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**Publications**

**Investigation of Site Dependent Donor-Acceptor (Al-N) Doping Effect into ZnO for Optoelectronic Applications**

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Abstract

In this study, the density functional theory (DFT) is used to investigate the effect of the incorporation of Al (donor) in the Zn-site and N (acceptor) in the O-site of ZnO. The detailed theoretical study highlights the confirmation of p-type conductivity and bandgap (0.58 and 0.21 eV) narrowing exhibits in N- and (Al-N)-doped ZnO systems. p-type nature is explicitly observed by introducing acceptor bands at the top of the valance band (VB). Whereas, degenerate n-type conductivity is seen in Al-doped ZnO and a widened bandgap of 2.70 eV is attributed to Burstein-Moss (BM) effect. The calculated value of the effective mass of the (Al-N)-doped ZnO system is lower than that of the un-doped ZnO. Enhancement of the absorption and photoconductivity in the visible region for N- and (Al-N)-doped ZnO could be due to the availability of more density of states. Importantly, reflectivity, refractive index, transmittance, dielectric constants, and optical band gap have also been calculated. Higher transmittance of the samples suggested that these could be suitable for the window material of solar cells. The optical bandgap value supports the electronic bandgap value. Therefore, our finding would be helpful to design high-performance homo-junction based electronic and optoelectronic devices.

*Keywords*: DFT; Semiconductor; Donor-acceptor; Electronic; Optoelectronic.

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1. Introduction

Zinc oxide (ZnO) is highly transparent, abundant, nontoxic and possesses unique physical, excellent electrical properties with a band gap of 3.2-3.4 eV and large exciton binding energy (~60 meV) at room temperature [1-8]. It has many advantages including the ability to sustain large electric fields, higher breakdown voltages, temperature, power operations and lower [electronic noise](https://en.wikipedia.org/wiki/Electronic_noise). Due to these basic properties, it is an important semiconductor for the applications in biosensors,solar cells,surface acoustic wave devices, spintronic, sensors, ultraviolet (UV) light emitting diode energy storage, catalysis, nano and information technology [9-17]. In addition, ZnO nanostructures have been attracted so much because of fabrication simplicity and large surface-to-volume ratio in conjunction with promising applications in fundamental nanoscience and nanotechnology fields [18]. Recently ZnO nanoparticles are being used as nano antibiotics and anticancer agents because of their antimicrobial activities. It should be noted that most of the aforementioned applications are realized based on n-type conductivity. n-type conductivity of ZnO is attributed to zinc interstitials (Zni), oxygen vacancies (Vo) and other intrinsic and extrinsic defects[19,20] as well as n-type doping is facile [21]. Different elements: Li, Al, Mn, Ni, Co, Cr, Cu, Ag, N, F and CdO, etc. have been doped in ZnO and studied their properties [3,5-7,10,22,23].It is shown that these doping elements act as n-type conductivity. It is noteworthy that the un-doped and doped n-type nature of ZnO hinders advanced applications. However, the fabrication of stable and reproducible p-type ZnO [24] is relatively difficult for advanced electronic, sensor and optoelectronic applications [25], etc. So, the key challenge that needs to be overcome to understand the p-type conductivity of ZnO for advanced applications is essential. It should be noted that an important step for designing advanced electronic and optoelectronic devices is band gap engineering which can be modulated by elemental doping of ZnO. Various elements have been doped in ZnO to produce stable p-type, and modulate the properties of ZnO [5,7,22,23]. In this regard, a lot of research works have been experimentally and theoretically studied [26-28]. It is reported that Al-doping enhanced the electrical conductivity of ZnO [29-31]. Several works reported that N-doped ZnO showed unstable p-type ZnO at ambient temperature and pressure [32-35], however, higher N doping showed promising results [36,37]. It is well known that dual doping is the most favorable technique to tune the dopant population, optical and electrical properties of ZnO [32-37]. Yamamoto *et al*. have theoretically studied the dual (Ga, In, Al) and acceptor (N) doped ZnO. They noticed that the electrical properties were enhanced and ensured p-type semiconductors [37-41]. There are also some experimental reports on p-type conductivity ZnO making using (Al-N) co-oping [42-48]. A quantum-chemical approach based on the Hartree–Fock theory [49]of Al doping ZnO showed n-type nature with changes in structural, electronic and electrical properties. Slassi *et al*. [50] have studied the effect of Al doping on the structural, optical, transport and electronic properties of ZnO using the DFT+TBmBJ and Boltzmann equation. Gsiea *et al*. [51] reported the structural, electronic and vibrational properties of N impurities doping in ZnO.

