

Electronic structure of β - Si_3N_4 crystals with substitutional icosagen group impurities

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The β - Si_3N_4 crystals are widely used in industrial and electronics areas. Therefore, β - Si_3N_4 has drawn the attention of researchers for many years. In this study, effects of icosagen group impurity atoms in the IIIA group on the electronic properties of the β - Si_3N_4 crystal were analyzed by using the density functional theory. As a result of these analyses, it was determined that the electronic properties of the crystal change significantly. Basic electronic characteristics for pure β - Si_3N_4 crystal and icosagen group impurity β - Si_3N_4 crystals, such as band structures, densities of states, binding energies, and formation energies were investigated. We identified that the band gap of the β - Si_3N_4 crystal was affected significantly by the impurity, and this change was varying linearly in line with the formation energy for the impurity cases. As a result of calculations, the Al-impurity was found to be the lowest-energy impurity state.

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1. Introduction

Due to its wider band gap, the Si_3N_4 material became a useful crystal in electronic, mechanic and thermal applications [1, 2]. Since it can operate at high temperatures, it is widely used in industrial areas such as thermally conducting heating elements, automobile engines and gas turbines [3]. Besides the industrial applications, it is widely used in the semiconductor industry as gate dielectrics due to its dielectric properties and as a passivation layer in silicon solar cells because of its surface passivation properties [4, 5].

Together with its cubic (γ) phase, as well as its well-known natural phases of alpha (α) and beta (β), it has a total of 3 crystalline forms [6]. β - Si_3N_4 can change phase at high temperatures and turns into γ or α - Si_3N_4 crystal [7]. β - Si_3N_4 has a hexagonal crystal structure having $P6_3m$ space group containing 6 silicon atoms and 8 nitrogen atoms in a 14-atom unit cell [8].

Recently, it became possible to grow the β - Si_3N_4 crystal using Chemical Vapor Deposition (CVD) and Molecular Beam Epitaxy (MBE) methods [9, 10]. When growing GaAs and GaN based semiconductor alloys (AlGaAs, AlGaN, InGaAs, InGaN, etc.) by these methods of growth, some impurity atoms, such as Aluminum (Al), Gallium (Ga) and Indium (In) can be deposited in the growth chamber, and can be a dopant as an impurity atom in a crystal grown afterwards. Such impurity atoms can affect the electronic properties of the doped crystal significantly [11].

The β - Si_3N_4 crystal is defined as a dielectric material in its pure state. Dielectric properties of these

materials can deteriorate if they contain one or more of the aforementioned impurities [12]. Considering this fact, it is important to study the effects of these impurity atoms on the electronic properties of the β - Si_3N_4 crystal.

In this study, the changes in the electronic properties of the β - Si_3N_4 crystal doped with Al, In and Ga impurity elements were investigated against the pure β - Si_3N_4 crystal. The electronic band structure, density of states (DOS) and total energy values obtained after doping each impurity atom into β - Si_3N_4 crystal were analyzed by calculating the formation energies and binding energies through density functional theory (DFT). In addition, the change in the formation energy was also examined according to the place of the atoms in the periodic table and band gap in impurity cases.

2. Calculation methods

In this study, Al, Ga and In impurity atoms were doped into the crystal independently, and the most stable states for each impurity atom were determined using Eq. (1) and Eq. (2). For these steady states, band structures, band gaps, densities of states, and the partial DOS (PDOS) calculations were performed. In the calculations, 14-atom β - Si_3N_4 unit cell, having the $P6_3m$ space group, consisting of 8 nitrogen atoms and 6 silicon atoms, shown in Fig. 1 was used. Then, the electronic properties of β - Si_3N_4 were calculated and examined through a DFT-based pseudo-potential method using the Atomistix Toolkit-Visual NanoLab (ATK) software [13-15]. The Local Density Approximation (LDA) approach was used as the exchange-correlation in the

calculations. The cut-off energy and k-points were taken as 280 eV and $4 \times 4 \times 10$ respectively, and $a=7.6015 \text{ \AA}$ and $c=2.9061 \text{ \AA}$, which are calculated as lattice constants with minimum total crystal energy values, were used. The lattice parameters were used as compatible with the literature [8, 16]. In addition, the maximum force applied to the crystal was 0.05 eV/\AA .

