Role of hydrogen co-doping on opto-electronic behaviors of Na-H co-doped zinc oxide: a first principle study

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Abstract
In this work, the electronic structure and optical properties are investigated within the framework of the density functional theory (DFT) for different Na-H co-doping scenarios to find out the suitability of H co-doping technique for achieving p-type conductivity in ZnO. Very low formation energies were found for the H co-doped systems compared to others which suggests that they can suppress other n-type impurities and increase the effect of p-type Na_{2n} defects in the lattice. From the electronic structure calculations, we have found that Na_{2n} doped structures with 50% H co-doping produces the best p-type behavior indicating importance of controlling annealing time. Moreover, from the optical calculations, it has been found that Na_{2n} creates impurity states 174 meV above the valence band and electron concentration in these states can be controlled by H co-doping concentration. H co-doping has not produced any substantial lattice strain as compared to other dopants and structures with Na-H co-doping is transparent in the visible light range.

1. Introduction
A wide range of useful properties displayed by ZnO have made this wide band gap semiconductor a research attraction in recent years [1, 2]. ZnO shows a band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV [3]. This enables applications in optoelectronics in the blue or UV region, including light-emitting diodes, laser diodes and photodetectors [4]. Due to a strong luminescence in the green-white region of the spectrum, ZnO is also a suitable material for phosphor applications. One of the most striking features of ZnO as a semiconductor is that large area single crystals are available, and epi-ready substrates are now commercialized.

Bulk crystals can be grown with a variety of techniques, including hydrothermal growth [5], vapor-phase transport [6] and pressurized melt growth [7]. Growth of thin films can be accomplished using chemical vapor deposition (MOCVD) [8], molecular-beam epitaxy [9], RF magnetron sputtering [10] and spray pyrolysis [11]. The epitaxial growth of ZnO on native substrates can potentially lead to high quality thin films with reduced concentrations of extended defects. Despite the many attractive applications of ZnO, obtaining p-type doping has not produced any substantial lattice strain as compared to other dopants and structures with Na-H co-doping is transparent in the visible light range.

The cause of this difficulty is the unintentional incorporation of impurities that act as shallow donors, such as hydrogen which is present in almost all growth and processing environments [13]. By means of density-functional calculations it has been shown that interstitial H forms a strong bond with O in ZnO and acts as a shallow donor, contrary to the amphoteric behavior of interstitial H in conventional semiconductors [14]. This shallow donor suppresses acceptor behavior generated by any p-type dopants specially by substitutionally doped Na in our case. This suppression of p-type behavior by H is termed as H compensation. Interestingly, hydrogen co-doped with Na into ZnO films can be the solution to the p-type doping difficulty as shown by S S Lin et al [15]. They showed Na-H co-doped sample shows reduced resistivity and p-type conductivity after annealing at 550 °C. They proposed a model involving Na_{2n}, Na_{3n} and H to illustrate the mechanism of p-type behavior. In this qualitative model, the formation of compensating interstitials is severely suppressed, and the acceptor...
Here, the calculations performed of Na\textsubscript{2}Z\textsubscript{n}-H\textsubscript{i} resulting p-type conductivity. Many researchers have investigated behavior of native point defects, dissociation energy means that it can be easily diffused out by annealing and thus achieving higher concentration solubility is greatly enhanced by forming H-acceptor complexes during the growth process. The low Na\textsubscript{2}Z\textsubscript{n}-H\textsubscript{i} sites rather than the tetrahedral interstitial sites[16]. We have showed that in the regime of high dopant concentrations, the dominant defect is the dopant–H complex[19]. As we are modelling a system with high doping concentration the Na–H complex has been taken as the most stable complex in our models. U Wahl et al have shown that Na\textsubscript{a} prefers the octahedral interstitial sites rather than the tetrahedral interstitial sites[20]. Moreover, in the Na\textsubscript{2}Z\textsubscript{n}–H\textsubscript{i} defect complex, the antibonding site of the O atom, which forms three Na\textsubscript{2}Z\textsubscript{n}–O bonds off the c-axis, is the most stable position[17]. To investigate the overall effect of H co-doping it is compared with substitutional (Na\textsubscript{2}Z\textsubscript{n}) and interstitial (Na\textsubscript{a}) doping (figures 2(a)–(c)). To understand the compensation process of H in Na\textsubscript{2}Z\textsubscript{n} doped ZnO, the supercell was doped with two Na atoms in substitutional positions amounting about 5.56% doping. It is compared with 50% compensated (2Na\textsubscript{2}Z\textsubscript{n}–H\textsubscript{i}) and 100% compensated (2Na\textsubscript{2}Z\textsubscript{n}–2H\textsubscript{2}) models (figures 2(d)–(f)). Finally, to investigate the effect of p-type and n-type condition on H co-doping the 50% compensated (2Na\textsubscript{2}Z\textsubscript{n}–H\textsubscript{i}) model is compared with H compensated supercell also doped at the interstitial position (Na\textsubscript{2}Z\textsubscript{n}–Na\textsubscript{a}–H\textsubscript{i}) (figures 2(e), (g)). We have calculated total ground state energy for all possible configurations (except the symmetric ones) for multi-doped systems and have chosen the configuration with the lowest energy for further calculations. We expect that this work will provide a theoretical basis for understating the H co-doping technique for fabrication of p-type ZnO semiconductor thus broadening its current application space.

