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A computational study of MoS$_2$ for band gap engineering by substitutional doping of TMN ($T$ = transition metal (Cu), $M$ = metalloid (B) and $N$ = non-metal (C))

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Abstract

Tunable electronic properties of two dimensional Molybdenum disulfide (MoS$_2$) make it a potential material. In this study, we inspect electronic and structural properties of TMN-doped MoS$_2$ ($T$ = Transition metal (Cu-copper), $M$ = Metalloid (B-boron) and $N$ = Nonmetal (C-carbon)) by using first principles DFT (density functional theory) calculations. Cu is substituted by Mo with varying concentration, which ranges from 2.08 to 8.33%, whereas B and C are replaced by S atoms with varying concentration of 2.08 to 4.16%. The substitutions result into significant variations in electronic and structural properties of MoS$_2$. Moreover, the importance of substitutional site has been elaborated. The substitution of these impurities, variation in concentration and the replaced sites of MoS$_2$ cause to modify the structure and energy gaps. Resulting bandgap fluctuates remain between 0.16 eV to 0.48 eV relative to 1.95 eV of pristine MoS$_2$. The PDOS calculations show good bonding relation among the host MoS$_2$ and the foreign impurity TMN. Therefore, substitution of impurities gives the opportunity to vary the bandgap as required for its valuable applications as semiconducting materials.

1. Introduction

Being most attractive class of materials, three dimensional materials exhibit vast range of applications that involve super lubricants [1], solar converters [2], half metallic magnets [3] and catalyst in redox based reactions [4]. Besides three dimensional materials, unique and regular atomic arrangement of monolayered graphene exposes its outstanding properties. A new scope to the 2D material research has been introduced by the isolation of monolayer of graphene that is expected to facilitate the resembling transition metal dichalcogenides (TMDs) [5, 6]. A representative role in nanoscience has been played by graphene because of its physiochemical properties. However scholars are taking a stance on graphene to overcome its defects including thermal stability [7], vacancies [8], weaker anchoring of shape of atoms and clusters [9]. These defects are necessary to be overthrown just to beat the restrictions that lemmatize its applications. Basically 2D materials have drawn a considerable interest as potential basis for next generation of electronics with exceptional properties. Nonmetallic materials generates 2D semiconducting and insulating material due to their intrinsic chemical properties. Ab-initio calculations have confirmed that the semi-conductive monolayer MoS$_2$ possess direct bandgap of nearly 1.95 eV, whereas in bulk form it has indirect bandgap of 1.2 eV [10, 11].

Graphene because of its bounded properties, is replaced by MoS$_2$. MoS$_2$ being transition metal dichalcogenide material, with properties of large surface area, high mechanical robustness has opened a new
gateway for the 2D material usage in energy storage applications [12]. In addition, MoS2 has attained great interest in the fields of sensors, organic light emitting diodes, memory and power nano devices [13]. It can also produce oscillating piezo electric voltage and current outputs because of odd number of layers [14].

As TMDs exhibits unique electrical and optical properties that has triggered the researchers towards 2D materials like graphene. Out of all TMDs, MoS2 has attained a distinctive position because of its good mobility, high on/off ratio, large optical absorption and much more. Hence, the use of single 2D material is lemmatized because of its inability to meet up the functional performance requirements for 2D practical applications. Graphene has good conductive ability but the zero band gap is the obstacle in its use for switch control. MoS2 possess inconsistent band gap that is commanded by several layers. Although it’s matchless electron mobility as compared to graphene make it ineligible for transparent electrode usage. The absorption and electronic properties of MoS2 are modiﬁed through bandgap tuning via quantum conﬁnement. Thus for practical application of MoS2 based nano materials, more struggle is required from integrating to modernizing the physiochemical properties.

