b = 3.1803 \, \text{Å}$ and $c = 5.17 \, \text{Å}$. The lattice constants show little deviation from other computed works [42] and are closer to the experimental value with 0.29% error [43] which makes our simulation reliable. The lattice constants, band gap energy (GGA, GGA + U), volume change, and the magnetic moment per formula unit for undoped and doped configurations are summarized in table 1.

Impurity addition increased the ratio between lattice parameter $c$ and $a$ (c/a ratio) compared to intrinsic GaN except for Ga$_{14}$C$_1$Fe$_2$N$_{15}$. The volume expansion of all the doped materials is due to the larger radius of the dopant than the lattice atom. The pristine wurtzite GaN has an average Ga-N bond length of 1.949 Å [44]. The Ga-C bond length in Ga$_{16}$C$_1$N$_{15}$ and Fe-N bond length in Ga$_{14}$Fe$_2$N$_{16}$ are 1.965 Å and 2 Å respectively. Due to carbon doping, the Ga-N bond length varies from 1.938 Å to 1.965 Å in the [001] direction. However, Fe doping alters the Ga-N bond length to 1.950 Å being very slight modification compared to carbon doping. In the co-doped structure, the Ga-N bond length varies from 1.938 Å to 1.962 Å, whereas the Fe-N bond length is 1.947 Å in the [100] direction and 1.987 Å in the [001] direction. Fe-C bond length (1.934 Å) being smaller than the Fe-N implies more interaction between Fe and C than N resulting in a relatively stronger hybridization. In the next section, it will be discussed in detail that this strong interaction between Fe and C in the spin-down direction caused the ferrimagnetic behavior of the co-doped material.

The Mulliken charges associated with the atom for different structures are tabulated in table 2. From the table, it is observed that the dopant atom has a lower Mulliken charge than the lattice atom it substituted. Interestingly, monodoping of carbon and iron reduces the Mulliken charge of the nearest neighboring atoms. But co-doping reduces the Mulliken charges of the nearest neighboring atoms more and causes more variation in charge transfer values across the lattice. The bond population of Ga-C in C doped GaN and Fe-N in Fe doped GaN is (0.72|e| 0.76|e|) and (0.55|e| to 0.62|e|) which is lesser than the pristine Ga-N bond population 1.80|e|. In addition, the Fe-C and Fe-N bond population is (0.61|e|) and (0.55|e| to 0.64|e|) respectively in the co-doped structure.

For evaluating the formation energy of C-Fe co-doped GaN, we considered configuration 1 where the Fe atoms were at the closest distance. All the stable structures for calculating formation energy are shown in figure 1. The Fe-Fe distance and energy differences between parallel and anti-parallel spin arrangement for 5 configurations of the C-Fe co-doped GaN supercell are given in table 3.

The evaluation of the formation energy expresses the stability of the defect incorporated structure upon forming. The negative value of formation energy denotes the ease of growth of the structure in equilibrium conditions [45]. The formation energies are calculated according to the following formula under Ga-rich and N-rich conditions:

$$E_f = E_{\text{C doped GaN}} - n\mu_C + n\mu_N \tag{1}$$

$$E_f = E_{\text{Fe doped GaN}} - n\mu_Fe + n\mu_Ga \tag{2}$$

$$E_f = E_{\text{C–Fe co–doped GaN}} - E_{\text{GaN}} - n\mu_Fe + n\mu_Ga - n\mu_C + n\mu_N \tag{3}$$

Here, $E_{\text{C doped GaN}}$, $E_{\text{Fe doped GaN}}$ and $E_{\text{C–Fe co–doped GaN}}$ represent the total energies of Ga$_{16}$C$_1$N$_{15}$, Ga$_{14}$Fe$_2$N$_{16}$, and Ga$_{14}$C$_1$Fe$_2$N$_{15}$ respectively. $E_{\text{GaN}}$ is the total energy of pristine GaN. $n$ represents the number of chemical species. $\mu_Ga$, $\mu_Fe$ and $\mu_C$ denote the chemical potential of Ga, N, Fe, and C respectively. The formation energies are summarized in table 4. It can be observed from the table that, all three materials can be formed easily under N-rich conditions due to their negative formation energy. Zinc-Blende GaN co-doped with a transition metal and carbon showed similar ease of formation under N-rich conditions [32].