### 2. Computational methods

Here, the calculations performed (i.e. scf, nscf and optical) were carried out using the Cambridge Serial Total Energy Package (CASTEP) code[21]. Plane wave basis set with pseudo-potential approach based on DFT was used as implemented in the code.[22, 23] Accuracy of a DFT calculation mainly depends on choice of exchange-correlation functionals used for a model. In our study we used Perdew–Burke–Ernzerhof (PBE) with generalized gradient approximation (GGA) parameterization scheme[24]. As GGA approach greatly underestimates the band gap and over or underestimates other properties[25], we used GGA + U method implemented via spin polarized, using formal spin as initial conditions with oxidation state of each element for charge neutralization. Hubbard (U) parameter of 10.5 eV and 7 eV were used for d-orbital of Zn and p-orbital of O, respectively. The interactions between ions and electrons are represented with Vanderbilt-type ultrasoft pseudopotential[26] for all atoms. All calculations including electronic structures (band structure and DOS) and optical were performed with a plane-wave cut off energy of 370 eV with a SCF tolerance of $1 \times 10^{-6}$ eV/atom. For the sampling of the Brillouin zone, $4 \times 4 \times 4$ k-point grids were generated according to the Monkhorst-Pack scheme[27]. Optical properties due to electronic transitions were calculated with polycrystalline geometry using a smearing value of

![Figure 1.](image-url)

(a) $3 \times 3 \times 2$ supercell used as the backbone for all our calculations and (b) reciprocal lattice and the high symmetry k points $\Gamma(0 \ 0 \ 0)$, $A(0 \ 0 \ 1/2)$, $H(-1/2 \ 1/2 \ 0)$, $K(-1/2 \ 0 \ 0)$, $M(0 \ 1/2 \ 0)$ and $L(0 \ 0 \ 1/2)$. 

[16] T. Kudo, T. Ohno, T. Asano, K. Tanaka, K. Kitamura, J. Phys. Soc. Jpn. 66 (1997) 1916.
[17] B. Bolotin, M. N. Reza, A. Z. Hamrock, B. Dutta, J. Phys. Chem. C 113 (2009) 14171.
[18] M. N. Reza, B. Bolotin, A. Z. Hamrock, B. Dutta, J. Phys. Chem. C 114 (2010) 12084.
[19] G. A. Samara, D. B. Binnemans, Phys. Rev. B 81 (2010) 165208.
[20] M. N. Reza, B. Bolotin, A. Z. Hamrock, B. Dutta, J. Phys. Chem. C 114 (2010) 12084.
[21] C. J. Pickard, J. C. Goodenough, D. Orozco-Segovia, K. Syme, J. Phys.: Condens. Matter 21 (2009) 403201.
[22] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[23] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. B 54 (1996) 16533.
[24] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. B 54 (1996) 16546.
[25] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. B 54 (1996) 16569.
[26] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. B 54 (1996) 16575.
[27] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. B 54 (1996) 16585.
0.5 eV and drude damping of 0.05 eV. The standard Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS) was used for the variable cell optimization where the self-consistence convergence tolerance for the total energy is $1.4 \times 10^{-5}$ eV/atom, the maximum force of the atom is 0.03 eV/Å, the maximum stress is 0.05 GPa using code as implemented in Quantum espresso (pwSCF) [28]. These parameters are found to be sufficient for good convergence of total energy and internal forces.

3. Results and discussions

3.1. Structural properties

Optimized lattice parameters of experimental and theoretical calculations and bond lengths of different ZnO models have been listed in Table 1. Our first principle predictions of lattice parameters agree well with the experimental results, for example, for c lattice parameter it agrees within 0.04% [29], much better than the other theoretical calculations [30, 31], indicating that our method of calculation is reliable. Lattice parameters a and c increase with increasing Na concentration, and this is due to the fact that the atomic radius of Na (0.95 Å) is larger than that of Zn (0.74 Å). However, Na affects the parameters more and isotopically compared to Na$_2$Zn, as
can be seen from the $c/a$ values. These behaviors have been shown by others [18]. Position of Na in interstitial doped ZnO is at the octahedral site. However, four Na-O atomic distance along the positive $c$ direction are different from the negative direction indicating shift from ideal octahedral position along the $c$ axis which agrees with the shift determined by angular distribution of $\beta^-$ particles emission [20].