From the literature, it is evident that Al is an ideal element for n-type doping because of its earth abundance, low cost and one more valence electron than Zn. On the other hand, N possesses high electronegativity to form shallow acceptors easily compared to P and As of group-V elements for p-type doping. Due to the similarity of the ionic radius of N (1.46 Å) with O (1.40 Å) [52], N doping on the O site is suspected to form p-type ZnO. For these intriguing properties, Al and N have been chosen as donor-acceptor (Al, N) doping elements.

In this work, single Al and N atoms are replaced on Zn and O atoms sites separately, and simultaneously dual (Al-N) is substituted on Zn and O atoms sites in ZnO, respectively to investigate the doping effects on the structural, electronic and optical properties using density functional theory (DFT). This is the first report on the investigation of site-dependent (Al, N) doping effects in ZnO and hence the obtaining results would be very beneficial and supportive for making stable p-type ZnO.

**2. Methodology**

The space group symmetry of wurtzite ZnO is p63mc and each primitive cell contains two Zn atoms and two O atoms. Parameters of the primitive cells are a=b=3.25 Å, c=5.21 Å, α=β=90°, and γ=120° [53-55]. These parameters were used in geometrical optimization to get optimized properties of un-doped and doped ZnO crystals. The geometry optimization was performed using the ultrasoft pseudopotential [56] method based on the DFT as implemented in the Cambridge Serial Total Energy Package (CASTEP) [57]. The generalized gradient approximation (GGA) with Perdew–Burke-Ernzerhof (PBE) functional [58] was used to describe the exchange-correlation interactions, core region and valence electrons of the atoms in the supercell (2×2×2) of un-doped, single (Al, N) and dual (Al, N) doped ZnO. The valence electrons configurations are 3d104s2 for Zn, 2s22p4 for O, 3s²3p¹ for Al and 3s23p3 for N atoms, respectively. The kinetic energy cutoff, 400 eV for the plane waves was chosen as the energy convergence criterion. A detailed theoretical procedure is described elsewhere[22]. k-Point in the first Brillouin zone was chosen as 4×4×2. A (2×2×2) supercell of ZnO holds 32 atoms with 16 Zn and 16 O atoms which is shown in Fig. 1(a). The substitution doping performed by introducing one Al atom on one Zn site atom is equivalent to 6.25 % in the supercell. This is shown in Fig. 1(b). Similarly, for 6.25 % N doping, one N substituted on one O atom site is shown in Fig. 1(c). For dual Al-N doping (Fig. 1(d)), one Al and one N atom are substituted on one Zn and one O sites atoms, respectively.

**3. Results and Discussion**

**3.1. *Crystal structure***

In this study, the geometry optimization was performed and the obtained optimized lattice parameters are shown in Table 1, which are in good harmony with experimental, [6,59] and theoretical [59-61] results. These optimized values suggest the reliability of the computational method. The deviation of the lattice parameters of (Al, N) doped ZnO systems from un-doped ZnO confirms the structural distortion, which is attributed to introduction of impurity (Al, N) into the ZnO lattice[22,62]. It is also seen that the lattice constant ‘*a*’ decreases while the value of ‘*c*’ increases for single (Al, N) and dual (Al-N) doping as compared to un-doped ZnO. These results confirm that tensile stress acts along the a-axis while increasing of ‘*c*’ value indicates lattice expansion due to impurity doping in ZnO. The structural distortion occurs due to the lattice mismatch and difference in ionic radius of Al (0.54 Å), Zn (0.74 Å), N (1.46 Å) and O (1.4 Å) [52].

