Silicon Atom doped Mono layer InN; a DFT Study

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Abstract
The electronic and optical parameters of monolayer Indium Nitride (InN) are modified by Silicon (Si) atom substitution using first-principles DFT. Si atom doping (with varying concentration) causes the graphene like Dirac cone of InN to move up or down the Fermi Energy (E_F) level or induces some energy gap at high symmetric K-point depending upon Si atom concentration. The overall absorption spectrum shows reduced strength; however the static reflectivity of InN is improved after Si atom substitution in its lattice.

Keywords — *Grapheme, Electronic structures,* InN *co-doping, Absorption, Reflectivity.*

I. INTRODUCTION

Discovery of two-dimensional (2D) graphene in 2004 [1] introduced a unique materials family known as FLAT LAND materials [2, 3]. Among these 2D materials, group III-V nitrides are now being considered as promising candidates for solid state semiconducting devices [4-6]. A member of group III-V nitrides i.e. monolayer InN has been experimentally and theoretically investigated and it contains higher thermal stability, high charge mobility, drifty velocity, excellent absorption and a sizeable band gap [7]. However, unlike graphene InN is a direct band gap semiconductor material; the outstanding characteristics like graphene along with direct band gap nature, InN is a functional candidate for nano-electronic devices [8]. Although, till now significant amount of work is dedicated to the manipulation of optical properties of InN layer, while the work on electronic properties manipulation remains unfinished [9, 10]. Here, we investigate the opto-electronic properties of monolayer InN decorated with Si atom having variable concentration through first- suggest that, Si atom doping in InN makes it display half metallic behavior and absorption coefficient of InN layer is overall reduced.

II. Computation methodology

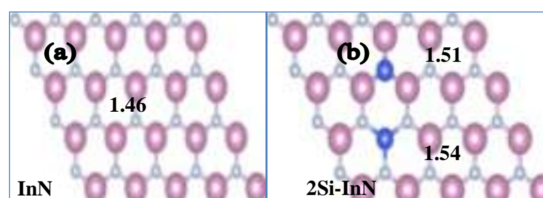
First-principles DFT calculations were carried out using VASP simulation package [11, 12] with PAW (projector augmented wave) scheme [13]. PBE (Perdew–Burke–Ernzerhof) function [14] with GGA (generalized-gradient approximation) technique was utilized for exchanges and correlations. Structure model consist of 5 × 4 InN supercell having 20 Å in Z-direction, on which 450eV cut-off energy was applied for expansion of its plane waves. Brillouin zone (BZ) was sampled using 7×7×1 *Gamma*-centered k-mesh. Si atom-doped InN systems were optimized till the Hellmann–Feynman force and total energy parameters did not gain 0.02 eV/Å and 10^{-5} eV values, respectively. Band structure was calculated using 30 points along *Gamma- M - K - Gamma* path in the irreducible BZ, in order to gain fine quality electronic structures. For optical parameters, Random Phase Approximation (RPA) technique was adopted. Brief explanation on the extraction of optical parameters can be easily found in previous studies [15, 16].

III. Results and discussions

Structural and opto-electronic parameters of Si atom-doped monatomic InN material are investigated in this section. Obtained results during accompanied with appropriate analysis follow as under:

A. Structure and electronic behaviors of Si doped monatomic InN layer

Typical relaxed geometry of pristine and Si decorated InN layer, depicting bond lengths between In-N, In-Si and N-Si atoms is shown in Figs. 1(a)-(d), respectively. Si incorporation in InN layer modifies the lattice constant attributed to the difference of the covalent radii of Si, N and In atoms, in that order. Average equatorial bond lengths of In-N, In-Si and N-Si atoms were obtained in range of 1.44-1.46Å, 1.49-1.51Å and 1.54-1.56Å, respectively. Moreover, when Si atom replaces In atom and is bonded with neighboring 3 N atoms, the Si atom bulges upward from the InN plane; whereas when Si atom is placed at N atom site and it has 3 neighboring In atoms, impurity Si atom holds its position in the InN plane [17-19].



