Indian Journal of Pure & Applied Physics
Vol. 60, April 2022, pp. 293-299

Non-magnetic Ge Functionalized Magnetism in 2D-GaN Monolayer

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Received 25 January 2022; accepted 23 March 2022

Exotic properties are predicted to be functionalized by the adsorption of non-magnetic Ge atom on the two-dimensional GaN (2D–GaN) monolayer. They include the existence of spin filtering, high magnetism and continuous emission of electromagnetic radiation. A comprehensive ab-initio study of structural, electronic, magnetic and optical properties of 2D–GaN monolayer possessing several Ge atoms as adsorbents has been performed. We employ the norm-conserving pseudopotentials for atoms and plane waves in a generalised gradient approximation within density functional theory (DFT). The semiconducting pure GaN monolayer is converted into a metallic one in far 2-Ge atoms adsorbed above Ga in 2D-GaN monolayer systems. The behaviour of magnetism is found to be site-independent. The binding energies per adatom of the Ge-atoms adsorbed above N are larger than those of the Ge-atoms adsorbed above Ga atoms. Along with the main strong absorption lying in the ultraviolet region in all the Ge-adsorbed GaN monolayers, strong continuous absorption from the far infrared region to the visible region has been seen in some systems. These systems may be useful for development of light-emitting devices that will emit in various regions of the energy spectrum including visible region. The emission in the deep ultraviolet region may also be used for sterilization, water purification, *etc.*

Keywords: Ab-initio study; 2D-GaN monolayer; Adsorption; Magnetism; Optical absorption

1 Introduction

The electronic devices based on bulk III-V compounds have been extensively investigated for their applications in various fields such as solar cells[1], photodetectors[2], light-emitting diodes[3], and so on, particularly in the ultraviolet and visible regions. Currently, two-dimensional (2D) systems have drawn great attention towards their study because of their fascinating mechanical, electronic, magnetic, and optical properties, *etc.* The 2D material layers are thinner than the bulk materials and their physical properties are very different from those of bulk materials. Experimental investigations of the 2D-GaN monolayer are very scarce. Recently, some workers have prepared 2D-GaN crystals using different experimental techniques[4-6].

The 2D-GaN monolayer having a comparatively large band gap will be useful in developing electronic and optoelectronic devices. The magnetic properties of two-dimensional materials may be very useful in developing nano-spintronic devices in future. The magnetic properties of the 2D-GaN monolayer have not been much investigated. Thus, it is essential to conduct a detailed investigation of the magnetic behaviour of the functionalised 2D-GaN monolayer. In this paper, we have made a comprehensive ab-initio study of the induced magnetism and spin filtering in a 2D-GaN monolayer by the adsorption of the Ge–atoms on the different types of Ga or N sites of the host lattice. Our results predict that the magnetism can be tuned by the number of non-magnetic atoms as adsorbent.

2 Method

We have used plane waves and norm-conserving pseudopotentials which are expected to predict more reliable results. For the conversion of wave function between the real and reciprocal lattices, we employ an efficient fast Fourier-transform algorithm[7]. Using the conjugate gradient algorithm[8,9], we calculate the wave function in a fixed potential state by state or band by band. The non-local norm-conserving pseudopotential of Troullier and Martin[10] within a separable approximation has been considered. An exchange-functional of Perdew *et al.*[11] produced by the FHI code[12] has been used. We also consider the long-range dispersion interactions (LRDI) as considered by Grimmes[13] in the ABINIT package in the present investigations. These long-range interactions have been ignored in earlier studies.

3 Results and Discussion

We have performed the spin-polarized self-consistent calculations and optimized the various

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structures by relaxing both the lattice parameter and the atomic positions simultaneously, in contrast to other earlier calculations where the optimization for the lattice vector and atomic positions has been done separately. A total system energy convergence of 10^{-5} eV is achieved. On all atoms, Hellmann-Feynman forces of less than 5×10^{-2} eV/Å are obtained. A two-dimensional super cell containing 32 atoms in a 4x4x1 two-dimensional lattice has been employed. We present here the results after using a plane wave cut-off energy of 80 Ry and a grid of 10×10×1 k-points in the Brillouin zone within the Monkhorst-Pack scheme. We have tested the convergence up to 1 % using a larger value of the cut-off energy and a larger number of k-points.

