



# Band Gap Modulation of Hydrogenated Silicene with Increased Fluorine Occupancy

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**Abstract.** The structural and electronic properties have been calculated with increased occupancy of fluorine upon hydrogenated silicene using first-principle DFT calculations. The indirect band gap has been observed for hydrogenated silicene. Band gap behavior has been changed with increasing fluorine occupancy on hydrogenated silicene. With the replacement of hydrogen atoms with fluorine step by step with direct band gap of 12.5% is obtained. The band gap is reduced with the increase of fluorination due to increased electronegativity, increasing the bowing character of energy bands in the band structure the reported values and the calculated structural parameters are in a straight line. For the first time band gap behaviour for different levels of fluorination upon hydrogenated silicene is calculated.

**Keywords:** Generalized gradient approximation (GGA) · DFT calculations · hydrogenated silicene

## 1 Introduction

In the last decade, researchers have shown enormous importance in studying 2-D graphene-like materials such as silicene, germanene, transition metal dichalcogenides, etc. They show high mobility, current carrying capacity, linear Fermi Dirac distribution, unusual quantum Hall Effect, high spin-orbit coupling, etc. compared to bulk structures and crystals. The Si atoms in silicene are unsaturated, unlike bulk silicon due to this silicene is anticipated to have a higher surface reactivity. Due to its higher reactivity for atomic and molecule adsorption graphene, silicene shows promise for possible uses in gas sensors and Nano electronic devices. However, IV group 2-D materials are necessary for excellent switching capacity in traditional field effect transistors (FETs) to achieve their potential.

Hydrogenation and fluorination are the chemical functionalization's that are used to an open band gap [1–6]. Hydrogenation of silicene has been investigated theoretically and experimentally [7–9], showing an indirect band gap that is not applicable for several optoelectronic applications. Authors have thought that the performance of the band gap can be modified with the addition of fluorine atoms occupancy in hydrogenated

silicene. The structural properties, such as lattice constants, bond lengths, and bond angles between silicon, hydrogen, and fluorine atoms, have been calculated in this paper and also band structures with increased fluorine occupancy are analyzed.

## 2 Computational Details

The calculation based on the first principle was done using the Material Studio 8.0 simulation package with CASTEP [10]. The generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof scheme (PBE), which is a popular density functional theory (DFT) method for electronic structure calculations, were used for the analyses [1–4, 11]. The ultra soft pseudo-potential method is a widely used approach for electronic structure calculations that enables efficient computations by reducing the size that is needed to describe the wave function of the system.

The symmetrical optimization was performed using the Broyden, Fletcher, Goldfarb, and Shanno (BFGS) algorithm, which is a commonly used algorithm for optimization in DFT calculations [12]. The algorithm aims to reduce the total energy of the system by iteratively adjusting the atomic positions until the forces on each atom are minimized.

## 3 Results and Discussion

According to theoretical predictions, hydrogenation of silicene causes several structures such as the chair, boat, tricycle, etc. Among all the configurations chair structure is the most stable structure [1, 4, 11]. The different views such as top and side views of hydrogenated silicene in the chair configuration are shown in Fig. 1. Calculated the total energy of a unit cell of hydrogenated silicene is structured for 100 iterations and the energy obtained is  $-372.254$  eV. The calculations of bond length and bond angles are shown in Table 1.

The lattice constants ( $a$ ), bond lengths ( $d$  Si-H,  $d$  Si-Si), bond angles ( $\theta$  Si-Si-H, and  $\theta$  Si-Si-Si), energy band gap (e.g.) of hydrogenated silicene and fluorinated silicene.

Together with the high symmetry points in the  $7*7*4$  k-point set's monkroost pack grid, the band structure has been calculated. Figures 2(a) and 2(b) are band structures for silicone and hydrogenated silicone.