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Fig. 1. Crystal structure of (a) un-doped, (b) Al-doped, (c) N-doped and (d) (Al-N) dual-doped ZnO.

Table 1.Calculated theoretical lattice parameters, cell volume, band gap, of un-doped and (Al, N)-doped ZnO.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Type of doping | Method | Lattice Parameters | | | | Band Gap (eV) |
| *a* = *b* (Å) | *c* (Å) | *c*/*a* | Volume (Å3) |
| Un-doped ZnO | Theo. | 3.298a, 3.298b, 3.258c, 3.295g | 5.299a, 5.286b, 5.220c, 5.290g | 1.60a, 1.60b,  1.60c, 1.605g | 49.82a, 49.61g | 0.73a,  0.74g |
| Expt. | 3.245d, 3.250e | 5.209d, 5.207e | 1.61d, 1.61e |  | 3.196h |
| Al-doped ZnO | Theo. | 3.285a, 3.27f | 5.344a, 5.335f | 1.62a, 1.63f | 49.94a | 2.42a |
| N-doped ZnO | Theo. | 3.283a, 3.286g | 5.348a, 5.310g | 1.63a, 1.616g | 49.91a, 49.51g | 0.61a,  0.69g |
| Expt. | 3.256d | 5.223d | 1.604d |
| Al-N co-doped ZnO | Theo. | 3.280a | 5.298a | 1.62a | 51.54a | 0.21a |

aPresent work, fRef. 46, b,cRefs. 6,55,58,59, dRef. 56, eRefs. 55,71, gRef. 22, hRef. 67

The Mullikan bond populations and bond length of un-doped, Al-, N- and (Al-N)-doped ZnO are presented in Table 2. It is seen that the volume of Al- and N-doped ZnO varies slightly compared to that of pure ZnO. This small variation of the volume occurs due to the shorter Al-O and Zn-N bond lengths as compared to that of Zn-O of the ZnO system. Besides, the bond population of Al-O and Zn-N is larger than that of the Zn-O bond which indicates more covalency effect, results smaller volume of the doped systems. In the case of dual Al-N doped ZnO system, the decrease in volume is observed as compared to single doping. This happened due tolower bond length and higher bond populations of O-Al, N-Al and Zn-N as compared to Zn-O (Table 2) and hence decreases the volume of dual-doped ZnO.

Table 2. Calculated theoretical bond length, bond population, optical band gap and effective mass of un-doped and (Al, N)-doped ZnO.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Type of doping | Bond length | | Bond population | Optical Band gap (eV) |  |  |
| Un-doped ZnO | Zn-O | 1.9996 | 0.39 | 2.05 | 0.316 | 2.057 |
| Al-doped ZnO | Zn-O | 1.9675 | 0.44 | 2.72 | 0.324 | 2.322 |
| Al-O | 1.8140 | 0.50 |
| N-doped ZnO | Zn-O | 1.9697 | 0.45 | 2.01 | 0.322 | 2.441 |
| Zn-N | 1.9572 | 0.58 |
| Al-N dual-doped ZnO | Zn-O | 1.9764 | 0.50 | 1.94 | 0.332 | 2.229 |
| Al-O | 1.8550 | 0.47 |
| Zn-N | 1.9550 | 0.58 |
| Al-N | 1.8256 | 0.72 |

* 1. ***Electronic structure***

The analysis of the electronic band structure of a material is essential in solid state physics because it provides information to explain the electro-optical and sometimes magnetic properties of a compound. The energy band structures of un-doped, Al-, N- and (Al-N)-doped ZnO as a function of (E-EF), along different high symmetry points (Z-G-F-Q-G-F-B for un-doped ZnO and G-A-H-K-G-M-L-H for doped ZnO) in the first Brillouin zone are shown in Fig. 2(a-d). The Fermi energy (EF) level is set to zero which is indicated by the horizontal dotted line. From Fig. 2(a), it is seen that the conduction band minimum (CBM) and valence band maximum (VBM) are located at the same k-point G. This implies that ZnO is a direct bandgap semiconductor with the value of 0.73 eV, which shows excellent agreement with the previously reported values [3,22,63-66]. But the theoretical result is far from the experimental value [7,67,68]. The underestimation of the bandgap value is well-known in GGA because this discrepancy occurs due to the lower exchange correlation between electrons made by GGA [62,69]. However, the underestimation of bandgap does not affect the calculation of other physical properties. The large dispersion in the CBM as compared to VBM indicates a small electron effective mass and higher carrier mobility as compared to the effective mass of hole.