To enhance the signiﬁcant potential of 2D materials for use in optoelectronic, sensing and memory devices, energy storage and catalysis ‘doping’ is one of the important processes to modify the band gap of 2D materials. Different schemes have been considered for this purpose as for nano devices chemically doped/modifed carbon nanotubes (CNTs) and graphene and n-p type doped graphene via chemical vapor deposition (CVD) [15, 16]. Basically substitutional and surface charge doping are implemented in case of 2D semiconductors [17, 18]. Dolui et al [19]. Theoretically proved that transition metal elements prefer to substitute at Mo site instead of S site. Substitution of some of transition metal like as Pd, Ag, Cd, Nb, Zr, and Y on MoS2 categorize the Mo as n-type (Pd, Ag and Cd) or p-type (Nb, Zr and Y). One of electron is added or removed from Mo site by this substitution. The transition metals such as Fe, Ni, Co and Cu have been doped at Mo and S edge site by Wang et al [20]. Besides this, the doping of the transition metals on both Mo and S edge sites of MoS2 has been observed by them. Ramasubramaniam et al [21]. Applied DFT to examine the electronic properties of Mn-doped monolayer MoS2. Lu et al [22]. Inspected the electronic characteristics of deformities of the doped MoS2. They discussed therein the band gap opening of monolayer MoS2 due to adatoms of various number of impurities. Cheng et al [23]. Calculated the structural, electronic and magnetic properties of doped MoS2 with numerous transition metals by ﬁrst-principles based calculations. Wang et al [24]. Explored the magnetic and electronic properties of Co-doped monolayered MoS2 by ﬁrst-principles calculations. Andriotis et al [25]. Carried out the electronic and magnetic properties of transition metal doped and co-doped MoS2 using ab-initio calculations. As a result a noticeable energy gap reduction has been observed by TM doping in MoS2, above all this in TM dopants magnetic features as ferromagnetic coupling has been observed. Hussain et al [26]. Studied the effect of dopant site and dopant concentration of Cu on the band gap of MoS2 using DFT calculations. They revealed that electronic and structural properties of MoS2 are modiﬁed due to the Cu doping. Joseph et al [27]. Used hydrothermal technique and analyzed the inﬂuence of Cu doping on thermoelastic properties of MoS2, X-ray diffraction (XRD) and high resolution transmission electron microscope (HRTEM) investigations veriﬁed the interaction between Cu and MoS2. Xia et al [28] also used the hydrothermal process for synthesis of Cu-doped MoS2 nanosheets and characterized the binding properties of Cu with Mo and S through energy dispersive X-ray (EDX) mapping and X-ray photoelectron spectra (XPS). Thus, MoS2 being a non-zero bandgap material with good thermal stability, has dragged a noticeable interest. Moreover MoS2 based devices exhibits great prospective to use in energy harvesting and semiconducting applications.

In this paper, we have provided a systematic study of electronic properties of TMN-doped MoS2, Cu, B and C are chosen as dopant which are experimentally [27, 29] and computationally [30] proved to have a good chemistry with MoS2. Furthermore, TMN assists in ﬁne bandgap tuning by changing its substitutional site and concentration variation which advocates for its good conducting role close to metallic character. The purpose of our study is to ascertain the outcomes of TMN concentration, effect of variation of substitutional site on the bandgap of MoS2, and the chemistry of foreign element with the host that suggests it practicable as semiconductor. Further, we have reported the stability of the system based on cohesive energy. As an inference a signiﬁcant variation in bandgap value has been observed which is advantageous to enhance the electronic properties for its use in the applications towards on/off and semiconducting gadgets.

2. Computational methodology

We performed DFT computations employing Vienna ab-initio simulation package (VASP) [31], which implies projector augmented wave (PAW) potentials [32] using the scheme of exchange correlation functional Perdew–Burke–Ernzerhof (PBE) [33]. The cut off kinetic energy of plane wave basis set was set to be 400 eV. We used a $4 \times 4$ supercell of MoS2, comprising of 16 and 32 atoms of Mo and S respectively. To avoid interlayer interactions, the vacuum in z-direction is kept 15Å. A Monkhorst Pack mesh of $5 \times 3 \times 1$ in brillian zone is used for geometry optimization [34], whereas a bigger grid of $15 \times 15 \times 1$ is employed for density of states (DOS) calculations. Energy minimization computations are performed until the complete Hellmann Feynman forces
were smaller than 0.02 eV Å$^{-1}$ [35]. In all the calculations, before and after the substitutions, the ionic positions were allowed to relax in the supercell. Cohesive energy was determined as:

$$E_{coh} = \frac{(E_{\text{System}} - N_{\text{Mo}}E_{\text{Mo}} - N_{\text{S}}E_{\text{S}} - N_{\text{Cu}}E_{\text{Cu}} - N_{\text{B}}E_{\text{B}} - N_{\text{C}}E_{\text{C}})}{N}$$

Where $E_{\text{System}}$ is the all-out energy of the framework. $E_{\text{Mo}}, E_{\text{S}}, E_{\text{Cu}}, E_{\text{B}}$ and $E_{\text{C}}$ are energies of confined Mo, S, Cu, B and C separately. $N_{\text{Mo}}, N_{\text{S}}, N_{\text{Cu}}, N_{\text{B}}$ and $N_{\text{C}}$ are the quantity of Mo, S, Cu, B and C atoms of the framework separately and $N$ is absolute number of atoms in supercell.

Table 1. Summary of the results obtained owing to the impurity concentration of Cu, B and C. The energy gap values, Cu–S, Cu–B and Cu–C bond lengths and their respective cohesive energies are given. The subscript with the symbols of substituted atoms represent the number of such atoms replaced.