3.2. Electronic and magnetic properties

We have calculated the band structure, and total and partial density of states depicted in figures 2 and 3 to understand the electronic properties. The band structure was calculated along with the high symmetry points (Γ→M → K→Γ→A → L). The GGA + U calculation of the band structure of GaN shows that the bandgap is 3.49 eV. The GGA and GGA + U band gaps are reported in table 1. The LDA and GGA greatly underestimate the bandgap. According to a similar DFT study of GaN, the LDA and GGA show a bandgap of 1.66 eV and
2.01 eV respectively [46]. However, our work is in close agreement with the experimental band gap of 3.44 eV [47]. There is no split between the spin-up and spin-down bands which proves GaN as a nonmagnetic material [48]. C doped GaN has a metallic character in both spin-up and spin-down states. PDOS shows that the C-2p orbital is above the Fermi level. That’s why the semiconducting nature of GaN has turned into metallic. Rico et al conducted a theoretical investigation that also confirms the metallic nature of carbon-doped wurtzite GaN [49]. The non-magnetic nature of C doped GaN is understood by the symmetry of TDOS. The valence band (VB) is divided into several parts. The d-orbital of Ga and the s orbitals of Ga and C contribute to the lower VB. C-2p, N-2p, and Ga-4p show a major contribution to the near Fermi level states in VB whereas Ga-4s and C-2s hybridize from $-9.80$ eV to $-9.45$ eV. Strong s-p hybridization is observed by the Ga-4s and 4-p orbitals in lower conduction band (CB). Monodoped Fe doped GaN has 2.211 eV band gap. As previously said, the Fe-doped GaN has two Fe atoms with exact opposite spins. Since the antiferromagnetic structure is stable, the total magnetic moment of the supercell is 0 $\mu_B$. Defect states due to Fe doping emerge from 2.16 eV to 3.04 eV reducing band gap. P-d hybridization is observed in VB near the Fermi level and defect states. In the upper valence band and defect states, N-2p and Fe-3d contribute more respectively. This p-d hybridization is also observed when other transition metals are doped in GaN [50–53]. In contrast to the C doped GaN, the Fe doped GaN didn’t show hybridization by the s orbital of dopant with Ga-4s around $-9$ eV because Fe-3s lies in much lower energy in the valence band.

The bandgap of C-Fe co-doped GaN is 0.177 eV (spin-up) and 1.708 eV (spin down). Observing figure 3(b), it becomes evident that the C-2p state is responsible for the reduced bandgap in the spin-up state. PDOS further shows 2p spin-up states of C and N overlaps near the Fermi level. In the valence band, the C-2s and Ga-4s hybridization shifted to lower energy ($-10.5$ eV to 10.10 eV) compared to C doped GaN. Spin up Fe-3d and N-2p show p-d hybridization from 0.91 eV to 1.92 eV. In the spin-down direction Fe-3d, N-2p, and C-2p show hybridization from 1.07 eV to 1.93 eV. There’s an asymmetry in the TDOS which results in $-1.02 \mu_B$ in the supercell. Fe$^{3+}$ has 5 unpaired electrons in the d orbital which gives a $5.0 \mu_B$ magnetic moment. In co-doped GaN, the Fe atom close to the C atom has a magnetic moment of 3.76 $\mu_B$ whereas the C atom has $-0.28 \mu_B$. 

Figure 4. The spin density distribution for C and Fe co-doped GaN. The isosurface value is set to 0.02 e/Å. The blue and yellow colors represent spin up and spin down respectively.
The spin from the bond population of Fe-C is $-0.13 \mu_B$. The other Fe atom’s magnetic moment is $-4.23 \mu_B$. So, the majority of spin of the supercell generates from 1 C and 1 Fe atoms. From the analysis of DOS, it can be understood that the ferrimagnetic behavior of C-Fe co-doped GaN is due to the interaction between Fe-3d, C-2p, and N-2p states.

Spin density distribution will help to further help to visualize the spin contribution of different atoms of the co-doped structure which is shown in figure 4. The isosurface value is set to 0.02 e/Å. The blue and yellow colors represent spin up and spin down respectively. The spin distribution is observed around Fe atoms, C atoms, and some N atoms located near them.