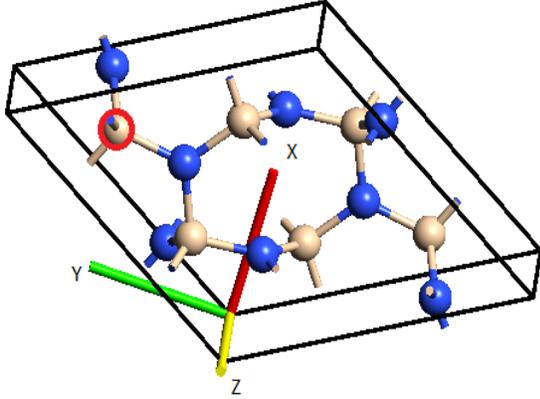


Fig. 1. 14-atom β - Si_3N_4 unit cell

3. Results and discussion

The most stable state for an impurity atom to be doped into the crystal is shown with a red circle. In our calculations, the locations of impurity atoms in the crystal were found by calculating the formation and binding energies.

As a result of these calculations, the states with lowest binding energy and the lowest formation energy were determined as the most stable states. In the binding energy given with Eq. (1), E_b is the binding energy, E_t is the total energy, and E_{atoms} is the sum of free energies of the crystal and impurity atoms doped into the crystal [18]. In the formation energy given with Eq. (2), E_{tot}^{dop} is the total energy in the impurity case, E_{tot}^{pure} is the total energy of the pure crystal, chemical potential values of Si, Al, Ga and In are taken as total energy per atom of bulk states. For a nitrogen atom, chemical potential is taken from the energy of N_2 molecule ($\mu_{\text{N}}=1/2\mu(\text{N}_2)$). μ_{imp} is the chemical potential of impurity atoms which are Al, Ga and In [19].

$$E_b = E_t - E_{atoms} \quad (1)$$

$$E_F = E_{tot}^{dop} - [E_{tot}^{pure} + \mu_{imp} - \mu_{\text{Si}}] \quad (2)$$

The most stable states found as a result of the calculations are shown in Table 1. When a comparison is made between the states with impurity, it is seen that the state with the lowest binding energy is the case with the Al impurities. Therefore, it can be said that the most stable state among these structures is β - Si_3N_4 with Al impurity. Negative binding energies are an indication of higher stability and are also the lowest energy states [20].

Table 1. The formation and binding energies for pure β - Si_3N_4 crystal and the β - Si_3N_4 crystal with Al, Ga and In impurity atoms

Impurity Atoms	Formation Energy (eV)	Binding Energy (eV)
No impurity	-	-164.2161
Aluminum	5.7512	-158.4648
Gallium	10.2658	-153.9502
Indium	15.2026	-149.0135

Fig. 2 shows the band structures of Si_3N_4 crystals for pure and impurity states. In the pure case, it is seen that the β - Si_3N_4 crystal has an indirect band gap. As a result of the calculations, the band gap for the pure β - Si_3N_4 was found as ~ 4.95 eV, and this result was observed to be rather consistent with the literature [2, 8]. In calculations performed with LDA, our calculations yielded values highly consistent with the experimental values, despite the lower band gap values in the literature [2].

When these impurity atoms in the IIIA group bind with nitrogen a loss of electron occurs. In contrast with the pure case, it is observed that valence band in the band structures of β - Si_3N_4 crystals with impurities is close to the Fermi level, an even it is seen that some of the bands form impurity levels above the Fermi level [21]. These impurity levels are the result of the hybridization of impurity atoms with surrounding nitrogen atoms.

The conduction bands of β - Si_3N_4 structures with Al and Ga impurities are pretty similar to each other, however, it is observed in the case with In impurity that the band gap becomes a direct one because of the additional band added to the conduction band. The band gap is observed to be reduced in β - Si_3N_4 crystals containing Al, Ga and In impurity atoms. The band gap values for β - Si_3N_4 crystals with Al, Ga and In impurity were 4.37 eV, 4.19 eV and 3.60 eV, respectively. It can be said that the In impurity atom changes the band gap of the β - Si_3N_4 crystal significantly and almost transformed it into a semiconductor material.