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Fig. 2. Band structures along high-symmetry k-points of (a) un-doped, (b) Al-doped, (c) N doped and (d) (Al-N) dual-doped ZnO.

The calculated total and partial density of states (TDOS and PDOS) of un-doped and (Al, N) doped ZnO are shown in Fig. 3(a-d). The PDOS of each atom has been calculated to realize the effect of each atom in the TDOS. From Fig. 3(a), it is shown that the valence band is divided into three regions: the deep level from -16 to -17.5 eV, which is attributed to the O-2s state only. The middle part from -2.7 to -7.2 eV, which originated from the hybridization between Zn-3d and O-2p states. The upper valence band (VB) ranges from 0 to -2.7 eV concerning the highest occupied state which is originated mainly from the 2p states of O (O-2p). The Zn-3d, 4p states and the O-2p states contribute to form the conduction band primarily. Figs. 2(b) and 3(b) show the band structure and DOS of Al-doped ZnO, respectively. From Fig. 2(b), it is confirmed that Al-doped ZnO is still a direct bandgap degenerate semiconductor. It is also observed that the gap between CB and VB decreases due to Al doping but the EF level deeply enters into the CB at 2.42 eV, which is attributed to the available occupied states below the CB. These results imply that the optical bandgap must be increased due to the well-known Burstein-Moss (BM) effect [70,71]. Since the EF level shifted into the CB, hence Al-doped ZnO shows n-type conductivity with higher carrier concentration than that of intrinsic ZnO. From DOS (Fig. 3b) of Al-doped ZnO, it is evident that TDOS shifts toward lower energy and the CBM enters into the VB. The upper VB contributed to the hybridization of Al-3p, O-2p and Zn-3d states. The middle VB is due to Al-3p, Al-3s, O-2p and Zn-3d orbital but the core VB is generated due to O-2s, Al-3p and Al-3s states. Thus, the main distinction of Al-doped ZnO is depicted in the VB, where, the donor impurity bands are introduced which are strongly hybridized among Al-3p, O-2p and Zn-3p orbitals, however, there is a small contribution from Zn-4s, Zn-3p and Al-3s orbitals. But the CBM is mainly originated from Al-3p state and the upper CB is due to Zn-4s, Zn-3p and O-2p states. From Fig. 3d it is evident that the donor impurity bandwidth is increased which indicates the increase of carrier concentration in this system.



Fig. 3. Total and partial density of states of (a) un-doped, (b) Al-doped, (c) N-doped and (d) (Al-N) dual-doped ZnO.