### 3.3. Optical properties

Optical properties help to determine the response of a material to light. For optoelectronic applications the analysis of the optical properties of materials is essential. When an incident photon falls upon a material, electrons transmit from the valence band to the conduction band. Since the valence and conduction band change due to various impurities and defects, the optical response becomes different for dissimilar materials. In addition, quantum confinement effects also alter the electronic bandgap and optical response when the particle interacts with light.
size becomes comparable to the wavelength of light. Due to the application of an electric field to a material, the separation of positive and negative ions gives rise to a net dipole moment. This polarization is ionic in most materials and contributes significantly to the dielectric response of a material at low frequencies [54]. The structural change by the addition of impurities in the material changes the ability and extent of ion separation. This is how the dielectric properties are altered due to doping in the bulk structure [55]. All the optical responses like absorption coefficient $\alpha(\omega)$, reflectivity, refractive index $\eta(\omega)$, conductivity $\sigma(\omega)$ can be described by the dielectric function, $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$ [55]. The real $\varepsilon_r(\omega)$ and imaginary part $\varepsilon_i(\omega)$ of the dielectric function accounts for the polarizing ability and energy absorption, respectively. So, it becomes important to evaluate and tune the dielectric response by the addition of impurity and regulate the optical properties accordingly. The imaginary part of the dielectric function is calculated from the following expression [56],

$$\varepsilon_i(\omega) = \left( \frac{4\pi^2e^2}{m^2\omega^2} \right) \sum_{i,j} \text{d}M | j^2 f_i(1 - f_j) \delta(E_f - E_i - \omega)d^3k$$

where $M$ is the dipole matrix; $i$ and $j$ are initial and final states respectively; $f_i$ is the Fermi distribution function for the $i_{th}$ state; $E_f$ is the energy of the electron in the $i_{th}$ state and $\omega$ is the frequency of the incident photon. The real part is derived from the imaginary part by the Kramers-Kronig transformation [57],

$$\varepsilon_r(\omega) = 1 + \frac{2}{\pi} \rho_0 \int_{0}^{\infty} \frac{\omega' \varepsilon_i(\omega')}{\omega'^2 - \omega^2} d\omega$$

where $\rho_0$ is the principal value of the integral.

Optical transition due to the energy of the photon is determined by the imaginary part of the dielectric function ($\varepsilon_i$). The transition occurs between the occupied states (valence band maximum or VBM) and unoccupied states (conduction band minimum or CBM). Pristine GaN shows the kink at ~3.75 eV (figure 5(b)) which accounts for the electron jump from N-2p states to Ga-4s states. This transition of the electrons is in conformity with another DFT + U study for wurtzite GaN [58]. We found the peaks of $\varepsilon_i$ for pure GaN at 8.14 eV, 9.16 eV, and 12.4 eV where the maximum value of $\varepsilon_i$ was obtained at ~12.4 eV (UV region). This denotes that GaN is suitable for absorbing light in the UV region. The experimental peaks were obtained at 7.0 eV, 7.9 eV, 9.0 eV [59] and 12.6 eV [60]. The optical band gap (observed by the kink) for Fe doped GaN appears at ~2.1 eV. For C doped GaN and C-Fe co-doped GaN the transition due to light absorption emerge further at lower energies. An interesting fact can be noted that, monodoped and co-doped material significantly absorbs light in the VIS-IR region because some major peaks are found at the (0–3) eV range.

The real component of the dielectric function ($\varepsilon_r$) is calculated in the range of (0–15) eV energy plotted in figure 5(a). The static dielectric constant is defined as the dielectric value at zero frequency of light. For pure GaN the static dielectric constant is 4.1 which increases with increased energy reaching a maximum value of 7.11 at 6.48 eV then dropping gradually. The static dielectric constant in our study is slightly lower than the experimental reported value of 5.35 [56, 61]. The reason behind it can be described by Penn’s model [62] ($\varepsilon(0) \approx 1 + (\hbar\omega_p/E_g)^3$) that the higher bandgap obtained by DFT + U gives a lower dielectric constant. From the figure, it is noted that the static dielectric constant has increased up to ~4.7 times for co-doped GaN. The static dielectric constants by DFT + U calculation for monodoped and co-doped structures are reported in table 5. C-Fe co-doped GaN and Fe doped GaN show new peaks in the visible region because of doping. The decrease in dielectric constant in the IR region for C doped GaN compared to pure GaN can be due to the breaking of polarizing bonds due to the addition of dopants. At this frequency range, electrical fields no longer affect the electric dipoles. The dielectric peaks have broadened due to doping and are prominent in the UV regions. C-doped GaN shows a higher dielectric constant than C-Fe co-doped GaN and Fe doped GaN in the UV region.