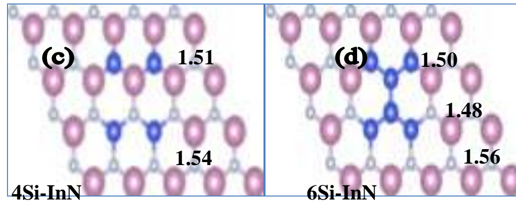


Fig 1. *(a)-(d) Atomic structures of Si-doped InN layer showing In-N, N-Si, In-Si and Si-Si bond lengths in Å*

Electronic structures of pristine and Si (varying concentration) decorated InN layer are described in Figs. 2(a)-(d), respectively. The electronic structure of pure InN layer depicts semiconducting behavior having 0.7eV band gap value as evident in Fig. 2(a). The electronic structure of pure InN layer is in accord with few of preceding studies [7, 8]. However, the variation in the energy levels of calculated electronic structures with the previous reports may be credited to the disparity of super cell size and adopted K-points during this study. When Si atoms are inserted in InN layer, they tend to modify the energy bands of electronic structure of InN.

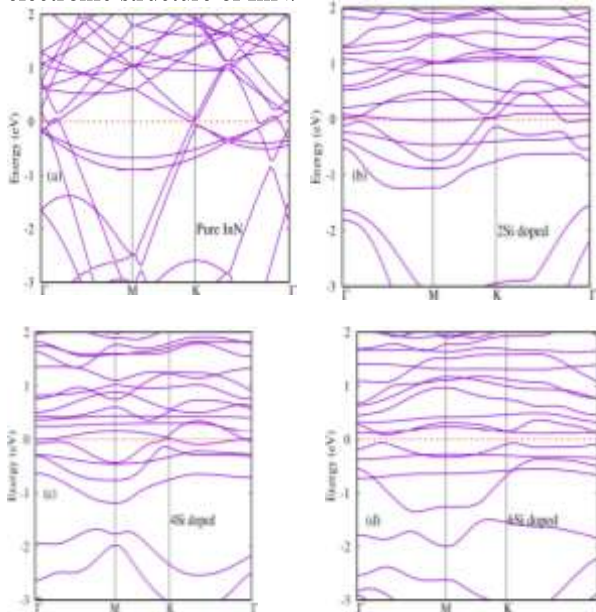


FIGURE 2. (a)-(d) *Band diagrams of pure and Si (2, 4 and 6) atom substituted monolayer 5 × 4 InN super cell structures.*

When 2Si atoms are incorporated in InN layer, the Si-InN hybrid system displays half metal property as some of the energy bands (i.e. impurity states) appear at the Fermi energy (EF) level as shown in Fig. 2(b). Similarly 4Si atoms substitution in InN layer makes it display metallic behavior, since valence and conductions bands are almost overlapping each other in the electronic structure as shown in Fig. 2(c). Lastly, when 6Si atoms are placed in InN layer, this system displays indirect band gap semiconducting behavior having band gap of 0.6eV, as evident in Fig. 2(d). In a summarized way, it can be predicted that, individual Si atom substitution in InN layer cannot add energy gaps in its electronic structure rather it tries to convert it into a half metal or conducting material by nature as demonstrated in Figs. 2(a)-(d), respectively [20, 21].