| Sr No | Configurations         | $d_{\text{Cu-S}}$(Å) | $d_{\text{Cu-B}}$(Å) | $d_{\text{Cu-C}}$(Å) | Band Gap (eV) | $E_{\text{coh}}$ (eV/atom) | $E_{\text{tot}}$ (eV) |
|-------|------------------------|----------------------|----------------------|----------------------|----------------|--------------------------|------------------|
| 1     | Cu$_1$B$_1$C$_1$        | 2.3                  | 2.1                  | 1.9                  | 0.38           | -5.08                    | 7.31             |
| 2     | Cu$_1$B$_1$C$_1$        | 2.6                  | 2.1                  | 1.9                  | 0.46           | -4.89                    | 16.50            |
| 3     | Cu$_1$B$_1$C$_1$(with changed sites) | 2.3                  | 2.1                  | 1.9                  | 0.48           | -4.89                    | 16.40            |
| 4     | Cu$_1$C$_1$B$_1$(with changed sites) | 2.4                  | 2.0                  | 1.9                  | 0.38           | -4.89                    | 16.30            |
| 5     | Cu$_1$B$_1$C$_1$        | 2.5                  | 2.0                  | 2.5                  | 0.46           | -4.85                    | 18.71            |
| 6     | Cu$_1$B$_1$C$_2$        | 2.3                  | 2.5                  | 1.9                  | 0.35           | -4.85                    | 18.40            |
| 7     | Cu$_1$B$_1$C$_2$        | 2.2                  | 2.1                  | 2.2                  | 0.30           | -4.85                    | 18.74            |
| 8     | Cu$_1$C$_2$            | 2.3                  | —                    | 2.0                  | 0.30           | -4.64                    | 28.4             |
| 9     | Cu$_1$B$_1$C$_1$        | 2.3                  | 2.5                  | 2.2                  | 0.37           | -4.71                    | 25.16            |
| 10    | Cu$_1$B$_1$C$_1$(Hexagonal) | 2.4                  | 2.1                  | 1.9                  | 0.27           | -4.56                    | 32.10            |
| 11    | Cu$_1$B$_1$C$_2$(Hexagonal) | 2.5                  | 2.2                  | 1.9                  | 0.16           | -4.62                    | 29.40            |
| 12    | Cu$_1$B$_2$C$_2$(Hexagonal) | 2.5                  | 2.2                  | 2.0                  | 0.16           | -4.59                    | 31.19            |
| 13    | Cu$_1$B$_2$C$_2$(Rectangular) | 2.5                  | 2.0                  | 2.0                  | 0.34           | -4.57                    | 32.05            |
| 14    | Cu$_1$B$_2$C$_2$(Rectangular) | 2.5                  | 2.1                  | 2.0                  | 0.28           | -4.63                    | 32.04            |

Figure 1. (a) Optimized (4 × 4 supercell) structure of Cu$_1$B$_1$C$_1$-doped MoS$_2$ monolayer (b) Energy gap patterns (c) Partial density of states patterns.
The formation energies reported in Table 1 have been calculated employing the following formula:

$$E_f = E(\text{doped}) - E(\text{pristine}) - E(\text{dopant}) + E(\text{removed})$$

Where $E(\text{doped})$, $E(\text{pristine})$, $E(\text{dopant})$ and $E(\text{removed})$ are respectively, the calculated total energy of the doped system, pure system, dopant and removed host atom.

### 3. Results and discussions

We incorporated Mo atom(s) in MoS$_2$ with Cu and, S atom(s) with B and C and observed that the change in bandgaps depends upon the impurity substitution, variation in impurity concentrations and substitutional sites.

#### 3.1. Substitution by single impurities

##### 3.1.1. Cu substitution by Mo and, B and C by S

We substituted one Mo with one Cu and, two S atoms with B and C atoms. Optimization process caused to change distances between Mo, S and impurity atoms. The bond lengths of $d_{\text{Cu-S}}$, $d_{\text{Cu-B}}$, $d_{\text{Cu-C}}$, $d_{\text{Mo-B}}$ and $d_{\text{Mo-C}}$ are determined to be 2.3, 2.1, 1.9, 2.1 and 1.9 Å respectively. A comparable substitutional doping of Cu in MoS$_2$ and Be in h-BN have been accounted for in our previous investigations [26, 36]. The Cu is displaced from the original position of Mo by 0.042 Å, whereas B and C by 0.98 Å and 0.88 Å respectively after geometry optimization process. The C–Cu–B, C–Cu–S and B–Cu–S bond angles are determined as 116°, 107° and 89° respectively relative to their 82° values in pristine MoS$_2$ [26].

In order to find the energy gap of the model given in figure 1(a), we computed the band structure computations. The results obtained are depicted in figure 1(b). At Fermi level, the energy gap is observed to be 0.17 eV. A similar energy gap with Mg doping in graphene has been accounted in our recent research [37]. The presence of impurity lines divide the wide bandgap into three parts having widths 0.38, 0.31 and 0.39 eV. The impurity lines near to Fermi level appear due to Cu atom. Our outcomes are in agreement with pervious detailed examinations [26, 36–38].
To investigate the role of dopants, we performed the PDOS calculations. The consequences are represented in figure 1 (c). The participation to DOS around the Fermi level is due to the orbitals of Cu, S and Mo. The hybridization appears just below the Fermi level due to p orbitals of B and d orbitals of Cu. A little participation comes to the PDOS from the pₓ of C, pₓ of S, and d of Cu at 0.5 eV. A sharp peak can be noted in conduction band, which mainly comes due the d-orbitals of Cu, pₓ of S, p orbitals of B, and pₓ of C. An intense peak in the conduction band shows that a strong overlapping among the B, Cu, S and Mo is observed around 1.2 eV energy. These results are consistent with our recent reported results [26].