Co-doping of H with Na$_{2zn}$ increases $c$ parameter more than both Na$_{2zn}$ and Na$_i$ models and the $c/a$ is in between the two models. Change of the parameter $c$ is important in case of hexagonal ZnO because it preferentially crystalizes along the $c$ direction ([0001] direction) [33] thus controlling the in-plane stress of deposited thin films which can be modeled by the biaxial strain model [34] as,

$$\sigma = 4.5 \times 10^4 \frac{c_o - c}{c_o}$$

where $c_o$ is the corresponding value for bulk undoped ZnO (5.2047 Å) and $c$ is the lattice parameter calculated from other models. The positive (negative) sign of $\sigma$ indicates that the films are in a state of tensile (compressive)

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**Table 1.** Theoretical and experimental lattice parameters and bond distance values of pure, doped (Na$_{2zn}$) and co-doped (Na$_{2zn}$-H$_i$) ZnO. $d_{Zn-O}$ denotes bond distance between Zn and O atoms, here C1 means Zn-O bond parallel to $c$-axis and C2 means other tetrahedral directions. $d_{Na-O}$ denotes bond distance between Na and O, for Na$_{2zn}$ D1 and D2 have the same meaning as C1 and C2. For Na$_i$ D1 means Na-O bond towards the positive $c$-axis and D2 towards negative and for Na$_{2zn}$-Na$_i$(H$_i$) D1 means Na-O bond distance for Na$_{2zn}$ and D2 for Na$_i$ along the $c$-axis. These bond distances are for the nearest neighbors of the defect complex and the largest in case of asymmetric distances. See figures 2(a), (b) and (g) for more detail.

| Model          | Method       | Doping [%] | $a$ [Å] | $c$ [Å] | $c/a$ | $d_{Zn-O}$ [Å] | $d_{Na-O}$ [Å] |
|----------------|--------------|------------|---------|---------|-------|----------------|----------------|
| undoped        | This work    | 0          | 3.2576  | 5.2047  | 1.5977 | 1.9842         | 1.9797         |
| undoped        | Exp$^{ab}$   | 0          | 3.2580  | 5.2200  | 1.6022 | 1.9875         | 1.9875         |
| undoped        | Exp$^{bc}$   | 0          | 3.2489  | 5.2066  | 1.6026 | 1.9876         | 1.9876         |
| undoped        | Theory$^{abc}$ | 0      | 3.2880  | 5.3060  | 1.6137 | 2.0073         | 2.0073         |
| Na$_{2zn}$     | This work    | 2.78       | 3.2626  | 5.2162  | 1.5988 | 2.0041         | 1.9243         |
| Na$_i$         | This work    | 2.78       | 3.2766  | 5.2198  | 1.5930 | 2.0239         | 2.0295         |
| Na$_{2zn}$ - H$_i$ | This work  | 2.78       | 3.2712  | 5.2217  | 1.5962 | 2.0177         | 1.9836         |
| Na$_i$ - Na$_{2zn}$ | This work | 2.78       | 3.2825  | 5.2162  | 1.5891 | 2.0116         | 2.0774         |
| Na$_i$ - Na$_{2zn}$ - H$_i$ | This work | 2.78       | 3.2907  | 5.2389  | 1.5920 | 2.0412         | 2.0851         |

**Compensation [%]**

| 2 Na$_{2zn}$ (0%) | This work | 5.56       | 3.2693  | 5.2273  | 1.5989 | 1.9384         | 2.0079         |
| 2 Na$_{2zn}$ - H$_i$ (50%) | This work | 5.56       | 3.2760  | 5.2357  | 1.5982 | 1.9926         | 1.9869         |
| 2 Na$_{2zn}$ - 2 H$_i$ (100%) | This work | 5.56       | 3.2782  | 5.2508  | 1.6017 | 1.9257         | 2.1347         |

a, b, c, d and e indicates Ref. [3, 29–31, 32]
stress. In our case, all our models show compressive in-plane stress according to equation (1) which is supported by experimental result provided by L W Wang et al [35].

In figure 3(a), effect of co-doping with H on bond lengths have been shown. Nearest neighbor Zn–O bond length along the c axis is increased by all types of doping condition which in turn increases the c parameter. NaZn has the largest (2%) and NaH has the lowest (1.7%) effect on the Zn–O bond length. Effect of H compensation on the Na–O bond lengths along c direction was compared. Both 0% and 50% compensation increased (2.7 and 9%, respectively) the Na–O bond length. However, 100% compensation decreased (2.1%) the bond length and thus, the length gets closer to the ideal Na–O bond length in NaZn-doped ZnO. From this observation, we can predict that H compensation technique may help stabilize doped ZnO thin films. As we have discussed earlier, H forms strong O–H bond in ZnO as evident by the small O–H values for all our models, the average value being 0.9563 Å, close to that of O–H bond length of 0.96 Å in water molecule. However, from the figure, we can infer that H co-doping and interstitial Na have little effect on O–H bond length.

3.2. Formation energy
Assuming thermodynamic equilibrium and neglecting defect–defect interactions (i.e. in the dilute regime), the concentration of a native defect in a solid is determined by its formation energy $E_f$ through the relation [36],

$$c = N_{site} \exp \left( \frac{-E_f}{k_B T} \right)$$

where $N_{site}$ is the number of sites (including different configurations) per unit volume the defect can be incorporated on, $k_B$ is the Boltzmann constant and $T$ the temperature in kelvin. Equation (2) shows that defects with high formation energies will occur in low concentrations. The energy appearing in equation (2) is, in principle, a free energy of formation. We have calculated the formation energy of the different neutral defect complex models using following equations:

$$E_f(\text{NaZn}) = E(\text{ZnO} + \text{NaZn}) - E(\text{ZnO}_{\text{undoped}}) + nE(\text{Zn}) - mE(\text{Na})$$

$$E_f(\text{Na}_i) = E(\text{ZnO} + \text{Na}_i) - E(\text{ZnO}_{\text{undoped}}) - mE(\text{Na})$$

$$E_f(\text{NaZn} + H_i) = E(\text{ZnO} + \text{NaZn} + H_i) - E(\text{ZnO}_{\text{undoped}}) + nE(\text{Zn}) - mE(\text{Na}) - pE(H)$$