B. Optical behaviors of Si decorated monoatomic InN layer

Lastly, optical parameters of pristine and Si decorated InN layers are investigated using Random Phase Approximation (RPA) DFT [22] technique. Local field effects are omitted and interband transitions are taken into account in this approach, which can produce some inaccurate results in lower energy range. The 13 × 13 × 1 *Gamma*-centered BZ sampling was performed during this work. Optical characteristics such as absorption coefficient 'α', reflectivity 'R' and energy loss spectrum were obtained for pure and Si doped InN layers. We need dielectric tensor values in order to gain these quantities. The imaginary dielectric tensor using following expression,

$$\varepsilon''_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2\omega_k \, \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \langle u_{ck+e_\alpha q} | u_{vk} \rangle \langle u_{ck+e_\beta q} | u_{vk} \rangle^* \quad (1)$$

Here, α and β are the Cartesian components, e_α and e_β stand for the unit vectors along the three directions, c and v symbolize conduction and valence bands, in that order. Conduction and valence band energies are denoted by ϵ_{ck} and ϵ_{vk} while u_{ck} term portrays the cell periodic part point K.

Similarly, real dielectric tensor can be obtained using Kramers-Kronig transformation,

$$\varepsilon'_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \quad (2)$$

Here, P describes the principle value. Abovementioned method is broadly elaborated in Ref. [22].

Absorption 'α', reflectivity 'R' and energy loss spectrum ELS parameters can be extracted from dielectric tensor values as explained in Ref. [15]. The absorption spectrum of pristine and Si decorated InN layers are demonstrated in Fig. 3(a). As visible in Fig. 3(a), the absorption spectrum of pure InN layer contains 2 main peaks at 0.2 eV and 9 eV energies having 2000 cm^{-1} and 7800 cm^{-1} peak intensities. When, InN is decorated with Si atoms, the absorption peaks at 0.2 eV and 9 eV energies gain reduced intensities. However, the absorption spectrum of InN layer is improved in between 2-8 eV and 10-13 eV energies, since in these intervals of energies InN layer has very low absorption as evident in Fig. 3(a) [21, 23]. In conclusion, Si incorporation in InN produces reduction in main absorption peaks while inducing greater absorbance in higher energy range.

Similarly, the 'R' parameter of pure and Si doped InN layer is demonstrated in Fig. 3(b). It can be seen in Fig. 3(b) that, the static 'R' parameter of pure InN layer has 0.8 intensity, while Si atom substitution reduces this value as shown in Fig. 3(b). The next main 'R' peak emerging at 10eV energy is

also reduced when Si atoms are placed in InN layer. In conclusion, the Si atom doping in InN layer reduces the overall reflectivity parameter of InN material. Lastly, the energy loss spectrum (ELS) of pure and Si doped InN is shown in Fig. 3(c). It can be observed that, the electrons of pure InN has larger ELS values at 4eV and 10eV energies but Si atoms try to reduces these peak intensities to a significantly low values as visible in Fig. 3(c), in that order [23, 24].