**Fig. 1.** The (a) side view and (b) top view of hydrogenated silicene

**Table 1.** The lattice constants ( $a$ ), bond lengths ( $d_{\text{Si-H}}$ ,  $d_{\text{Si-Si}}$ ), bond angles ( $\theta_{\text{Si-Si-H}}$ , and  $\theta_{\text{Si-Si-Si}}$ ), energy band gap ( $E_g$ ) of hydrogenated silicene and fluorinated silicene

| Hydrogenated silicene      |                     |                 | Fluorinated silicene       |                   |
|----------------------------|---------------------|-----------------|----------------------------|-------------------|
| Lattice constant ( $a$ ) Å |                     | $3.82^{10}$     | Lattice constant ( $a$ ) Å | 4.325             |
| $d_{\text{Si-H}}$ (Å)      | 1.512               | 1.5024, 1.51925 | $d_{\text{Si-F}}$ (Å)      | 1.637             |
| $d_{\text{Si-Si}}$ (Å)     | 2.372               | 2.3624          | $d_{\text{Si-Si}}$ (Å)     | 2.570             |
| $\theta_{\text{Si-Si-H}}$  | 107.750             |                 | $\theta_{\text{Si-Si-F}}$  | 103.614           |
| $\theta_{\text{Si-Si-Si}}$ | 111.136             | 110.717         | $\theta_{\text{Si-Si-Si}}$ | 114.639           |
| $E_g$                      | 2.186<br>(indirect) | $2.0^{10}$      | $E_g$                      | 0.375<br>(direct) |

The thickness of conditions of 3p-orbital of silicon cross-over at the Fermi level, causing zero bandgaps is shown in Fig. 3(a). The hybridization of p orbital with H-1s orbital and forms sp<sup>3</sup> hybridization due to hydrogenation of silicene.

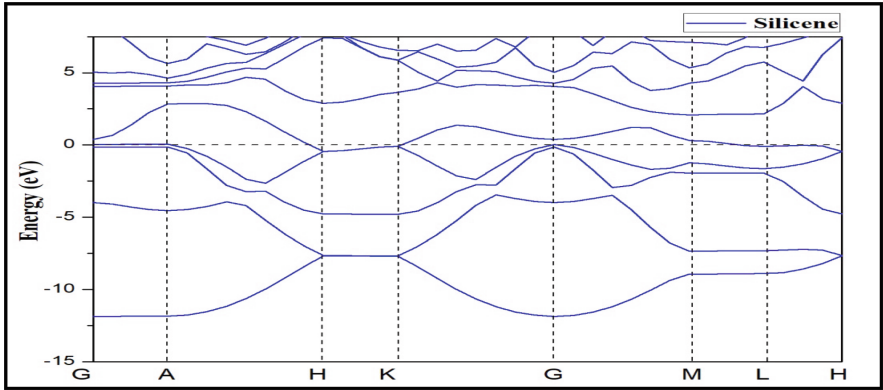
Figure 3(b) displays the gap formation between negative and positive levels of the 3p orbital of silicon. Thus one can say that hybridization of silicon with hydrogen plays a significant role in the band gap. The drawback here is the indirect band gap which will hinder the application in optoelectronics. To overcome this, fluorine atoms have been added in place of hydrogen step by step at 12.5%. The band structure of 12.5% fluorination on silicene is shown in Fig. 4, which shows a direct band gap of 1.862 eV. The addition of fluorine leads to an increase in the electronegativity of the material, which increases the bowing character of energy bands in band structure [9].

The 50% fluorination is viewed and calculated band structure for hydro fluorinated silicene (SiH<sub>0.5</sub>F<sub>0.5</sub>) shown in Figs. 5 and 6, which shows a band gap of 1.68 eV, respectively. Increase in fluorine content increases the bowing of energy bands at the Gamma point, which decreases the direct band gap [9]. The density of states of 50% fluorination in hydro fluorinated silicene is shown in Fig. 7. The calculated energy band gap with different fluorination upon hydrogenated silicene is plotted in Fig. 8.

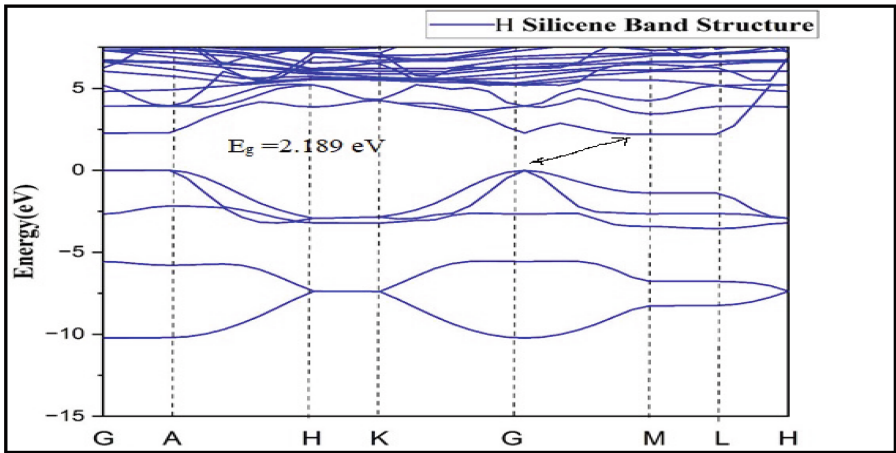
It demonstrates that the direct band gap narrows as fluorine occupancy rises. The side and top views of fluorinated silicene are shown in Fig. 9. The calculated band structure for 100% fluorination upon silicene is shown in Fig. 10, which shows a band gap of 0.3 eV. The calculated density of states for fluorinated silicene is shown in Fig. 11. The hydrogenation of silicene leads to a large bandgap, and fluorination converts the indirect bandgap to the direct bandgap, respectively.