Where, $E_f(\text{NaZn})$, $E_f(\text{Na}_i)$ and $E_f(\text{NaZn} + H_i)$ indicate the formation energies of the substitutional and interstitial Na defects and substitutional Na and interstitial H co-doped defect complexes, respectively, $E(\text{ZnO} + \text{NaZn})$, $E(\text{ZnO} + \text{Na}_i)$ and $E(\text{NaZn} + H_i)$ are the total energies of the supercell containing substitution, interstitial Na defects and co-doped NaZnH complexes, $E(\text{ZnO}_{\text{undoped}})$ is the total energy of a perfect supercell of ZnO, $E(\text{Zn})$, $E(\text{Na})$ and $E(\text{H})$ are the total energies per atom of Zn, Na and H in their reference states, respectively. They have been calculated using pseudo atomic calculation scheme. Pseudo atomic calculation is a method of calculating total energy of isolated atom as their reference state using the energy of their outermost orbitals. In our case, 3d$^{10}$–4s$^2$, 2s$^2$–2p$^4$, 2s$^2$–2p$^5$–3s$^1$ and 1s$^1$ orbitals have been used to calculate pseudo atomic total energy for Zn, O, Na and H, respectively. Lower formation energy indicates a more stable

Figure 4. Band structure of undoped ZnO along high symmetry k points ($\Gamma \rightarrow A \rightarrow H \rightarrow K \rightarrow \Gamma \rightarrow M \rightarrow L \rightarrow H$) with total density of states of ZnO and contribution from Zn and O. The Fermi level is set to zero.
All formation energy calculated from the above equations are used only for qualitative comparison. For more detailed quantitative approach readers can refer to these studies [14, 19].

As shown in table 2 and figure 5(b), the formation energy of the interstitial model is negative and lower than the substitutional one which indicates that, the interstitial model is more stable than the substitutional one. The same behavior has been reported by other groups [19, 37, 38]. Higher concentration of NaZn is unstable as has been shown by theoretical [18] and experimental results [35]. Presence of Na defects increases stability of NaZn defects thus, high solubility of Na atoms in ZnO lattice is only possible when both types of defect are present. H co-doping stabilizes both p-type (2NaZn) and n-type (NaZn-Na) structures. Thus, H co-doping is a good approach for higher NaZn concentration without increasing compensating Na defects. Although, H also acts as a donor in ZnO, it is much easier to diffuse out than Na defects [19, 39].

### 3.3. Electronic structure

According to the optimized lattice structure, we have calculated the electronic band structures along with the high symmetry directions in the Brillouin zone for both undoped ZnO and doped ZnO models. Figure 4 shows the band structure and total density of states (TDOS) of pure ZnO. The band structures for different defect positions, different levels of H co-doping and type of doping conditions (i.e. p or n type) are shown in figure 5, 6.

**Table 2.** Theoretical and experimental band gap ($E_g$) values of undoped and doped ZnO systems. $E_f$ denotes the formation energies for different doped and co-doped models.

| Model       | Method    | Doping [%] | $E_g$ [eV] | $E_f$ [eV] |
|-------------|-----------|------------|------------|------------|
| undoped     | This work | 0          | 3.394      | —          |
| undoped     | Exp [40]  | 0          | 3.440      | —          |
| undoped     | Theory [18]| 0          | 3.380      | —          |
| NaZn        | This work | 2.78       | 3.463      | 0.57921    |
| Na          | This work | 2.78       | 3.335      | -2.90704   |
| NaZn - H$_i$| This work | 2.78       | 3.298      | -5.94958   |
| Na$_i$ - NaZn| This work| 2.78      | 3.369      | -3.46181   |
| Na$_i$ - NaZn - H$_i$ | This work | 2.78 | 3.288 | -6.06575 |

| Compensation [%] | 2NaZn (0%) | This work | 5.56 | 3.637 | 3.82608 |
| Compensation [%] | 2NaZn - H$_i$ (50%) | This work | 5.56 | 3.458 | -2.79213 |
| Compensation [%] | 2NaZn - 2H$_i$ (100%) | This work | 5.56 | 3.438 | -9.75961 |

Figure 5. Band structure of (a) NaZn, (b) Na$_i$, and (c) NaZn-H$_i$ along high symmetry k points ($\Gamma \rightarrow A \rightarrow H \rightarrow K \rightarrow \Gamma \rightarrow M \rightarrow L \rightarrow H$). The Fermi level is set to zero.
and 7, respectively. The partial density of states (PDOS) of undoped ZnO is shown in figure 8. According to figure 4, we can see that ZnO is a direct bandgap semiconductor with a bandgap of 3.394 eV at the $\Gamma$ point, which is close to the experimental value 3.44 eV [40]. Our result is comparatively closer to the experimental measurement than those obtained by other methods such as LDA (0.76 eV) [41], GGA (0.731 eV) [42] and TB–mBJ (2.7 eV) [43]. The fermi level lies in the middle of the VBM (valence band maximum) and CBM (conduction band minimum) as expected from an intrinsic semiconductor. To clearly understand, which band corresponds to which orbital of which element, we have calculated the TDOS and PDOS for both undoped and doped models. From figures 4 and 8 we can see that, the top and bottom of the valence band and conduction band for undoped ZnO is mainly made out of O-2p and Zn-4s orbitals, respectively, which agrees with other results [30, 44].