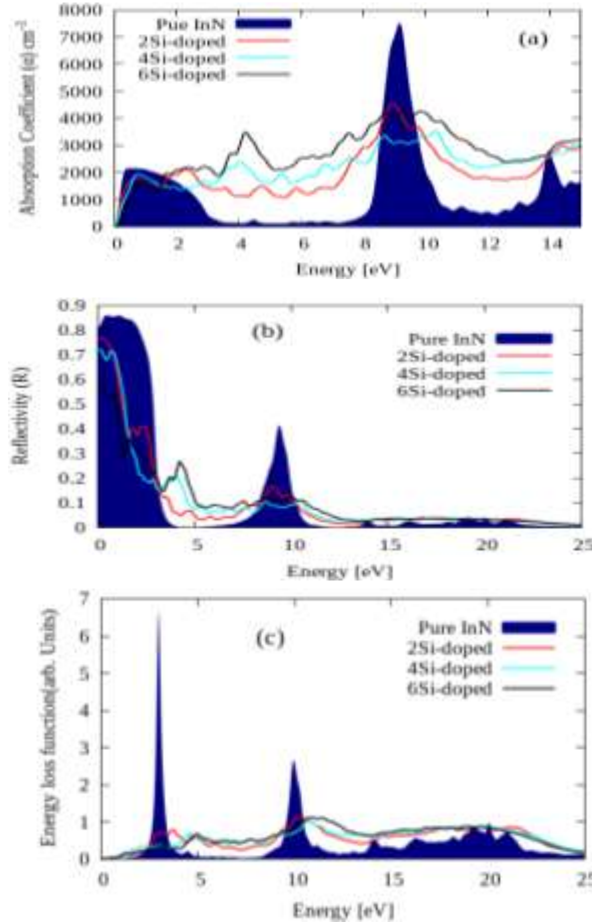


FIGURE 3. (a) Absorption coefficient 'α', (b) reflectivity 'R' and (c) ELS of pristine and Si decorated InN layer

C. Formation energies of Si decorated monatomic InN layer

The stability criteria for Si atom-doped InN structures is investigated by calculating the formation energies of given systems; Formation energies (E_F) can be obtained using following expression [25]:

$$E_{f(Si/InN)} = E_{(Si/InN)} - E_{pInN} + m\mu_{In} - n\mu_N - \mu_{Si} \quad (3)$$

Here, $E_{f\,(Si/I}$ and E_{pI} are complete energies of Si decorated InN layer and pristine InN, correspondingly. Chemical potentials ( ) of Indium, nitrogen and Si atoms were taken from intrinsic InN, NO_2 gas molecules and standard phase of Si crystals. Obtained formation energies for 2Si, 4SI and 6Si decorated monolayer InN structures were found as i.e. -2.63eV, -3.92eV and -4.43eV, respectively. Given Si atom-doped InN structures illustrate negative (E_F) values which indicates that, the Si substitution in InN layer is an exothermic stable process. These predictions are in consensus with previous literature [26-28].

VI. Conclusion

This study demonstrates the opto-electronic parameters of pristine and Si decorated monatomic InN material using first-principles DFT. Different Si (i.e. 2, 4 and 6) atoms were placed in InN lattice and their effects were investigated on abovementioned properties of InN layer. Si atom incorporation in InN layer makes it display half metal/semiconducting behavior, depending upon the quantity of Si atoms embedded in InN. When 6Si atoms were substituted, InN layer displayed indirect band gap semiconductor property having 0.6eV band gap. From optical parameters, it was observed that, Si atom substitution in InN reduced the absorption quantity in lower energy range, while significantly improving the absorption in higher energy intervals. The static reflectivity parameter of InN layer is reduced suggesting that, Si atom doping converts reflective InN layer to an antireflective layer in lower energy range. Likewise, the electron energy loss parameter of InN is also reduced significantly as Si atoms are placed in InN layer. The stability parameter of Si doped InN was determined by calculating the formation energies for all given systems. All Si atom-doped InN structures indicated negative formation energies suggesting that, the Si substitution is stable thermodynamic process. In a summarized way, it can be suggested that, Si atom doping in InN layer is a preferred technique to tune its opto-electronic parameters, so that a functional InN materials can be fabricated for nano-electronic and optoelectronic device applications.

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References

[1] Novoselov, K.S., et al., Electric field effect in atomically thin carbon films. science, 2004. 306(5696): p. 666-669.
[2] Pacile, D., et al., The two-dimensional phase of boron nitride: few-atomic-layer sheets and suspended membranes. Applied Physics Letters, 2008. 92(13): p. 133107.
[3] Vogt, P., et al., Silicene: compelling experimental evidence for graphenelike two-dimensional silicon. Physical review letters, 2012. 108(15): p. 155501.
[4] Vurgaftman, I., J.á. Meyer, and L.á. Ram-Mohan, Band parameters for III–V compound semiconductors and their alloys. Journal of applied physics, 2001. 89(11): p. 5815-5875.