The band structure and DOS of N-doped ZnO are depicted in Figs. 2(c) and 3(c). It reveals clearly that the band structure does not change the basic electronic structure, but only generates an additional fully occupied band above the VBM while the EF level is shifted into VB exhibiting p-type conductivity [37,66]. When excess N atoms are available, they will dope into the ZnO lattice and the transition will occur between the N defect levels and the fully occupied impurity bands, rather than the original valence bands. Band structure also reveals the direct bandgap nature and bandgap value is decreased to 0.61 eV. From the DOS of N-doped ZnO, it is seen that when one oxygen atom is substituted by one nitrogen atom, the partial density of 2p states of nitrogen contribute to unoccupied state which confirms that the localized state adjacent to EF level is attributed to the N-2p state coupled with O-2p state. This nature indicates that nitrogen is a deep acceptor for bulk N-doped ZnO. Besides, N-2s introduce a narrow band at around -14 and -12 eV. Therefore, p-type conductivity of ZnO can be introduced by N doping and hence N atom acts as an acceptor impurity agent that provides hole carriers. The band structure and DOS of (Al-N) dual-doped ZnO are shown in Figs. 2(d) and 3(d), respectively. It is clearly observed that (Al-N)-doped ZnO (Fig. 2d) also exhibits direct bandgap material and the energy gap is reduced to 0.21 eV. The decrease in bandgap value arises due to the introduction of donor and acceptor impurities levels below and above the CB and VB, respectively. Since the lower CB shifts downward and the impurity band just develops above the VB therefore dual (Al-N)-doped ZnO insights a p-type semiconductor and the obtained result is consistent with previously reported results [41-48]. The conductivity is also decreased due to the compensation between electrons and holes introduced by the Al and N, respectively. Thus, the band gap narrowing is possible by Al-N dual-doping into ZnO. From DOS analysis, it is clear that Al-3p and N-2p mainly contribute to the upper VB and lower CB. The decrease of carrier concentration is also confirmed from the height of the TDOS of (Al-N)-doped ZnO. The height of TDOS is lower than the un-doped and single Al and N-doped ZnO systems. At the EF level, the N-2p states show a strong coupling with the Al-3p states. A localized state appears around -13.7 and -12.4 eV is originated from the N-2s, Al-3s and Al-3p states.

**3.3.** ***Effective mass***

The effective mass of the electron ( and hole ( can be calculated from the bottom of the CB and the top of the VB respectively using the following equation:

where, is carrier effective mass, is the reduced Planck constant, and E(k) is the energy wave function of k. The effective masses of electrons can be obtained by fitting the E ~ k states at the CBM for the undoped and doped ZnO crystals. The calculated values of for the undoped, Al-doped, N-doped, and Al-N co-doped ZnO are 0.316, 0.324, 0.322, and 0.332, respectively. These values are quite small which indicates that the photogenerated electrons must exhibit excellent electrical conductivity. These values are similar to the electron effective mass of the conventional photocatalysts (e.g. 0.48-1.81 for different polymorphs of BaTiO3 [72]. It is interesting to note that the effect of Al doping on ZnO is greater than that of N doping in increasing the electron effective mass. But it is opposite in the case of hole effective mass, as we can see that the calculated values of at VBM for the un-doped, Al-doped, N-doped, and (Al-N) dual-doped ZnO are 2.057, 2.322, 2.441, and 2.229, respectively. The hole effective mass of (Al-N) dual-doped ZnO is lower than N-doped ZnO, which indicates that (Al-N) dual-doped ZnO is more stable than N-doped ZnO. The effective mass of photogenerated carriers is well known to be smaller in photocatalysis, implying that the carriers have a larger probability of reaching surface reaction sites over their lifetime, improving photocatalytic activity. In addition, these carriers can interact with other molecules at their surface, resulting in improved product selectivity and yield. From this discussion, it can be concluded that all the crystals are suitable for water-splitting reactions and pollutant degradations.

**3.4. *Optical properties***

Optical properties play an important role to recognize the nature of the material and represent a clear concept of a material in optoelectronic applications. It indicates the interaction of a photon with the electron/hole in the system that can be described by time dependent perturbation theory of the electronic ground state. The electric field of the photon explains the occupied and unoccupied states respectively. Fig. 4(a and b) shows real and imaginary parts of the dielectric function ε(ω) respectively for doped and undoped ZnO. The static dielectric constant ɛ1(0) is obtained to be 4.00 for undoped ZnO and ε1(ω) value increases slowly with the energy and reaches its maximum value of 4.33 at the photon energy of 0.97 eV. There are also two small peaks at the energy 5.57 and 8.8 eV, which originated from the optical transition of the electron from the VB to the empty CB. It is well known from the Penn model that the bandgap is inversely related to the static dielectric constant, implying that the smaller the bandgap the higher the static dielectric constant [73]. The value of ɛ1(0) is obtained as 2.88 for Al-doped ZnO which is smaller than undoped ZnO. This smaller value recommends that the band gap of Al-doped ZnO is higher than pure ZnO, which satisfies the Penn model [73]. Whereas, N-doped ZnO and dual (Al, N) doped ZnO, the values of ɛ1(0) are 12 and 5.58 respectively which insight that the band gap was decreased [73] from undoped ZnO. The peaks of ε2(ω) explain the optical transitions. The first peak obtained at 1.75 eV for pure ZnO is connected to the optical transition from O-2p states of VBM to the Zn-4s state of the CBM. The highest peak at around 6.42 eV is due to the transition from the VB deep Zn-3d state to the O-2p state of CBM. The first peak obtained at 3.6 eV for Al-doped ZnO is connected to the optical transition from the hybridized state of VBM to the hybridized state of the CBM. The highest peak at around 6.45 eV is also due to the transition from the hybridized VB deep state to the hybridized state of CBM.