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**Figure 6.** Band structure of (a) $2\text{Na}_2\text{Zn}$, (b) $2\text{Na}_2\text{Zn}-\text{H}$, and (c) $2\text{Na}_2\text{Zn}-2\text{H}$ along high symmetry k points ($\Gamma \rightarrow A \rightarrow H \rightarrow K \rightarrow \Gamma \rightarrow M \rightarrow L \rightarrow H$). The Fermi level is set to zero.

**Figure 7.** Band structure of (a) $2\text{Na}_2\text{Zn}$, $2\text{Na}_2\text{Zn}-\text{H}$, and (b) $\text{Na}_2\text{Zn}$, $\text{Na}_2\text{Zn}-\text{H}$ along high symmetry k points ($\Gamma \rightarrow A \rightarrow H \rightarrow K \rightarrow \Gamma \rightarrow M \rightarrow L \rightarrow H$) and ($\Gamma \rightarrow F \rightarrow Q \rightarrow Z \rightarrow \Gamma$) respectively. The Fermi level is set to zero.
In figure 5, we have calculated band structures of Na$_{2}$Zn$_{i}$, Na$_{i}$, and Na$_{2}$Zn$_{i}$-H$_{i}$. All of them show direct band gap characteristic. For Na$_{2}$Zn$_{i}$, the fermi level is near the VBM, indication of p-type conductivity. For both Na$_{i}$ and Na$_{2}$Zn$_{i}$-H$_{i}$, the fermi level is inside the conduction band, though shallower for Na$_{2}$Zn$_{i}$-H$_{i}$. Thus, both show degenerate n-type conductivity and can act as compensating centers in p-type ZnO which have been shown by previous studies [12, 14]. Band gap increases for Na$_{2}$Zn$_{i}$ and decreases for both Na$_{i}$ and Na$_{2}$Zn$_{i}$-H$_{i}$ (table 2). For Na$_{2}$Zn$_{i}$, two localize bands of Na-3s and Na-2p are present between—5 eV to 0 eV range thus contributing to upper valence bands and the conduction band is made of delocalized Na-2p orbital (figure 8). In Na$_{i}$ model the conduction band has contribution from both Na-2s and Na-2p delocalized states at a deeper energy level of around 5 eV. However, the upper valence band has much less contribution from Na-3s and 2p than Na$_{2}$Zn$_{i}$. In case

**Figure 8.** Partial density of states (PDOS) of undoped ZnO and doped Na$_{2}$Zn$_{i}$, Na$_{i}$ and Na$_{2}$Zn$_{i}$-H$_{i}$ models showing contribution from different channels (s and p). Dashed gray and red line indicate total contribution from Zn and O atoms respectively.

**Figure 9.** Partial density of states (PDOS) of 2Na$_{2}$Zn$_{i}$, 2Na$_{2}$Zn$_{i}$-H$_{i}$ and 2Na$_{2}$Zn$_{i}$-2H$_{i}$, models showing effect of different level of H compensation. Dashed gray and red line indicate total contribution from Zn and O atoms respectively.
of H co-doped model, the DOS is similar to NaZn model with a shift towards lower energy. The upper conduction band has a strong contribution from H-1s orbital. In figure 6, effect of different levels of H compensation on band structure has been shown. All band structures indicate direct band gap while decreasing with compensation. Fermi level indicates that both 2NaZn and 2NaZn-H1 models (corresponding to 0 and 50% compensation) are of p-type. However, for 50% compensation the fermi level is closer to the VBM (Δ 456 meV) indicating better p-type conductivity than no H co-doping. 100% compensation produces degenerate n-type conductivity. From figure 9, we can see that H-1s interacts with Na-2p and 3s channels and shifts the bands slightly towards higher energy which can explain the increased p-type behavior. In all the cases the valence band has a strong contribution from localized Na-3s and 2p orbitals and conduction band from delocalized Na-2p and H-1s (in case of compensation) orbitals. In figure 7, effect of p-type and n-type conditions on band structure is shown. Both Na−NaZn and Na−NaZn−H1 show n-type degeneracy. However, in Na−NaZn−H1 the fermi level is deeper in the conduction band region showing opposite result of what we have seen in case of 2NaZn and 2NaZn−H1. From the PDOS (figure 10) we can see that 3 s and 2p channels of NaZn defect centers show localized behavior around −5 eV while Na1 show delocalized behavior. Moreover, the upper and lower part of the valence

Figure 10. Partial density of states (PDOS) of (a) 2NaZn, 2NaZn-H1, (b) Na1−NaZn with contribution from both NaZn and Na defects centers and (c) Na1−NaZn−H1 models showing effect of p-type and n-type conditions.