[5] Ponce, F.A. and D.P. Bour, Nitride-based semiconductors for blue and green light-emitting devices. Nature, 1997. 386: p. 351.
[6] Liao, J., et al., Design of High-Efficiency Visible-Light Photocatalysts for Water Splitting: MoS2/AlN(GaN) Heterostructures. The Journal of Physical Chemistry C, 2014. 118(31): p. 17594-17599.
[7] Chen, X.-P., et al., Density-functional calculation of methane adsorption on graphenes. IEEE Electron Device Lett, 2015. 36(12): p. 1366-1368.
[8] Şahin, H., et al., Monolayer honeycomb structures of group-IV elements and III-V binary compounds: First-principles calculations. Physical Review B, 2009. 80(15): p. 155453.
[9] Abbas, A.N., et al., Black phosphorus gas sensors. ACS nano, 2015. 9(5): p. 5618-5624.
[10] Zhou, M., et al., Adsorption of gas molecules on transition metal embedded graphene: a search for high-performance graphene-based catalysts and gas sensors. Nanotechnology, 2011. 22(38): p. 385502.
[11] Kresse, G. and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Physical Review B, 1999. 59(3): p. 1758.
[12] Kresse, G. and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Computational Materials Science, 1996. 6(1): p. 15-50.
[13] Blöchl, P.E., Projector augmented-wave method. Physical Review B, 1994. 50(24): p. 17953.
[14] Perdew, J.P., K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple. Physical review letters, 1996. 77(18): p. 3865.
[15] Marinopoulos, A., et al., Ab initio study of the optical absorption and wave-vector-dependent dielectric response of graphite. Physical Review B, 2004. 69(24): p. 245419.
[16] Muhammad, R., Y. Shuai, and H.-P. Tan, First-principles study on hydrogen adsorption on nitrogen doped graphene. Physica E: Low-dimensional Systems and Nanostructures, 2017. 88: p. 115-124.
[17] Rafique, M., et al., Structural, electronic, and magnetic behaviors of 5d transition metal atom substituted divacancy graphene: A first-principles study. Chinese Physics B, 2017. 26(5): p. 056301.
[18] Rafique, M., et al., Manipulation of inherent characteristics of graphene through N and Mg atom co-doping; a DFT study. Physics Letters A, 2018. 382(16): p. 1108-1119.
[19] Muhammad, R., Y. Shuai, and H.-P. Tan, A first-principles study on alkaline earth metal atom substituted monolayer boron nitride (BN). Journal of Materials Chemistry C, 2017. 5(32): p. 8112-8127.
[20] Sun, X., et al., Adsorption of gas molecules on graphene-like InN monolayer: A first-principle study. Applied Surface Science, 2017. 404: p. 291-299.
[21] Jalilian, J., et al., Tuning of the electronic and optical properties of single-layer indium nitride by strain and stress. Physica E: Low-dimensional Systems and Nanostructures, 2016. 83: p. 372-377.
[22] Gajdoš, M., et al., Linear optical properties in the projector-augmented wave methodology. Physical Review B, 2006. 73(4): p. 045112.
[23] Strite, S. and H. Morkoç, GaN, AlN, and InN: a review. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena, 1992. 10(4): p. 1237-1266.
[24] Rani, P., G.S. Dubey, and V. Jindal, DFT study of optical properties of pure and doped graphene. Physica E: Low-dimensional Systems and Nanostructures, 2014. 62: p. 28-35.
[25] Li, D., et al., Structural and electronic properties of MnO 3 (4) superhalogen clusters embedded in graphene. Chemical Physics Letters, 2014. 601: p. 16-20.
[26] Sun, M., et al., Tuning electronic and magnetic properties of blue phosphorene by doping Al, Si, As and Sb atom: A DFT calculation. Solid State Communications, 2016. 242: p. 36-40.
[27] Sun, M., et al., Magnetism in transition-metal-doped germanene: A first-principles study. Computational Materials Science, 2016. 118: p. 112-116.
[28] Wan, Q., et al., First-principles study of Ag-based p-type doping difficulty in ZnO. Optical Materials, 2008. 30(6): p. 817-821.

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