In the case of N-doped ZnO, a significant and intense peak is observed at ~0.41 eV due to the optical transition from the hybridized O-2p, N-2p states of VBM to the Zn-4s state of the CBM which indicates that a large number of electron-hole pairs can be generated in N-doped ZnO. Whereas, there is no distinct peak observed for dual (Al-N) doped ZnO at the lower energy could be due to a narrow energy gap. For Al-doped, the first peak of ε2(ω) obtained at 3.6 eV shifts toward the higher energy suggesting an increase in the energy bandgap.



Fig. 4. Calculated (a) real and (b) imaginary part of dielectric function, (c) refractive indices, and (d) extinction coefficient of un-doped and (Al,N)-doped ZnO.

The real and imaginary refractive indices for pure and doped ZnO are shown in Fig. 4(c-d). Refractive index is obtained by the root of the dielectric constant, [74]. For pure ZnO, the calculated static refractive index nr(0) value is 2.0 and the maximum value of nr(ω) is 2.10. It is apparent that nr(ω) decreases with the increase of photon energy. There are some small peaks which explain the optical transition from the different VB level to the CB. For Al-doped, the values of nr(0) and nrmax(ω) are 1.69 and 1.90. These values reveal that the band gap for Al-doped is increased. The static refractive index nr(0) of N and (Al-N) doped are obtained to be 2.31 and 3.24 which indicates the bandgap decreases. The imaginary refractive is obtained similar phenomena as the imaginary dielectric function because of this equation [74]. The absorption coefficient of pure and doped ZnO has been shown in Figure 5 (a). The first critical point of α(ω) for pure, Al, N and Al-N doped ZnO is at the energy 0.80, 2.20, 0.60 and 0.50 eV, respectively. These are very close to the calculated energy gap and are known as the absorption edge and confirm the direct optical transitions. In the IR region, α(ω) is the lowest value for Al-doped ZnO and indicates n-type conductivity. It is also observed low absorptivity in the visible region for pure and doped ZnO. While N- and (Al-N)-doped ZnO shows similar absorption as ZnO in the IR region but higher than ZnO. This enhancement of the α(ω) at the low energy supports the p-type conductivity [41-48]. The prominent large peak is located between 10 to 11 eV for all samples indicating the increases of α(ω) in the UV region. However, the value of α(ω) decreases sharply above 13.0 eV photon energy. So, these materials can be used as good absorbers of UV rays in p-n based electronic and optoelectronic devices.



(e)

Fig. 5. Calculated (a) absorption coefficient, (b) reflectivity, (c) conductivity, (d) transmittance, (e) loss function and (f) optical band gap of un-doped and (Al,N)-doped ZnO.

Fig. 5(b) shows the reflectivity nature of pure and doped ZnO. The reflectivity at low energy (IR region) is higher for N-doped and dual-doped ZnO than pure ZnO. These results indicate that N- and (Al-N)-doped ZnO appear a better reflector than pure ZnO. But Al-doped ZnO possesses low reflectivity in the low energy region. In the visible region, low reflectivity is observed for both doped and un-doped ZnO. It should be noted that low absorptivity and reflectivity in the visible region indicates a transparent conducting oxide (TCO) semiconductor.