Figure 11. (a) Dielectric function of undoped ZnO, (b) real and (c) imaginary part of the dielectric functions of doped NaZn, Na1 and NaZn−H1 models.
and conduction band respectively are influenced more by the Na$_{zn}$−3s and 2p channels than Nai defect complexes. Delocalization of the 3s channel in the Na$_{ai}$-Na$_{zn}$-Hi model specially for Na$_{zn}$ defect complex is due to interaction with H−1s channel. The interaction is more pronounced in the n-type model (Na$_{ai}$-Na$_{zn}$-Hi) than in the p-type model (2Na$_{zn}$-Hi). Contribution from H−1s orbital is much more pronounced in the n-type model than p-type in the lower conduction band region.

3.4. Optical properties
In the linear response range, the solid macroscopic optical response function can usually be described by the frequency dependent dielectric function $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, which is mainly connected with the electronic structures. The imaginary part $\varepsilon_i(\omega)$ of the dielectric function $\varepsilon(\omega)$ is calculated from the momentum matrix elements between the occupied and unoccupied electronic states. The real part $\varepsilon_r(\omega)$ is derived from the imaginary part $\varepsilon_i(\omega)$ by the Kramers–Kronig transformation. All other optical constants, such as the absorption coefficient $\alpha(\omega)$ and refractive index $\eta(\omega)$ are derived from $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ [45].

The calculated real and imaginary part of the dielectric function have been calculated for undoped, doped Na$_{zn}$-Na$_{ai}$ and Na$_{zn}$-Hi models in figure 11. The static dielectric constants $\varepsilon_r(0)$ for undoped, Na$_{zn}$, Na$_{ai}$ and Na$_{zn}$-Hi models are about 2.5, 1.2, 2.47 and 2.47, respectively. $\varepsilon_r(\omega)$ can be attributed to the transition of electrons. $\varepsilon_i(\omega)$ of undoped ZnO has three extreme peaks at the photon energy of 4.35 (E1), 9.15 (E2) and 15.3 eV (E3), respectively which is in close agreement with the other theoretical results of 1.4, 6.7, and 10.4 eV [46]. E1 can be attributed to the electron transition from the highest point of VB and the lowest point of CB. E2 can be attributed to the electron transition from the 2p states of O to 4s states of Zn. E3 can be attributed to the electron transition from the 3d states of Zn to the 2p states of O in the VB. A new and strong peak at about 174 meV is present for Na$_{zn}$ which is due to electron transition from Na−3s to the acceptor levels created by the unoccupied p states of O. No new peaks at different energy levels are observed for Na$_{ai}$ and Na$_{zn}$-Hi, indicating transition between Na−3s and 2p with other orbitals are weak and the unoccupied p states of O have been filled by H−1s electrons respectively, resulting compensation.

In figure 12, absorption spectrum for undoped and doped models have been calculated for a certain range of photon energy. The absorption edge in the higher energy area (3.3–4 eV/300–400 nm) in undoped ZnO spectra can be attributed to the transition between VB and CB, corresponds to absorption in the ultra-violet range. The absorption edge moves to the higher energy area (3.5–4.5 eV) for Na$_{zn}$, indicating that the band gap increase after doping, shows a blue shift compared to un-doped ZnO. Na$_{zn}$ shows a second absorption edge at a very low energy level range (92–790 meV) corresponding to electron transition between VB and impurity states above it. Absorption spectrum of Na$_{zn}$-Hi, is similar to Na$_{zn}$ except that the second absorption edge is missing, indicating the impurity states have been filled by H−1s electrons. All our models show very little absorption in the visible range (see insets in the 1.8–3.1 eV range) which is appropriate for transparent conductive oxide (TCO) applications.
The calculated refractive index $n(\omega)$ and extinction coefficient $k(\omega)$ of undoped, Na$_{2}$Zn, Na$_{i}$ single-doped, and Na$_{2}$Zn-H$_{i}$ co-doped ZnO are shown in figure 13. The static refractive indices $n(0)$ of undoped, Na$_{2}$Zn, Na$_{i}$ single-doped, and Na$_{2}$Zn-H$_{i}$ co-doped ZnO are about 1.58, 3.92, 1.573 and 1.573, respectively. In the energy range of 0–16 eV, the $k(\omega)$ of undoped, Na$_{i}$ single-doped, and Na$_{2}$Zn-H$_{i}$ co-doped ZnO increases. Though, Na$_{2}$Zn shows similar behavior, at 500 meV the value of $k$ is non-zero (1.96), similar to the $\varepsilon_{i}$ behavior.