The binding energy (BE) for one adatom for a system containing n-adatoms has been determined as,

$$BE = [E_{GaN} + nE_{ad} - E_T]/n$$

where E_{GaN} is the energy of all the Ga and N atoms of the unit cell, E_{ad} is the energy of isolated one adatom and E_T is the total energy of system containing all the Ga and N atoms and 'n' adatoms.

We define "buckling" in the plane of the 2D-GaN monolayer as the maximum difference in the heights of the host atoms normal to the plane of the monolayer. In all the electronic structure figures, the Fermi level (E_F) has been set at the value obtained in the calculation. Also, in all the figures containing the atomic configurations, the difference between the spin up and spin down charge densities, known as net charge density, has been plotted around some important atoms. The net spin charge density determines the magnetic moment of the unit cell.

3.1 Pure 2D-GaN monolayer

We consider a pure 2D-GaN monolayer whose atomic configuration is shown in Fig. 1(a). The optimised value of the lattice parameter is found to be 3.07 Å. A quite small buckling of 0.07 Å is observed. The cohesive energy per Ga-N pair is obtained as 8.38 eV. These values for the lattice constant and cohesive energy are quite different from the values reported by the earlier workers who did not include LRDI in their investigations considered here. As example, Sahin *et al.*[14] & Gonzalez *et al.*[15] have reported the values of the lattice constant as 3.20 and 3.21Å, respectively. Also, cohesive energy equal to 12.74 or 7.68 eV, has been obtained by these workers. In fact, the inclusion of LRDI in the present study contracts the GaN monolayer, which results in a smaller lattice constant and a higher electron energy band gap. The computed electronic structure for the pure 2D-GaN monolayer is depicted in Fig. 1(b). In our previous article[17], an indirect band gap of 2.93 eV between the top of the valence band at K-point and the lowest state in the conduction band at Γ-point has been reported. Earlier researchers reported much lower values of the indirect band gap. A value of 2.27 eV for the indirect band gap has been reported by Sahin *et al.*[14].

The absorption spectrum for the pure 2D-GaN monolayer is shown in Fig. 1(c). One does not observe any absorption in the visible region. The absorption in the near ultraviolet region is also small. The strongest absorption appears in the energy range from 5.4 to 6.3 eV and peaks at 5.7 eV. Tian *et al.*[16] have obtained this peak at 5.24 eV. The presence of absorption in the ultraviolet energy regions can be used in a variety of applications, such as optoelectronic devices, sterilization, water filtering and so on.

3.2 Adsorption of Ge atoms above Ga atom in 2D-GaN monolayer

3.2.1 1-Ge atom

For 1-Ge atom adsorbed above Ga atom, the optimised atomic structure and net charge density are

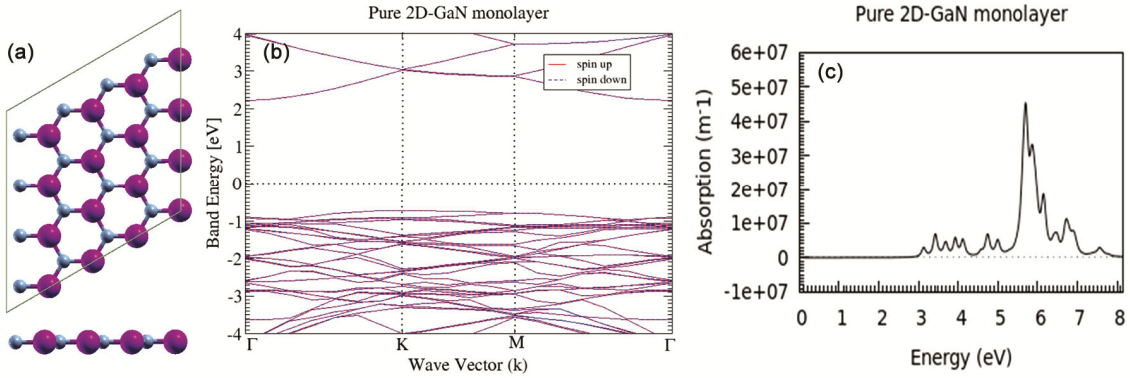

Fig. 1 — Pure 2D-GaN monolayer (a) Top and side views of atomic configurations having Ga (purple colour) and N (grey colour) atoms (b) electronic structure (c) optical absorption.