Optical absorption is calculated by the real and imaginary components of the dielectric constant. The equation is as follows [63],

$$\alpha(\omega) = \sqrt{2} \left[ \varepsilon_i^2(\omega) + \varepsilon_i^2(\omega) - \varepsilon_r(\omega) \right]^{1/2}$$

The absorption coefficient $\alpha(\omega)$ denotes the diminishing rate of the incident photon at certain energy with the thickness of a material. Absorption as a function of photon energy for pure GaN, monodoped, and co-doped structure is plotted in figure 5(c). This property is highly crucial to understanding the feasibility of materials in optoelectronic applications. Absorption for pure GaN starts at 3.5 eV (optical band gap) being lesser than the electronic bandgap. The absorption below the bandgap is close to zero and it goes on increasing as the photon energy increases up to a certain value which is ~12.95 eV in the UV region for pure GaN. The absorption maxima for C doped GaN, Fe doped GaN and C-Fe co-doped GaN is located at 13.47 eV (92.045 nm), 13.71 eV (90.42 nm) and 13.69 eV (90.56 nm) respectively. The dopant atoms enhance the absorption in VIS-IR and long-wavelength UV region because of quantum confinement effects [64]. Moreover, dopants add new states which causes optical transition at new photon energies. The absorption also enhanced from ~9.14 eV to ~11.4 eV and
above \(\sim \) 13.81 eV (short wavelength UV). More interband transitions increase the absorption coefficient for the doped materials. The impurity atoms have caused a redshift of the absorption edge for all the materials. The second absorption edge in the \((0–2)\) eV range for C doped GaN and C-Fe co-doped GaN is due to the transition of electrons from VB to C-2p impurity states which is observed by the PDOS plot. Doping causing redshifts and making the range of absorption wavelength wider were also observed for ZnO [65] and MoS\(_2\) monolayer [66]. Since the monodoped and co-doped materials possess the ability to absorb photons in the VIS-IR region and the UV region, this ability enables them not only to be used for power harvesting devices but also IR and UV photodetectors.

The Refractive index \(n(\omega)\) of materials depicts the transmission of light through a material. The trends will be like the real dielectric function because of the relation \(n(\omega) = \sqrt{\varepsilon(\omega)}\) [67]. Refractive index \(n(\omega)\) as a function of photon energy is plotted in figure 5(d). The peak value of 2.74 for GaN appears at 6.61 eV (187 nm). Impurity defects and total internal reflection may lower the refractive index. Fe monodoped and C-Fe co-doped GaN show new peaks in the low energy region. For Fe doped GaN, C doped GaN and C-Fe co-doped GaN peak value 2.36, 2.55 and 2.32 appears at 7.25 eV (171 nm), 6.9 eV (179 nm) and 2.87 eV (432 nm) respectively. Static refractive indices are the values of \(n(\omega)\) at zero frequency photons. E.Ejder reported the experimental static refractive index \(\sim 2.29\) for pure GaN [68]. Interestingly the DFT + U calculated static refractive index \(\sim 2.02\) in our work for pure GaN is slightly lower than the experimental value because refractive indices are obtained from static dielectric constants \((\varepsilon(0) = \sqrt{\varepsilon(0)})\) and dielectric constants are slightly underestimated according to Penn’s model mentioned above [62]. The static refractive indices for all the materials in this study are reported in table 5. C-Fe co-doped GaN shows the highest refractive index \(\sim 4.45\) which indicates its prospective optical applications.

Reflectivity denotes the amount of light reflected from the surface of the materials relative to the incident light. Peaks appear due to the VB to CB interband transitions. Reflectivity versus photon energy plot was
computed by the following formula [63] (plotted in figure 6(a)),

\[ R(\omega) = \left( \frac{\sqrt{\varepsilon_1 + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1 + i\varepsilon_2(\omega)} + 1} \right)^2 \]  
(7)

High reflectivity indicates the material reflection of incident light from the surface with no absorption at that particular energy level [69]. GaN shows reflectivity maxima at \( \sim 13.58 \text{ eV} \) (91.3 nm). The inclusion of defects in GaN gives reflectivity maxima in the UV region as GaN depicted in figure 6(a). In the high energy UV region (4.23 eV to 8.95 eV and above 11.47 eV) the reflectivity lowers due to impurity addition. Fe doped GaN and C-Fe co-doped GaN show the least reflectivity in the high energy region indicating better absorption properties. High reflectivity is observed below \( \sim 4.20 \text{ eV} \) for Fe doped GaN, C-Fe co-doped GaN and below \( \sim 1.1 \text{ eV} \) for C doped GaN.