The effect of H co-doping on absorption and dielectric function have been shown in figure 14. Other models show similar behavior to that of Na$_{2}$Zn, the only difference is that 100% compensation (2Na$_{2}$Zn-H$_{i}$) shows a red shift for absorption spectrum. Second absorption edge and non-zero value at near zero energy level for 0 and 50% compensation is the evidence of empty impurity states. 100% compensation fills the empty states. Decreased absorption near the second absorption edge of 2Na$_{2}$Zn-H$_{i}$ model compared to 2Na$_{2}$Zn, is evidence of partially filled impurity states because of H co-doping. In both compensated and non-compensated cases, for n-type condition a blue shift near the first absorption edge can be seen in their absorption spectrum (figure 15) with respect to p-type condition. Na$_{2}$Zn-Na$_{i}$ does not has a second absorption edge like 2Na$_{2}$Zn, which is evidence of Na$_{i}$-3s electrons filling empty states created by Na$_{2}$Zn in O-2p orbitals.
4. Conclusion

In this study, the structural, electronic and optical properties of undoped, Na single-doped, and Na-H co-doped ZnO were evaluated by first-principles calculations based on DFT. Na\textsubscript{i} sits in the slightly shifted octahedral position and increases both lattice parameters (a and c) compared to Na\textsubscript{Zn} for the same doping concentration. Co-doping of H increases lattice parameter c much more than both substitutional and interstitial doping. However, compensation can help stabilize the structure by reducing strain as it greatly reduces Na-O bond distance parallel to c-axis, however, it has to be done at a high concentration level. Strong O–H bond is formed in all our H co-doped models and they are not affected by both compensation level and doping condition. From all our models, H co-doped ZnO are the most stable and substitutional Na doped are the least stable. Additionally, the stability increases with H co-doping and decreases with Na doping in ZnO respectively for higher concentrations. Thus, p-type conductivity cannot be achieved in ZnO by mono-doping only, rather co-doping with donor atoms is necessary. From our calculations, H is a better candidate as it retains the host structure, forms stable complexes, and can be diffused out at a low temperature. From the electronic structure calculations, we have seen that 50\% H compensation produces the best p-type conductivity as H-1s interacts with Na-2p and 3s channels and shifts the bands slightly towards higher energy. Thus, during annealing process retention of some percentage of H can be beneficial for p-type conductivity. In summary, annealing temperature is not only the important factor here, annealing duration must be controlled too to get good p-type behavior. From the optical calculations, we have found that all our models are transparent in the visible range. A shallow acceptor level can be derived from the fact that a new and strong peak at about 174 meV is present for Na\textsubscript{Zn} which is due to transition of electrons from Na-3s to the acceptor levels created by the unoccupied p states of O. This acceptor level can be filled at different levels depending on the H co-doping level. From the results above, Na-H co-doping is a good strategy for achieving good p-type conductivity with the optimized level of H compensation by controlling annealing temperature and time.

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Data availability

The datasets are available upon request from the authors.
CRediT authorship contribution statement

MD Rajbanul Akhond: Conceptualization, Methodology, Software, Validation, Data curation, Writing - original draft, Writing - review & editing. 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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References