3.2. Effect of concentration and substitutional site
In this subsection we systematically changed the sites of B and C atoms by keeping the impurity concentration of Cu (4.16%) same, and have observed a variation in bandgap values. Furthermore, bonding mechanism is also considered.

3.2.1. Two Cu substituted by Mo and, B and C by S
We substituted two Mo atoms with Cu, which made the Cu concentration 4.16%. Two S atoms were additionally replaced, one with B and other with C as shown in figure 2(a). The bond lengths of $d_{\text{Cu1-S}}$, $d_{\text{Cu1-B}}$, $d_{\text{Cu2-S}}$, $d_{\text{Cu2-C}}$, $d_{\text{Mo-B}}$ and $d_{\text{Mo-C}}$ are observed to be 2.6 Å, 2.1 Å, 2.7 Å, 1.9 Å, 2.1 Å and 2 Å respectively. All $d_{\text{Mo-S}}$ bond lengths are found to be the same as the pristine MoS₂ [26]. The Cu is displaced from the original position of Mo by 0.16 Å, whereas B and C by 0.39 Å and 0.68 Å respectively after geometry optimization process. These findings are well agreed with our recent reported results [26, 30].

The electronic band structure calculations showed the direct and indirect band gaps having values 0.26 and 0.46 eV respectively as depicted in figure 2(b). This observed direct bandgap (0.26 eV) is smaller than the single Cu doped configuration (0.39 eV), while the direct bandgap moves 0.56 eV above from Fermi level. The indirect band gap (0.46 eV) is greater than the reported configuration (0.38 eV) in section 3.1.1. The indirect bandgap moves 0.41 eV below from Fermi level which is higher ups the single Cu–doped system. Many impurity lines are observed between direct and indirect band gaps. These impurity lines come from the p of C and B and d of Cu atoms. These results are in accordance with previous reported results [21, 26, 39].

Figure 3. (a) Optimized (4 × 4 supercell) structure of Cu₂B₁C₁-(with changed sites)-doped MoS₂ monolayer (b) Energy gap patterns (c) Partial density of states patterns.
The consequences of PDOS computations are shown in figure 2(c). These consequences show that the orbitals of S, B, C, Mo and Cu are overlapping in valence band. The major contribution to PDOS at Fermi level is from \( p_x \) orbitals of C, \( p \) of B and S and \( d \) of Cu and Mo. A hybridization is experienced due to \( p_x \) orbitals of C, \( p \) orbitals of B, \( p_z \) of S and \( d \) of Mo and Cu both at 0.5 and 0.85 eV. This hybridization results in sigma bond formation. \( p \) orbitals of B and C atoms are hybridized at 1.1 eV. In the conduction band, Mo and S atoms show major contribution in energy area 1.2 to 2.5 eV of PDOS.

3.2.2. Two Cu substituted by Mo and, B and C by S with changed sites

In this system, the concentration of impurity atoms was same as reported in section 3.2.1 but the dopant sites of B and C were changed. The atomic distances of \( d_{\text{Cu1-S}}, d_{\text{Cu1-B}}, d_{\text{Cu2-S}}, d_{\text{Cu2-C}}, d_{\text{Mo-B}} \) and \( d_{\text{Mo-C}} \) are determined to 2.3 Å, 2.1 Å, 2.5 Å, 1.9 Å, 2.1 Å and 1.9 Å respectively. The bond length between Cu and S decreases as we change the dopant sites of B and C atoms. All the bond lengths \( d_{\text{Mo-S}} \) are found to be same as in the pristine MoS\(_2\). Thus, by changing the dopant site a significant variation occurs in bond length values.

The indirect and direct bandgaps were induced of 0.32 and 0.48 eV respectively as presented in figure 3(b). The indirect bandgap shifts 0.42 eV beyond the Fermi level, while indirect band gap reported in section 3.2.1 was observed below the Fermi level. The direct bandgap goes 0.40 eV below the Fermi level, while direct band gap discussed in section 3.2.1 was observed above the Fermi level. Thus, by changing the dopant sites of B and C the location of direct and indirect band gaps are also changed. Many impurity lines are observed within direct and indirect band gaps which divide the big bandgap.

The outcomes from PDOS computations are showed in figure 3(c). These outcomes point toward the main contribution to DOS coming from the \( p_x \) of S, \( d \) of molybdenum and copper, and \( p_y \) orbitals of C-atom within the valance band. The orbitals of B, S and Mo are overlapping in energy area \(-1.4 \) to \(-0.9 \) eV. The hybridization occurs due to \( p_x \) of sulfur and \( d \) of Cu-atom at \(-0.4 \) eV. In the vicinity of Fermi level, the population of PDOS is observed due to \( p_x \) of C, \( p_y \) of S and \( d \) of Mo and Cu. These overlapping occur at 0.85 eV. Major contribution in conduction band to the PDOS comes from the Mo and S atoms in energy area 1.3 to 2.5 eV as shown in figure 3(c).
3.2.3. Two Cu substituted by Mo and, B and C by S with replaced sites