shown in Fig. 2(a). The lattice parameter is computed as 3.01 Å. The height of Ge atom lying above Ga atom is found to be 2.31 Å. The binding energy per Ge atom is found as 0.38 eV. Here, one observes a small buckling of 0.005 Å. The electronic structure for this system is shown in Fig. 2(b) which explains that this configuration is a semiconductor possessing an indirect band gap of 0.71 eV having bottom of the conduction band at Γ-point and top of valence band at K-point. The electronic state lying at bottom of the conduction band is due to spin down p-type states of Ge and N atoms and the electronic state lying at the top of valence band is because of spin up p-type state of Ge atom. The perusal of band structure of this system reveals that it will not work as a spin filter.

We present the absorption spectra for this system in Fig. 2(c). The absorption spectra seem to be weaker as compared to that of pure 2D-GaN monolayer with a red shift of absorption peaks by the energy of 1.24 eV. One observes the Ge-activated magnetic moment of 2 μ_B per unit cell. It is delocalized and comprised of 0.65, 0.11 and 0.13μ_B on Ge, Ga and each of the three neighbouring N atoms, respectively. The rest part of the contribution lies in the interstitial space {see Fig. 2(a)}.

3.2.2 Near 2-Ge atoms

We study near 2-Ge atoms adsorbed above Ga atoms Fig. 3(a) which depicts the optimized atomic configuration along with the net charge density. The lattice parameter is found to be 3.08 Å. A quite small buckling of 0.02 Å appears in the 2D-GaN monolayer. The optimized height of each Ge atom is found to be 2.36 Å. The two Ge atoms show a small repulsion with each other and their separation is 3.22Å. This Ge-Ge distance is larger than the separation of 3.08 Å of the two underlying Ga-atoms. It explains that the two Ge atoms form a molecule.

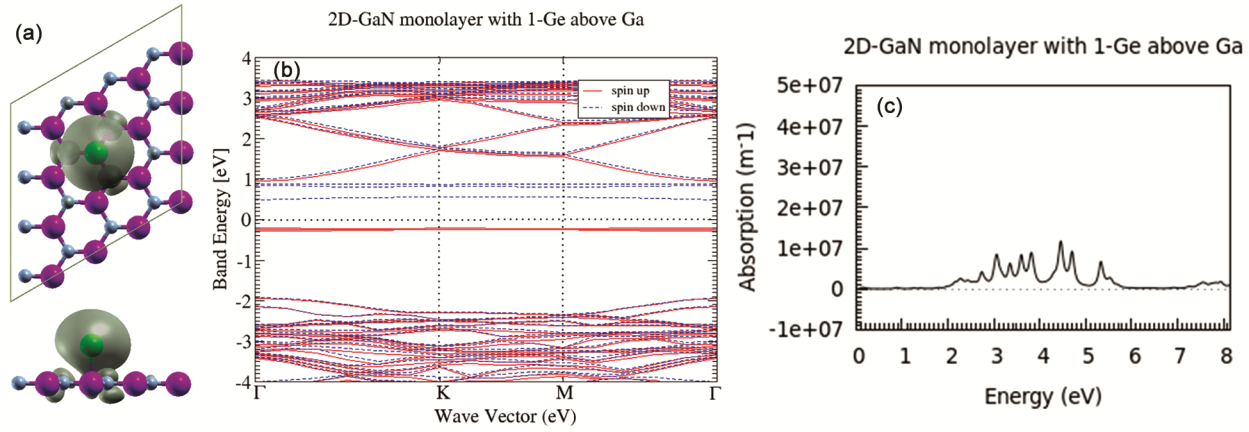

Fig. 2 — 2D-GaN monolayer with 1-Ge above Ga (a) Top and side views of atomic configurations having Ge (green colour) and net spin charge density with isosurface value 10^{-3} e Å^{-3} (b) electronic structure (c) optical absorption.