In the band structure of the pure β - Si_3N_4 crystal, the maximum point of the valence band was between A- Γ , whereas it is at the point Γ in all impurity states. Except for the In impurity, the minimum point of the conduction band is at A. In addition, the total energy values per atom for each state are shown in Table 2.

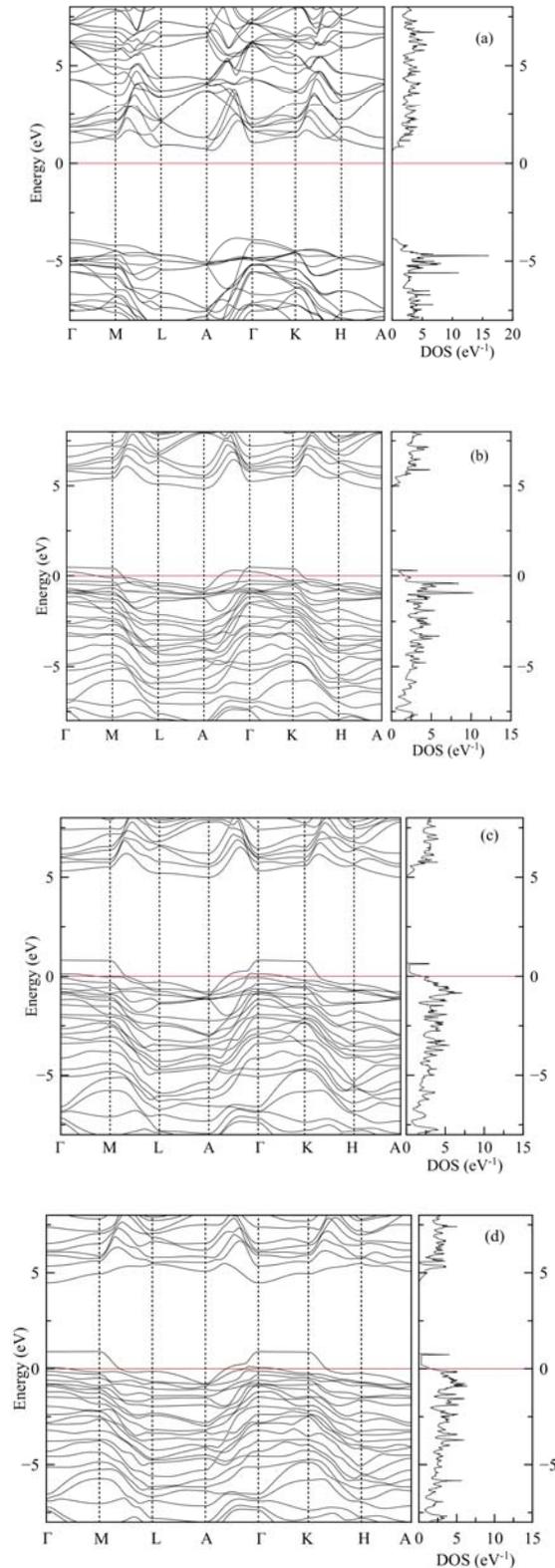


Fig. 2. Band structures and density of states, (a) pure β - Si_3N_4 , (b) β - Si_3N_4 doped with Al-impurity, (c) β - Si_3N_4 doped with Ga-impurity, (d) β - Si_3N_4 doped with In-impurity

Table 2. The total energy values per atom, band gaps and direct or indirect band gaps for pure β - Si_3N_4 crystal and β - Si_3N_4 crystals with Al, Ga and In impurities

Structures	VB _{max} point	CB _{min} point	Direct	Bandgap (eV)	Total energy per atom (eV)
Pure	A- Γ	A	No	4.95	-234.05
Aluminum	Γ	A	No	4.37	-231.27
Gallium	Γ	A	No	4.19	-238.19
Indium	Γ	Γ	Yes	3.60	-260.56

Fig. 3 shows the total DOS and the PDOS graph for pure β - Si_3N_4 crystal. The contribution from the orbitals of the atoms contributing to the total DOS is shown in the figure. The major contribution to the valence band comes from the p shell of the nitrogen atom, whereas the major contribution to the conduction band comes from the p and d shells of the silicon atom. The atomic orbital calculations performed for pure β - Si_3N_4 are found to be consistent with the literature [22, 23].