Optical conductivity is related to the dielectric constant by the following formula [63] (plotted in figure 6(b)),

\[ \sigma(\omega) = -\frac{i}{4\pi} [\varepsilon(\omega) - 1] \]  
(8)

Monodoping and co-doping increase conductivity in the low-frequency area (up to \( \sim 5.9 \text{ eV} \)). The conductivity also enhances in the region from \( \sim 9.2 \text{ eV} \) to \( \sim 10.3 \text{ eV} \) and above \( \sim 13 \text{ eV} \). The conductivity peaks are in a similar trend with a slight shifting of the maxima. Pure GaN has conductivity maxima at 12.2 eV whereas the impurity added GaN shows the maxima at C doped GaN \( \sim 12.65 \text{ eV} \), Fe doped GaN \( \sim 12.71 \text{ eV} \), and C-Fe co-doped GaN \( \sim 12.68 \text{ eV} \). The enhancement of the conductivity is due to the incident light penetrating deep inside the material increasing absorptivity. Likewise, the diminution can be due to a lowering of absorption at a certain frequency range due to quantum confinement effects [64]. The sharp peak in the UV region can be caused due to more interband transitions from the valence band to the conduction band. Conductivity peaks may have shifted due to p-d hybridization for monodoped and co-doped materials. The shifting due to hybridization is also observed for other dopants with d and f orbitals [63].

The loss function is an important property to assess the optical applications of materials. It denotes the energy loss in a material and the strength of light absorption at a definite frequency. The plot of \( k \) versus energy is shown in figure 6(c). Mathematical loss function \( k \) and absorption coefficient \( \alpha \) are related by the following formula [32].

\[ k = \frac{\alpha \lambda}{4\pi} \]  
(9)

Thus, similar trends for absorption and loss function will be observed. In (0–2.5) eV new peaks of \( k \) have appeared due to the emergence of defect states due to doping which is observed in the PDOS. This is analogous to the absorption spectra. The \( k \) values of C doped GaN, Fe doped GaN, and C-Fe co-doped GaN are in the (0–0.15) range which is lower than the experimentally calculated \( k \) value (0.26) at 1.98 eV for pure GaN [70].

4. Conclusion

In the current work, we conducted the DFT + U study using CASTEP code to obtain the monodoping and co-doping effects of C and Fe on the structural, electronic, magnetic, and optical properties of GaN. Volume expansion due to larger dopants was observed for all the doped structures. The formation energy showed the stability of the monodoped and co-doped GaN with C and Fe under N-rich conditions. C doped GaN was metallic, and the bandgap was reduced for Fe doped GaN. The interaction between Fe-3d, C-2p, and N-2p states reduced the band gap asymmetrically in both the spin directions for C-Fe co-doped GaN. C doped GaN, Fe doped GaN, and C-Fe co-doped GaN were nonmagnetic, antiferromagnetic, and ferrimagnetic respectively. The absorption edge redshifted leading to enhanced absorption in long-wavelength UV and VIS-IR regions. C-Fe co-doped GaN showed better absorption in this region. Our study explores the suitability of C and Fe monodoped and co-doped GaN in technological fields like power harvesting devices, UV and IR optoelectronics photodetectors, and sensors.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Credit authorship contribution statement

Akib Zaman: Conceptualization, Methodology, Software, Validation, Data curation, Writing - original draft, Writing - review & editing. Homayra Tabassum Mumu: Conceptualization, Methodology, Software, Validation, Data curation, Writing - review & editing. Rafat Hussain Aunkon: Conceptualization, Methodology, Software, Validation, Data curation. Faharia Hasan Bhuiyan: Conceptualization, Methodology, Software, Validation, Data curation. Ahmed Sharif: Conceptualization, Methodology, Writing - review & editing, Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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