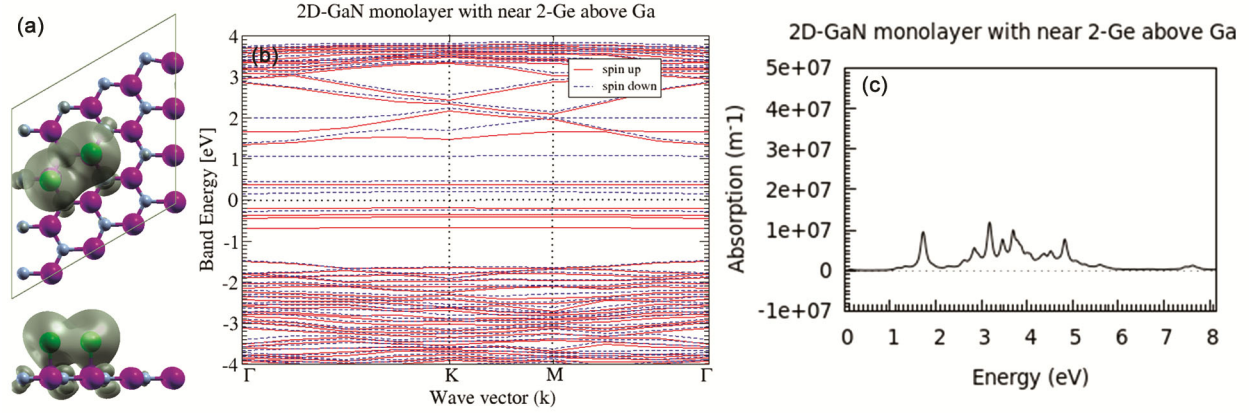

Fig. 3 — 2D-GaN monolayer with near 2-Ge above Ga (a) Top and side views of atomic configurations and net spin charge density with isosurface value 10^{-3} e Å^{-3} (b) electronic structure (c) optical absorption.

The binding energy of Ge molecule with 2D-GaN monolayer turns out to be 4.59 eV. The electronic structure for the near 2-Ge atoms is presented in Fig. 3(b). This Fig. 3(b) explains the semiconducting nature with an indirect band gap of 0.35 eV having bottom of the conduction band at Γ-point and top of valence band at K point. The electronic states at the edges of conduction band and valence band are due to spin down p-type states and spin up p-type states of Ge atom respectively. Again, this system will not act as spin filter.

The corresponding absorption spectrum is depicted in Fig. 3(c). The four major peaks in the absorption spectra lie at 1.81, 3.23, 3.72 and 4.95 eV. The major peak lies at 3.27 eV. There appears continuous absorption starting from the near infrared region at 1.81 eV up to the far ultraviolet energy region. The Ge molecule possesses a magnetic moment of 2.42 μ_B. It arises from the contributions of 0.36 μ_B made by each Ge atom, 0.08 μ_B by Ga and 0.22 μ_B by each of the nearest N atoms. The remaining part lies in the interstitial space {see Fig. 3(a)}.

3.2.3 Far 2-Ge atoms

Further, we consider far 2-Ge atoms adsorbed above two Ga atoms for which the optimized atomic configuration and calculated net charge density are shown in Fig. 4(a). The lattice parameter is found to be 3.02 Å. A much reduced buckling of 0.005 Å is seen. The height of each Ge atom is found to be 2.59 Å. The binding energy per Ge atom is 1.22 eV which is greater than that of a single Ge atom adsorbed on the GaN monolayer. The electronic structure for this system is presented in Fig. 4(b). One observes a number of flat bands in the vicinity of E_F. This system behaves like metallic character. All the occupied and the unoccupied bands around the E_F possess the spin up character. Further, these flat band are comprised mainly of the hybridized p-type states of Ge and N atoms. The phenomenon of spin filtering is seen. The system will filter the electrons having spin down. Hence this system will act as a spin filter.