[1] Mang A, Reimann K and Rübenack S 1995 Band gaps, crystal-field splitting, spin–orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure Solid State Commun. 94 251–4
[2] Nicklow N H and Tsukamoto E (eds) Zinc Oxide - A Material for Micro- and Optoelectronic Applications: Proc. of the NATO Advanced Research Workshop on Zinc Oxide as a Material for Micro- and Optoelectronic Applications, held in St. Petersburg, Russia, from 23 to 25 June 2004. (Netherlands: Springer) 2005
[3] Özgür U et al 2005 A comprehensive review of ZnO materials and devices J. Appl. Phys. 98 041301
[4] Look D C 2001 Recent advances in ZnO materials and devices Mater. Sci. Eng. B 80 383–7
[5] Maeda K, Sato M, Niikura I and Fukuda T 2005 Growth of 2 inch ZnO bulk single crystal by the hydrothermal method Semicond. Sci. Technol. 20 549–54
[6] Look D C et al 1998 Electrical properties of bulk ZnO Solid State Commun. 105 399–401
[7] Nause J and Nemeth B 2005 Pressurized melt growth of ZnO boules Semicond. Sci. Technol. 20 S45–8
[8] Iye T, Ren-Yu-Yao, T, Van de Walle C G, Mishra U K, DenBaars S P and Speck J S 2008 Step-flow growth of ZnO(001) on GaN(001) by metalorganic chemical vapor epitaxy J. Cryst. Growth 310 3407–12
[9] Heizne S et al 2007 Homoepitaxial growth of ZnO by metalorganic vapor phase epitaxy in two-dimensional growth mode J. Cryst. Growth 308 170–5
[10] Kang D W, Kuk S H, Ji K S, Hah Y H and Han M K 2011 Effects of ITO precursor thickness on transparent conductive Al doped ZnO film for solar cell applications Sol. Energy Mater. Sol. Cells 95 138–41
[11] Nair V G, Jayakrishnan J, John J, Salam J A, Anand A M and Raj A 2020 Anomalous photocconductivity in chemical spray pyrolysis deposited nano-crystalline ZnO thin films Mater. Chem. Phys. 247 122849
[12] Park C H, Zhang S B and Wei S H 2002 Origin of p-type dopings in ZnO Phys. Rev. B 66 073202
[13] Janotti A and Van de Walle C G 2007 Hydrogen multicentre bonds Nat. Mater. 6 1
[14] Van de Walle C G 2000 Hydrogen as a cause of doping in zinc oxide Phys. Rev. Lett. 85 1012–5
[15] Lin S S, He H P, Lu Y F and Ye Z Z 2009 Mechanism of Na-doped p-type ZnO: suppressing Na interstitials by codoping with H and Na of appropriate concentrations J. Appl. Phys. 106 6
[16] Janotti A and Van de Walle C G 2007 Native point defects in ZnO Phys. Rev. B 76 165202
[17] Lee E-C and Chang K J 2006 P-type doping with group-I elements and hydrogenation effect in ZnO Phys. B Condens. Matter 376–377 707–10
[18] Ahmoun H, Roughara M, Su’ait M S, Choqra S and Keroud M 2019 Impact of position and concentration of sodium on the photovoltaic properties of zinc oxide solar cells Phys. B Condens. Matter 560 28–38
[19] Lee E-C and Chang K J 2006 Possible p-type doping with group-I elements in ZnOPhys. Rev. B 70 151210
[20] Wahl U, Correia J G, Amorim L, Decoster S, da Silva M R and Pereira L M C 2016 Lattice sites of Na dopants in ZnO Semicond. Sci. Technol. 31 095005
[21] Clark S J et al 2005 First principles methods using CASTEP Z. Först Krist. - Cryst. Mater. 220 567–70
[22] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas Phys. Rev. 136 B864–71
[23] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects Phys. Rev. 140 A1133–8
[24] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[25] Perdew J P and Levy M 1983 Physical content of the exact kohn–sham orbital energies: band gaps and derivative discontinuities Phys. Rev. Lett. 51 1884–7
[26] Vanderbilt D 1990 Soft self-consistent pseudopotentials in a generalized eigenvalue formalism Phys. Rev. B 41 7892–5
[27] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92
[28] Giannozzi P et al 2009 Advanced capabilities for materials modelling with Quantum ESPRESSO J. Phys. Condens. Matter 21 395502
[29] Desgreniers S 1998 High-density phases of ZnO: structural and compressive parameters Phys. Rev. B 58 14022–5
[30] Zhang Y G, Zhang G B and Wang Y X 2011 First-principles study of the electronic structure and optical properties of Ce-doped ZnO J. Appl. Phys. 109 053510
[31] Schleife A, Fuchs F, Furthmüller J and Bechtstedt F 2006 First-principles study of ground- and excited-state properties of MgO, ZnO, and CdO polyamorphs Phys. Rev. B 73 245212
[32] Decrepins F et al 2003 Local structure of condensed zinc oxide Phys. Rev. B 68 104110
[33] EbrahimiFard R, Abdizadeh H and Golobostanfard M R 2020 Controlling the extremely preferred orientation texturing of sol–gel derived ZnO thin films with sol and heat treatment parameters J. Sol-Gel Sci. Technol. 93 41–52
[34] Tsai C-L et al 2012 Erratum: ‘Effects of Li content on the structural, optical, and electrical properties of LiZnMgO films’ J. Appl. Phys. 107, 113717 (2010) J. Appl. Phys. 111 109901
[35] Wang L W et al 2015 Effects of Na content on structural and optical properties of Na-doped ZnO thin films prepared by sol–gel method J. Alloys Compd. 623 367–73
[36] Kittel C and McEuen P 1996 Introduction to solid state physics 8 (New York: Wiley) pp 105–30
[37] Huang G-Y, Wang C-Y and Wang J-T 2009 First-principles study of diffusion of Li, Na, K and Ag in ZnO J. Phys. Condens. Matter 21 345802
[38] Wardle M G, Goss J P and Briddon P R 2005 Theory of Li in ZnO: a limitation for Li-based p-type doping Phys. Rev. B 71 155205
[39] Ip K et al 2003 Hydrogen incorporation and diffusivity in plasma-exposed bulk ZnO Appl. Phys. Lett. 82 385–7
[40] Reynolds D C, Look D C, Jogia B, Litton C W, Cantwell G and Harsch W C 1999 Valence-band ordering in ZnO Phys. Rev. B 60 2340–4
[41] Charifi Z, Bazzi H and Roshak A H 2007 Ab-initio investigation of structural, electronic and optical properties for three phases of ZnO compound Phys. Status Solidi b 244 3154–67
[42] Si X et al 2015 The interaction between oxygen vacancies and doping atoms in ZnO Mater. Des. 87 969–73
[43] Slassi A, Naji S, Benyoussef A, Hamedoun M and Kenz A E 2014 On the transparent conducting oxide Al doped ZnO: first principles and boltzmann equations study J. Alloys Compd. 605 118–23
[44] Liu W, Liu C, Chen X, Lu J, Chen H and Miao Z 2020 First-principles study on electronic and optical properties of S, N single-doped and S–N co-doped ZnO Phys. Lett. A 384 126172
[45] Gajdoš M, Hummer K, Kresse G, Furthmüller J and Bechstedt F 2006 Linear optical properties in the projector-augmented wave methodology Phys. Rev. B 73 045112
[46] Sun J, Wang H-T, He J and Tian Y 2005 Ab initio investigations of optical properties of the high-pressure phases of ZnO Phys. Rev. B 71 125132