The optical conductivity σ(ω) of undoped and doped ZnO is shown in Fig. 5(c). The first critical points of pure, Al, N and (Al-N) doped are obtained at 0.73, 2.0, 0.64 and 0.43 respectively. These correspond to the optical band gap of the respective materials. From Fig. 5(c), it is clear that the first peak of Al-doped shifts toward the higher energy but for N- and (Al-N)-doped shifts toward lower energy from pure ZnO. The enhancement of σ(ω) in the lower energy for N- and (Al-N)-doped ZnO insights p-type conductivity and de-enhancement for Al doping ZnO indicates n-type conductivity nature of the systems. It is also noticed that at higher energy the value of σ(ω) for N- and (Al-N)-doped ZnO lie under the ZnO spectrum. Importantly, the N-doped ZnO system insights into the higher mobility of the charge carrier which coherence with the exceptional peak is exhibited in absorption coefficient, reflectivity and conductivity nature at the lower incident photon energy. The transmittance can be enumerated from the value of absorption coefficients, reflectivity (R), and thickness (d) of the film by the following formula. Fig. 5(d) describes the transmittance of the undoped and doped ZnO and the assumed film thickness was 200 nm. For Al-doped ZnO, the transmittance in the visible and ultraviolet regions is higher than N-doped and (Al-N) dual-doped ZnO. So, (Al-N)-doped ZnO could be used as a window material for photovoltaic systems.

Loss function indicates the amount of energy losses a fast electron when it passes through a material. It can be determined by absorption and reflection of a substance. Fig. 5(e) represents the loss function of un-doped and doped ZnO and shows that the peak value of L(ω) is at 13.9 eV, where R(ω) decreases rapidly. This value indicates the bulk plasma resonant energy, which appears where. Above 13.9 eV all the material (undoped and doped ZnO) becomes fully transparent and depicts insulator properties.

The band gap represents the minimum energy that an electron in the valence band must acquire to move into the conduction band and become a free electron. The size of the bandgap is an important property of a material, as it determines its electronic and optical properties. By using Tauc’s relation [76], graph is plotted and shown in Fig. 5(f) and tabulated in Table 2. It can be said from Table 2 that each of the un-doped and doped ZnO crystals has a bandgap in the visible range (1.6-3.1 eV). So, they have the potential for application in photovoltaic applications. While Al as a dopant increases the bandgap, N decreases it and it nullifies the effect of Al when both dopants are used as can be seen from Table 2. One interesting thing to note is that un-doped, N-doped, and (Al-N)-doped ZnO have bandgaps in the red side of the EM spectrum while the bandgap of Al-doped ZnO is in the blue region of the EM spectrum. To conclude, almost the whole visible EM spectrum can be covered by adjusting the doping level of ZnO by the use of Al and N as dopants, and the efficiency of the current photovoltaic devices can be increased using the aforementioned materials.

1. **Conclusion**

A systematic theoretical study has been performed on the structural, electronic and optical properties of undoped, Al-, N- and (Al-N)-doped ZnO systems, respectively. The optimized lattice parameters are in good agreement with theoretical and experimental reports. However, the value of ‘*c*’ is increased in Al-, N- and (Al-N)-doped ZnO systems while the value of ‘*a*’ is decreased. The band structure calculation shows that all the structures are direct bandgap semiconductors which are satisfactory values in comparison with reported results. The bandgap is reduced linearly from 0.73 eV to 0.21 eV for undoped, N- and (Al-N)-doped ZnO. However, for Al doping, the bandgap is widened to 2.42 eV. The absorption increases in the visible region for N- and (Al-N)-doped ZnO. The values of the static dielectric constant and the photoconductivity are significantly enhanced for N and Al-N doping rather than undoped and Al-doped ZnO indicating distinct carrier types are possible by Al and N doping agents. The other optical properties related to the imaginary dielectric constant are also reported. Thus, these obtained features of Al-, N- and (Al-N)-doped ZnO would be suitable for modern electronic and optoelectronic applications.

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