The absorption spectrum for this system is shown in Fig. 4(c). A broad absorption peak lies at very low energy of 0.30 eV. Approximately similar two absorption peaks appear at 2.72 and 3.81 eV. As compared pure 2D-GaN monolayer and 1-Ge adsorbent lying above Ga atom, the absorption spectrum is shifted towards low energy side. The total magnetic moment is 4 μ_B which is double of the magnetic moment of 1-Ge atom adsorbed on the Ga atom. This magnetic moment is delocalized. It is comprised of 0.66, 0.04 and 0.09 μ_B on each Ge, Ga and N-atoms, respectively. The remaining part lies in the interstitial space {see Fig. 4(a)}.

3.3 Adsorption of Ge atoms above N atoms in 2D-GaN monolayer

3.3.1 1-Ge atom

For 1-Ge atom adsorbed above N atom, the optimized atomic configuration and net charge density are shown in Fig. 5(a). The lattice parameter is little reduced to 3.0 Å. There appears a small buckling of 0.005 Å in 2D-GaN monolayer. The height of the Ge atom is found to be 2.12 Å. The binding energy per Ge atom is quite high equal to 1.28 eV which explains a much stronger binding to 2D-GaN monolayer as compared to the binding of 1-Ge atom adsorbed above Ga-atom. Fig. 5(b) presents the electronic structure for this system. The present configuration is a semiconductor possessing an indirect band gap of 1.17 eV. Again, the existence of bottom of conduction

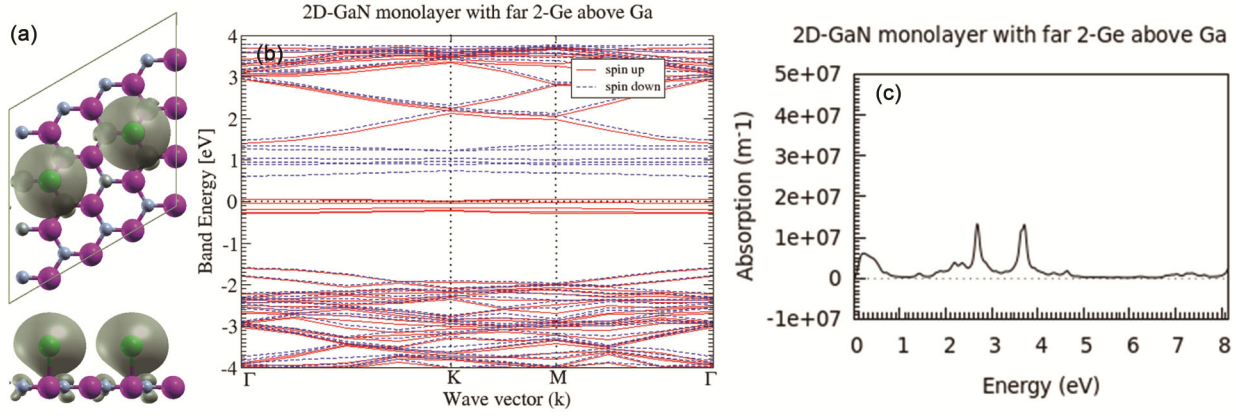

Fig. 4 — 2D-GaN monolayer with far 2-Ge above Ga (a) Top and side views of atomic configurations and net spin charge density with isosurface value 10^{-3} e Å^{-3} (b) electronic structure (c) optical absorption.