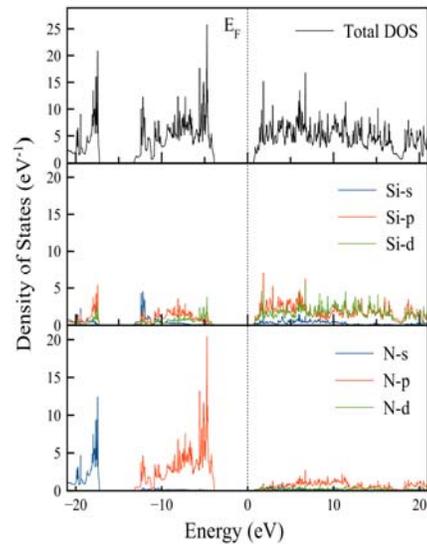


Fig. 3. Density of state for the β - Si_3N_4 crystal

Fig. 4 shows the PDOS for β - Si_3N_4 crystal with Al, Ga and In impurities. The p orbitals of Al, Ga and In impurity atoms are seen to interact with binding nitrogen's p orbitals mostly. As a result of this interaction, it is observed that the valence band is pulled down under the Fermi level, creating levels to receive. However, the graph in Figure 4(c) shows that Fermi level overlaps valence band more for the In-impurity state, compared to other impurity states. The Fermi levels overlapping valence band were found to be 0.28 eV,

0.64 eV and 0.73 eV for Al, Ga and In impurities respectively.

In the comparison of states of pure and impurity states, a significant change is observed in the density of states of crystals with impurity given in Fig. 4, in comparison to the pure states. It can be seen that these densities of states created by contributions of particularly the impurity atoms above the Fermi level reduce the band gap of the pure β - Si_3N_4 crystal, leading substantial changes in the electronic properties of the crystal. Such impurities have changed the band gap of the pure β - Si_3N_4 crystal, and the states of the conduction and valence bands against Fermi level, compared to the pure β - Si_3N_4 case. Because of the significant change in the band gap especially, these impurity atoms may play a major role in adjusting the band gap of pure β - Si_3N_4 crystal.

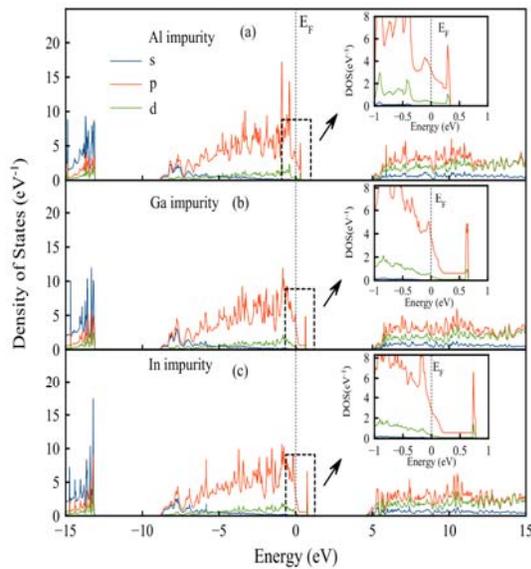


Fig. 4. PDOS for the β - Si_3N_4 crystal containing a) Al, b) Ga, c) In impurity atoms

Fig. 5 shows the contributions from s, p and d orbitals of the impurity atoms of the β - Si_3N_4 crystal with Al, Ga and In impurities. The density on the d orbital of the Al-impurity atom above the Fermi level was found to be more than of the p orbital. It is also seen that the density of states in the p and d orbitals for Ga and In impurity atoms were almost the same, with a bit more density in the p orbital.