The concentration of dopants is kept same as reported in sections 3.2.1 and 3.2.2, while the sites of B and C are interchanged relative to last discussed section. Geometry optimization procedure has been continued until to the required accuracy of the structure has reached. The optimized structure indicates very small variations in the bond lengths. The bond lengths of $d_{\text{Cu1–S}}$, $d_{\text{Cu1–C}}$, $d_{\text{Cu2–S}}$, $d_{\text{Cu2–B}}$, $d_{\text{Mo–B}}$ and $d_{\text{Mo–C}}$ are measured to be 2.4 Å, 1.98 Å, 2.5 Å, 2.01 Å, 2.1 Å and 2 Å respectively.

After electronic band structure computations, we noticed that the highest band gap is observed 0.38 eV which is below the Fermi level as indicated in figure 4(b). The observed band gap (0.38 eV) has smaller value as compared to the above reported band gaps. Emergence of impurity lines splits the bandgap into five parts having widths 0.38, 0.30, 0.22, 0.20 and 0.19 eV (see figure 4(b)). Thus, by changing the site of dopants a significant variation in band gap occurs.

The PDOS calculations results indicate that the main involvement to DOS originates from the orbitals of Cu, Mo, B, C and S in the energy area $-3$ to $-0.8$ eV as shown in figure 4(c). A peak is noticed due to hybridization of the orbitals of C, S, Cu and Mo at $-0.45$ eV. The hybridization is observed in the locality of Fermi level due to the orbitals of S and Cu. A small overlapping is noted at Fermi level due to the orbitals of C and Mo, while a large overlapping is found due to $p_z$ of S and d of Cu, Mo and C at 0.55 eV. We also determined a strong hybridization due to the orbitals of B, Mo and Cu at 0.85 eV, which indicates a sigma bonding. In conduction band, an overlapping can be seen due to the orbitals of C, S, Cu and Mo at 1 eV. The main overlapping in the conduction band originates from the orbitals of B, S and Mo as depicted in figure 4(c).

3.2.4. Three Cu substituted by Mo and, B and C by S

In the present case, the concentration of B and C are kept same as discussed above and only the concentration of Cu has been increased to 6.25% as depicted in figure 5(a). After geometry optimization, the bond lengths $d_{\text{Cu1–C}}$, $d_{\text{Cu2–C}}$, $d_{\text{Cu3–C}}$ and $d_{\text{Cu2–B}}$ are determined to be 2.05, 2.5, 2.06 and 2.03 Å respectively. The bond lengths between Mo and S are determined in ranging from 2.36 to 2.49 Å. The highest value of $d_{\text{Cu1–C–Cu3}}$ bond angle is noticed as 121°. The maximum displaced position of Cu from original position of Mo is determined to be 0.30 Å which is the heighest of all reported systems. These results are consistent with previous reported studies [26, 30].
The electronic band structure computations were performed for the present configuration. These results indicate that the direct and indirect bandgaps appear above and below the Fermi level. The highest value of indirect bandgap is found as 0.46 eV above the Fermi level. The same value of bandgap (0.46 eV) was observed in earlier reported section 3.2.1 below the Fermi level. The direct bandgap of 0.30 eV is determined below the Fermi level, while 0.26 eV direct band gap was determined above the Fermi level reported in previous section 3.2.1. Thus, by increasing the impurity (Cu) concentration the change of location of direct and indirect band gaps occur. We also observed a small band gap just below the Fermi level as shown in figure 5(b). We observed many impurity lines which cause the reduction in big band gap. Our results are well agreed with previous studies [26, 28].

The PDOS calculations indicate that an overlapping is observed due to p orbitals of B, S and C, and d orbitals of Mo and Cu at −0.7 eV. We also observed hybridization among p$_x$ of C, p$_y$ of S and d of Cu and Mo around 0.25 eV. A little peak is can be seen at 0.7 eV due to overlapping of concerned p and d orbitals of the elements involved. An overlapping is is noted due to p orbitals of B, C and S, and d orbitals of Cu and Mo in energy area 0.8 to 1.2 eV as shown in figure 5(c).

### 3.2.5. Three Cu substituted by Mo and, one B and two C by S

Keeping the concentration of Cu and B same as reported in section 3.2.4, only variation in C concentration has been made to observe its effect on bond length, which comes to be 2.5 Å, 1.97 Å and 2.3 Å of Cu–B, Cu–C and Cu–S respectively and other properties. All other atomic distances between Mo and S are determined to be 2.4 Å. Thus, a significant variation in bond lengths are noticed by playing with the concentration of C atoms.

Two direct bandgaps having widths 0.34 and 0.21 eV above and below the Fermi level respectively are observed. An indirect bandgap 0.35 eV is observed below the Fermi level. This value of indirect bandgap (0.35 eV) is smaller than the reported in section 3.2.4 (0.46 eV). We also noticed that the Fermi level shifts upward as compared with configuration reported in section 3.2.4. Thus, the position of Fermi level could be changed by changing the impurity concentration of C in MoS$_2$.