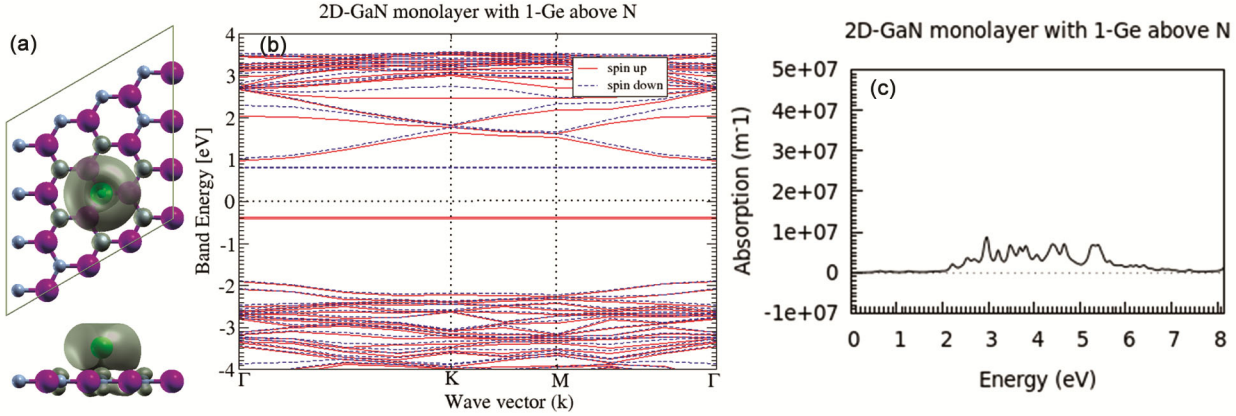

Fig. 5 — 2D-GaN monolayer with 1-Ge above N (a) Top and side views of atomic configurations and net spin charge density with isosurface value 10^{-3} e Å^{-3} (b) electronic structure (c) optical absorption .

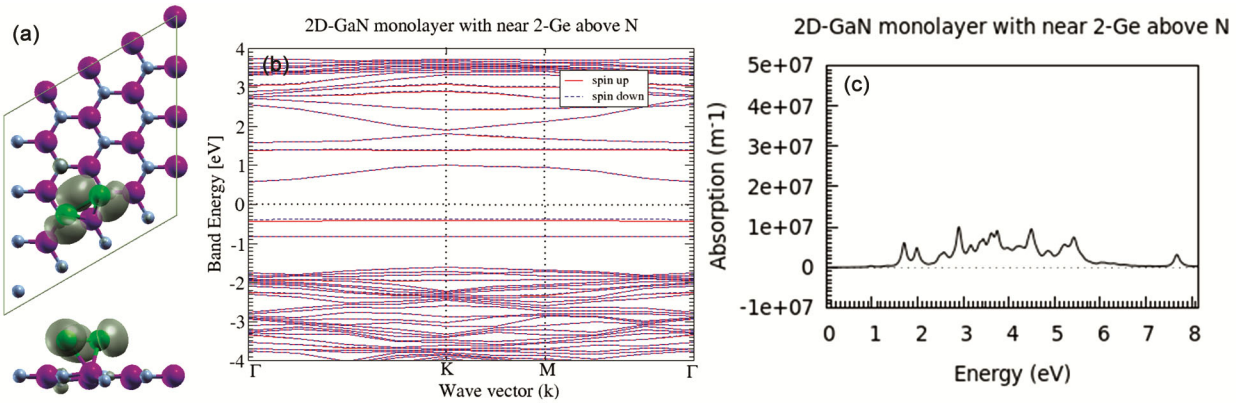

Fig. 6 — 2D-GaN monolayer with near 2-Ge above N (a) Top and side views of atomic configurations and net spin charge density with isosurface value 10^{-4}e Å^{-3} (b) electronic structure (c) optical absorption.

band and top of valence band is similar to the earlier systems. The states lying at the top of valence band have spin up character and are composed of hybridised p-type states of Ge, N and Ga atoms. The state lying at the bottom of conduction band has spin down character and is comprised with spin down p-type state of Ge atom. The perusal of band structure depicts that this system will not work as spin filter.

The absorption spectrum for this system is shown in Fig. 5(c). One observes a continuous electromagnetic absorption in the visible and ultraviolet regions starting from 2.24 eV. The net magnetic moment of 2 μ_B per unit cell is observed. This magnetic moment is delocalized and comprised of 0.61, 0.05, and 0.09 μ_B on Ge, N and each neighbouring Ga atom, respectively {see Fig. 5(a)}. The remaining part lies in the interstitial region of 2D-GaN monolayer.