Fig. 6 (a) shows the change in the formation energy of the examined structures according to the positions of the used impurity atoms Al, Ga, and In in the periodic table. It is seen that the formation energy increases substantially and exhibit a linear behavior as the atomic number increases in the IIIA group in the periodic table. Looking at the impurity states in the β - Si_3N_4 crystal for the other atoms in this group, it can be said that they will exhibit this sort of behavior.

Again, Fig. 6(b) shows the change in the formation

energy depending on the band gap for the β - Si_3N_4 crystal with Al, Ga and In impurities. It's observed that the formation energy decreases significantly as the band gap values increases. It's seen that the structures with larger band gaps have more localized impurity states.

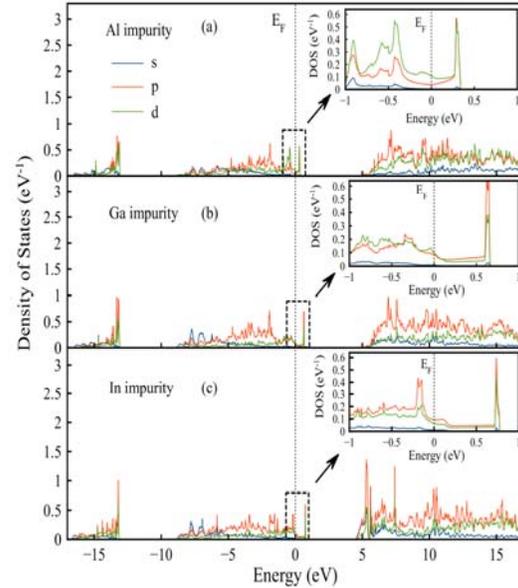


Fig. 5. PDOS of the a) Al, b) Ga, c) In impurity atoms only

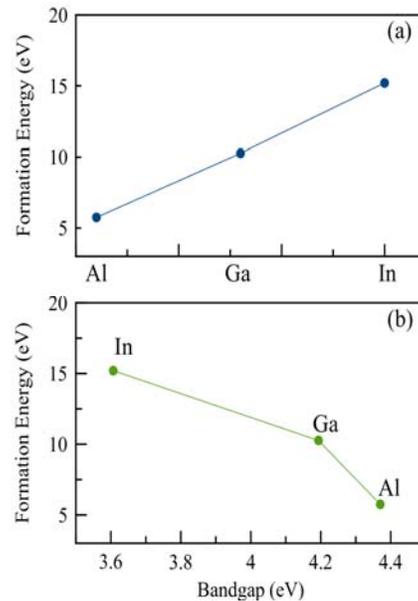


Fig. 6. Formation energy of systems with impurities; depending on the (a) atoms and (b) band gaps

Formation energy values and binding energy values of β - Si_3N_4 crystal with Al, Ga and In impurities are listed in Table 1. The lowest binding energy state is seen for Al impurity. Therefore, the steadiest state can be accepted for β - Si_3N_4 crystal doped with Al impurity. In addition, it is also

observed that the binding energy increases as the atomic numbers of the impurity atoms increase. It is known that steady state of the crystal increases as a result of the increasing binding energy values.

4. Conclusion

In this study, effects of Al, Ga and In atoms, on the electronic properties of the pure β - Si_3N_4 crystal were investigated. The LDA approach was used as the exchange-correlation in the calculations. As a result of the calculations, impurity atoms were shown to affect the electronic properties of pure β - Si_3N_4 crystal significantly. It was determined that the dopant impurity atoms have a p-type contribution for the crystal, and create impurity levels above the Fermi level, pulling the valence band under the Fermi level. The band gap of the crystal containing impurity was found to be lower than the band gap of the pure β - Si_3N_4 crystal. The change of the formation energy of the crystal was analyzed for the pure state depending on this change in the band gap, and as a result the formation energy was observed to be lower in higher band gaps. In addition, it was also observed that the formation energy of the β - Si_3N_4 crystal containing these impurities increases linearly as the atomic numbers of these atoms in the IIIA group increase. The steadiest structure among the impurity atoms was determined to be β - Si_3N_4 with Al-impurity, by looking at the lowest formation and binding energies. As a result of the analysis, the impurity atoms were observed to change the band structure, band gap and total energy per atom of the crystal in a pure state significantly.

Acknowledgements

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