The consequences of PDOS computations are revealed in figure 6(c), which show that the p of C, S and d of Mo and Cu participate in bonding in energy area −3 to −0.9 eV. The major contribution around the Fermi level

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**Figure 6.** (a) Optimized (4 × 4 supercell) structure of Cu$_3$B$_1$C$_2$-doped MoS$_2$ monolayer (b) Energy gap patterns (c) Partial density of states patterns.
arises from the p_y of S, p of C and d of Mo and Cu, while in conduction band, a strong hybridization is observed due to these atoms in 0.6 to 1.1 eV range. A small peak is also determined by the overlapping of C, Cu, and S and Mo atoms at 1.3 eV.

### 3.2.6. Three Cu substituted by Mo and, one C and two B by S

In this configuration, the concentration of Cu and C is kept constant as discussed in sections 3.2.4 and 3.2.5, only the variation in B concentration has been made to observe its effect on geometry parameters and other properties. The highest bond length value between Cu_1 and C is observed to be 2.18 Å. The bond lengths d_{Cu2-C} and d_{Cu3-C} are measured to be same being 2.06 Å. The atomic distance between Cu and B is determined as 2.01 Å. The bond lengths between impurity atoms and S are observed to be 2.24 Å, while bond length of 2.1 Å between Mo and B atoms is noticed. The bond length values between Mo and S are determined in ranging from 2.33 to 2.5 Å as shown in figure 7(a). The highest bond angle (Cu–B–Mo) is observed to be 121°. Thus, a significant variation in geometry parameters are observed on varying the concentration of B atoms.

Figure 7(b) indicates the pattern of band structure calculations. These results provide the indirect and direct band gaps of 0.21 and 0.30 eV above and below the Fermi level respectively. This value of direct bandgap (0.30 eV) is smaller than that discussed in section 3.2.5 (0.34 eV). We also noticed the position of direct bandgap just below the Fermi level, while in reported section 3.2.5 above the Fermi level. Similarly, the position of indirect bandgap is also observed to be changed relative to the configuration discussed in section 3.2.5. Hence, the position of bandgap could be altered by changing the impurity concentration of B in MoS_2 monolayer.

The orbitals of Mo, Cu, C, B and S mainly contribute to PDOS in energy area −3 to −0.45 eV as shown in figure 7(c). In the vicinity of Fermi level, the population of PDOS is observed due to p of S and d of Cu and Mo, while a small contribution of p orbitals of B also played a role. In the conduction band, an overlapping is determined among the orbitals of S, B, Mo and Cu as depicted in figure 7(c).

### 3.2.7. Four Cu substituted by Mo and, two C by S

In this system, we substituted four Mo atoms with Cu, which made the Cu concentration 8.33%. Additionally, two S atoms were replaced with two C atoms and creation of a single vacancy of S atom as depicted in figure 8(a).
After the procedure of geometry optimization, we found that the impurity atoms cause the alteration in bond lengths between Mo, S and impurity atoms. The bond lengths of $d_{\text{Cu-S}}$, $d_{\text{Cu-C}}$, $d_{\text{Mo-C}}$ and $d_{\text{Mo-S}}$ are observed to be 2.3 Å, 2.0 Å, 2.1 Å, and 2.4 Å respectively.

Figure 8(b) shows the results of the band structure calculations. Multiple band gaps appear having values 0.30, 0.25, 0.18, 0.16 and 0.13 eV. At the Fermi level, the indirect band gap is observed as 0.16 eV. The presence of impurity lines divide the large bandgap (1.95 eV) into smaller bandgaps. Around the Fermi level, the impurity lines come from the Cu and C atoms. A similar study was reported previously in which effect of Mn and B, C and N co-doping in MoS$_2$ [39].

A large overlapping is determined among the d of Mo and Cu, and p of C and S in ranging from $-3$ to $-0.8$ eV as shown in figure 8(c). The hybridization is observed due to the p of S and C, and d of Mo and Cu in energy area $-0.6$ to $-0.15$ eV. At the Fermi level, a small peak is observed which is from p of C and S, and d of Cu and Mo. Many peaks are also determined by overlapping of the orbitals of Cu, Mo, S and C in conduction band. In conduction band, orbitals of B and Cu also overlapping in energy area 1 to 2 eV.

3.2.8. Four Cu substituted by Mo and, B and C by S

The concentration of Cu is kept same as reported in section 3.2.7, only the one C from two is replaced by one B including the site change and after this the change in geometrical structure has been noticed. The bond length between Cu$_1$ and B is observed to be 2.5 Å, while all bond lengths between impurity atoms are determined as 2.2 Å. The atomic distance between S and Cu is found to be 2.3 Å.

The highest value of indirect bandgap is observed to be 0.37 eV above the Fermi level. We also observed the smallest value of indirect bandgap 0.18 eV just below the Fermi level as shown in figure 9(b).