3.3.2 Near 2-Ge atoms

The optimized atomic configuration and net charge density for near 2-Ge atoms adsorbed above two N atoms are shown in Fig. 6(a). The lattice parameter is found as 3.18 Å. Further, a weak buckling of 0.06 Å is found in 2D-GaN monolayer. The optimized height of each Ge atom is found to be 2.38 Å. The two Ge atoms attract towards each other and their separation is 2.44 Å which is smaller than that of two underlying Ga (3.14 Å). The Ge atoms form a molecule. The binding energy of the Ge molecule with the 2D-GaN monolayer turns out to be 14.25 eV which indicates further a stronger binding of Ge molecule to 2D-GaN monolayer. The electronic structure for this system is shown in Fig. 6(b). This system shows a semiconducting behavior with an indirect band gap of 0.94 eV. One finds that there is no splitting between the spin up and spin down states at the bottom of the conduction band. However, small splitted spin states do occur at the top of valence band. The features are quite different from that of system with near 2-Ge above Ga atom.

Figure. 6(c) includes the absorption spectrum for this system. Further, the occurrence of absorption in visible

and ultraviolet energy regions can be utilized in various applications like optoelectronic devices, sterilization and water filtering etc. The magnetic moment per unit cell for this configuration is quite small equal to 0.06 μ_B resulting a very weak magnetism.

3.3.3. Far 2-Ge atoms

Figure. 7(a) presents the optimized atomic configuration and net charge density for far 2-Ge atoms adsorbed above two N atoms. The lattice parameter is computed as 3.0 Å. No buckling is seen in 2D-GaN monolayer. The height of each Ge atoms in this system is found as 2.07 Å. The binding energy per Ge atom is found to be 1.04 eV which is greater than that of 1-Ge above Ga atom. The electronic structure for this system is shown in Fig. 7(b). The present configuration is a semiconductor possessing an indirect band gap of 0.98 eV. On the top of valence band, one observes a quite flat band having spin up character. This band originates from the hybridised p-type states of Ge, Ga and N atoms. The bottom of conduction band has spin down character and is comprised of hybridised spin down p-type states of Ge and Ga atom. Thus, this system will not act as spin filter.

The absorption spectrum for this system is contained in Fig. 7(c). Similar to Fig. 4(c), a small absorption peak lies at very low energy of 0.23 eV. The perusal of absorption spectra reveals that the absorption is found in both infrared and ultraviolet regions with almost no absorption in visible region. The total delocalized magnetic moment is 4 μ_B which is comprised of 0.59, 0.05 and 0.09 μ_B on Ge, N and each Ga atom. The remaining part lies in the interstitial space {see Fig. 7(a)}.

The lattice constant, binding energy, total magnetic moment, magnetic moment on each Ge adatom, the nature of system with band gap for the various Ge-adsorbed 2D-GaN monolayer systems are presented in Table 1. It is found that binding energy increases