The PDOS calculations indicate that a large overlapping is determined among the d of Mo and Cu, and p orbitals of C, B and S in valence band as shown in figure 9(c). An intense peak is found at $-0.45$ eV which comes from the orbitals of B, C, S, Mo and Cu. This overlapping forms a bond. At the Fermi level, an overlapping is observed which arises from the orbitals of S, Cu and Mo, while a small overlapping of the orbitals of B also played a role. At 0.4 eV, the p$_y$ of C is overlapping with d of Mo and Cu at 0.45 eV. A sharp overlapping is determined.
between \( p_x \) of C and B at 1.1 eV. The large overlapping is observed due to the orbitals of B, S and Mo in the conduction band ranging from 1.3 to 2.5 eV (see figure 9(c)).

3.2.9. Four Cu substituted hexagonally by Mo and, B and C by S
The concentration of Cu, B and C is kept the same as reported in section 3.2.8, only the site changing of dopants has been made to notice its effect on bond lengths and other properties. The results indicate the bond lengths between B and its nearest atoms (Cu and Mo) are 2.1 Å, while C and its nearest atoms (Cu and Mo) have 1.9 Å as depicted in figure 10(a). All other atomic distances are determined to be 2.4 Å. Hence, a small variation in bond lengths is produced by changing the dopant sites. A similar hexagonal doping of Cu in MoS\(_2\), Be in h-BN and Be in graphene have been studied in earlier studies [26, 36, 40].

The band structure computations results are depicted in figure 10(b). These results show that the bandgap value is observed to be 0.27 eV above the Fermi level. Fermi level moves 0.70 eV below the bandgap that indicates a p type doping. By keeping the same value of concentrations (Cu, C, B) as discussed in the previous section only the sites of dopant are changed to notice the effect on bandgap, a significant change is observed as outcome.

The PDOS calculations indicate that a large overlapping is determined among the orbitals of Mo, Cu and S in energy area –3 to 0.7 eV as shown in figure 10(c). In vicinity of Fermi level, the contributions from C, Cu, S and Mo atoms are populated in PDOS. A hybridization is observed due to p of B, C and S, and d of Mo and Cu at 1.1 eV.

3.2.10. Four Cu substituted hexagonally by Mo and, one B and two C by S
The hexagonal geometry of Cu is maintained by keeping the concentration and sites of Cu and B same as discussed in section 3.2.9. The variation in bond length value has been noted down by increasing C concentration. A 2.2 Å bond value is observed between Cu and B atoms. The bond length values between Cu and C atoms is determined as 1.97 Å. The bond length values between Mo and S are observed in ranging from 2.36 to 2.61 Å. Thus, a prominent variation in bond lengths can be observed by playing with the concentration of C atoms.
A modification in band gap has been noticed by altering concentration as shown in figure 11(b). Firstly the band gap is calculated by keeping the concentration in same ratio as narrated in section 3.2.9. Then the concentration of C is changed irrespective of the Cu and B. Resultantly, a remarkable decrease in band gap from 0.27 to 0.18 eV has been perceived.

The PDOS calculations indicate that a large overlapping is determined among the d of Mo and Cu, and p orbitals of S and C in energy ranging from $-3$ to 1 eV, while a small hybridization of the orbitals of B is also observed as shown in figure 11(c). An overlapping is determined due to the p of S and C, and d of Mo and Cu in energy area 0.6 to 1 eV. A peak is observed due to the orbitals of C, B, S, Cu and Mo at 1.2 eV.

### 3.2.11. Four Cu substitute hexagonally by Mo and, two B and two C by S

In this model, the concentration and sites of Cu and C are kept same as reported in the last case. The variation in bond lengths have been observed by increasing the B concentration as shown in figure 12(a). After geometry optimization, the bond lengths of $d_{\text{Cu1-C2}}$, $d_{\text{Cu2-B2}}$, $d_{\text{Cu3-C1}}$, $d_{\text{Mo-B1}}$, $d_{\text{Cu4-S}}$ and $d_{\text{Mo-B2}}$ are noted to be 2.04 Å, 2.21 Å, 2.04 Å, 2.11 Å, 2.5 Å and 2.09 Å respectively. All bond lengths of $d_{\text{Mo-S}}$ are found to same as in the pristine MoS$_2$. A similar hexagonal doping of Cu in MoS$_2$, Be in h-BN and Be in graphene have been reported in earlier studies [26, 36, 40].

Band structure results are displayed in figure 11(b). A variation in band gap has been seen by playing with concentration. Firstly, the band gap is measured by keeping the concentration in same ratio as narrated in section 3.2.10. Then the concentration of B is changed irrespective of the Cu and C concentrations. The surprising results have been noted by this strategy, as no variation in bandgap value has been identified.

The consequences of PDOS computations are shown in figure 12(c) that points out large contribution to PDOS arises from d of Mo and Cu, and p of B, C and S atoms in energy ranging from $-3$ to 0.8 eV. In the conduction band, hybridization occurs between B and C atoms in energy ranging from 1 to 2.5 eV.

### 3.2.12. Four Cu substituted rectangularly by Mo and, one B and two C by S

In this case, the concentration of dopants is same as discussed in section 3.2.10 only the dopants sites are changed. Cu-C bond distance is found 2.01 Å. We observed a bond separation between Cu and S of 2.5 Å. The bond distance between Mo and B is determined to 2 Å as shown in figure 13(a).
Figure 11. (a) Optimized (4 × 4 supercell) structure of Cu$_4$B$_1$C$_2$ (hexagonal)-doped MoS$_2$ monolayer (b) Energy gap patterns (c) Partial density of states patterns.

Figure 12. (a) Optimized (4 × 4 supercell) structure of Cu$_4$B$_2$C$_2$ (hexagonal)-doped MoS$_2$ monolayer (b) Energy gap patterns (c) Partial density of states patterns.
A variation in band gap has been observed by playing with substituational sites. Firstly, the band gap is calculated by keeping the site same as narrated in section 3.2.10. Then the sites of dopant are changed irrespective of the concentrations. This causes a considerable increase in band gap from 0.18 eV to 0.34 eV. The PDOS results as depicted in figure 14(c) indicate that main contribution of the orbitals of S, B, C, Mo and Cu contribute to PDOS at Fermi level and around energy gaps, while in the valence band it comes from the S, B, C, Mo and Cu atoms. However, hybridization is observed between the p orbitals of B and C in energy range 1.1 to 1.3 eV.

3.2.13. Four Cu substituted rectangularly by Mo and, two B and two C by S
In the present model, the concentration and sites of Cu and C are kept same as reported in section 3.2.12. The variation in bond lengths have been observed by increasing the B concentration as shown in figure 14(a). After geometry optimization, the bond lengths of $d_{\text{Cu1-C1}}$, $d_{\text{Cu2-C2}}$, $d_{\text{Cu3-B2}}$, $d_{\text{Cu4-S}}$ and $d_{\text{Mo-B1}}$ are calculated as 2.03 Å, 2.02 Å, 2.1 Å, 2.51 Å and 2.13 Å respectively. All other bond lengths of $d_{\text{Mo-S}}$ are same as in the pristine MoS$_2$.

Electronic band structure outcomes are exhibited in figure 14(b). These outcomes indicate that the highest value of bandgap is found as 0.28 eV above the Fermi level. A variation in band gap is noticed by keeping the same concentration of dopants discussed in section 3.2.12 but the locations of dopants are altered. Hence, the significant variations in band gaps have been determined after changing the sites and concentration of dopants. The PDOS calculations indicate that a very large overlapping is found among the d of Mo and Cu, and p of S, B and C in energy ranging from $-3$ to $-1$ eV as shown in figure 14(c). An overlapping is determined due to the orbitals of S, C, Mo and Cu in energy ranging from $-0.6$ to $0.8$ eV. In the conduction band, the population of PDOS arises from the p of B and S, p$_{x}$ of C and d of Mo and Cu in energy ranging from 1.1 to 1.3 eV. The p of C, B and S, and d of Mo show main contribution in conduction band.

Inspired by the investigations carried out by Ouma et al [41], where they have reported the lanthanide substitutions in host MoS$_2$ and resulting magnetic moments indicating dilute magnetic semiconductor behavior; we also repeated some of our configurations employing spin polarized DFT calculations. The configurations reported in figures 1, 2, 7, 9, 10 and 14 have been recalculated as these models contains all the concentrations of Cu substituted (i.e. Cu 1–4 atoms) in addition to hexagonal and rectangular patterns. It was
interesting to note that only two systems described in figures 2 and 9 have in respective order, the total magnetic moments of 1.08 and 0.54 μB. However, the magnetic moments on Mo were negligibly small. Additionally, the band gaps being main focus of this study are not altered. However, this interesting behavior could be observed by devoting a comprehensive study on MoS2 by varying substituents, concentration and positions to ascertain the reported alike characteristics in MoS2 which we intend to report in future.

4. Conclusions

Via first principles DFT calculations, we studied the geometrical and electronic properties of TMN doped MoS2. We substituted Mo by Cu and, B and C by S. We determined the effect of variation of concentration of impurities in addition to replaced position. We do note the changes in geometrical parameters of the host material after optimization procedure. However, from PDOS calculations we noticed that the impurity atoms make bonding with host MoS2 advocating good interaction of the foreign elements with the pristine. The maximum change in Cu–C bond distance is determined 0.51 Å comparative to pure MoS2. We also observed a variations in bond angles and buckling heights of dopants. However, despite these variations, overall geometry of the system remains intact. However, the impurities cause to decrease the Ecoh as low as −4.56 eV relative to −5.2 eV of MoS2. Due to doping the impurity lines appear in the big energy gap of MoS2 causing to divide it into small energy gaps. For TMN-doped structures, the change in concentration and site of impurities in doped structure modifies energy gaps. These efforts exhibit a variety of band gaps in the range 0.16 to 0.48 eV. Thus having achieved the band gap of desired value, MoS2 become a valuable material for its use as semiconducting materials.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
Conflict of Interest

The authors declare that they have no conflict of interest.

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