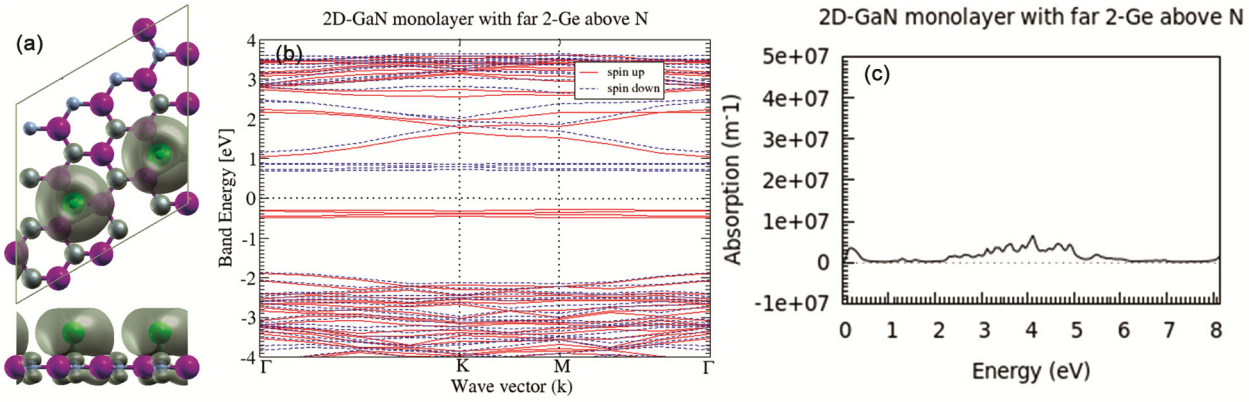

Fig. 7 — 2D-GaN monolayer with far 2-Ge above N (a) Top and side views of atomic configurations and net spin charge density with isosurface value 10^{-3} e Å^{-3} (b) electronic structure (c) optical absorption.

Table 1 — Lattice constant, binding energy, total magnetic moment, magnetic moment on each Ge adatom and nature of system with band gap for various Ge-adsorbed 2D-GaN monolayer systems.

Systems	Lattice constant (Å)	Binding energy (eV)	Total magnetic moment (μ_B)	Magnetic moment on each Ge adatom(μ_B)	Nature of system with band gap
Pure 2D-GaN monolayer	3.07	8.38	0.0	-	Semiconductor, indirect bad gap of 2.93 eV
2D-GaN monolayer with 1-Ge above Ga	3.01	0.38	2.0	0.65	Semiconductor and an indirect band gap of 0.71 eV
2D-GaN monolayer with near 2-Ge above Ga	3.08	4.59(molecule)	2.42	0.36	Semiconductor, an indirect band gap of 0.35 eV
2D-GaN monolayer with far 2-Ge above Ga	3.02	1.22	4.0	0.66	Metallic and spin filter
2D-GaN monolayer with 1-Ge above N	3.0	1.28	2.0	0.61	Semiconductor, an indirect band gap of 1.17 eV
2D-GaN monolayer with near 2-Ge above N	3.18	14.25(molecule)	0.06	0.01	Semiconductor, indirect band gap of 0.94 eV
2D-GaN monolayer with far 2-Ge above N	3.0	1.04	4.0	0.59	Semiconductor and an indirect band gap of 0.98 eV

with the number of Ge-atoms. Further, the magnetic moment of various configurations lies in a range of 2-4 μ_B except for the Ge-molecule adsorbed on the N atoms. Most of the systems have semiconducting nature except one which is far 2-Ge above Ga atom with metallic nature. Only this system with metallic nature will work as spin filter. On the other hand, the system with semiconducting nature will be useful for their future applications in electronics and spintronics.

4 Conclusions

A comprehensive ab-initio study has been performed for the structural, electronic, magnetic, and optical properties of a 2D-GaN monolayer possessing several Ge atoms as adsorbent on two types of the host atoms. The norm-conserving pseudopotentials have been employed in the calculation in contrast to other earlier workers who have used soft or ultra-soft pseudopotentials. We predict the existence of several exotic properties e.g. spin filtering, high magnetism, and continuous emission of electromagnetic radiation in different Ge adsorbed 2D-GaN monolayer. The behaviour of magnetism is found to be site-independent. The binding energies per adatom of the Ge-atoms adsorbed above N are larger than those of the Ge-atoms adsorbed above Ga atoms. Along with the main strong absorption lying in the ultraviolet region in all the Ge-adsorbed Ga-N monolayer systems, strong continuous absorption from far infrared region to visible region has been seen in some of these systems. These systems may therefore be useful for the development of light emitting devices which will emit in various regions of the energy spectrum including white emission. The emission of 2D-GaN monolayer lying in the deep ultraviolet region may also be used for sterilization, water purification, etc.

Acknowledgements

The authors are thankful to University Grants Commission, New Delhi and Department of Science and Technology, New Delhi and for their financial support. We are also thankful to the Super Computing Center, IIT, BHU for allowing us to use the facility for running test jobs.

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