## 4 Conclusions

The reported values for hydrogenated, hydro fluorinated, and fluorinated silicene are consistent with the lattice constants, bond lengths, and bond angles. The most stable chair-structured shows indirect band gap of 2.186 eV by hydrogenated silicene. Amount of the energy bandgap is in great concurrence with the announced qualities. By replacing hydrogen atoms with fluorine atoms, the band gap has been changed to a direct bandgap.



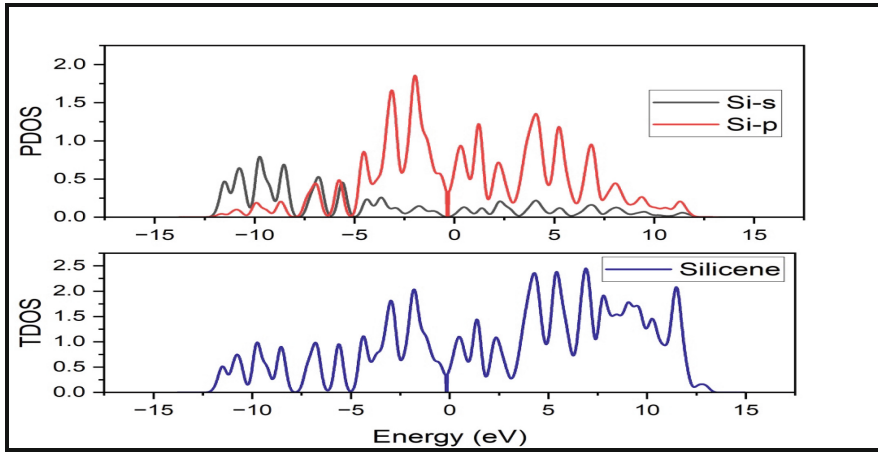
(a)



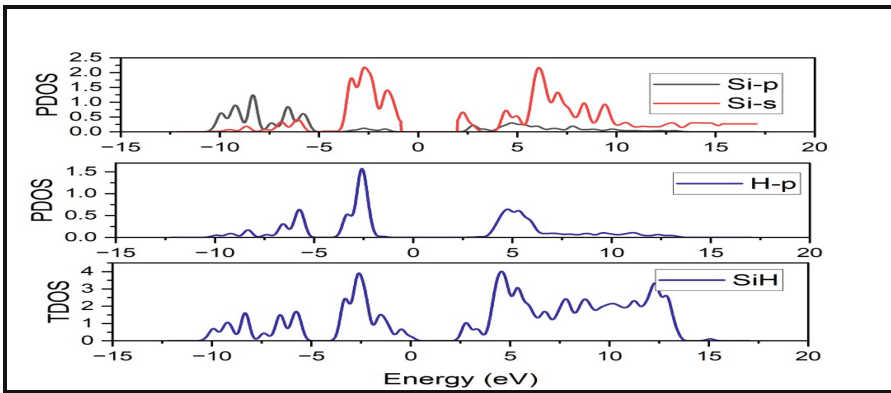
(b)

**Fig. 2.** Calculated band structure of (a) silicene and (b) hydrogenated silicene along the high symmetry points

For 12.5% fluorination and 87.5% hydrogenation on silicene, the direct bandgap is 1.86 eV. The direct bandgap has been diminished with the increment of fluorine inhabitation up to 87.5% of fluorination and 12.5% hydrogenation, which becomes 1.21 eV because of the ascent of electronegativity in the semiconductor. The 100 percent fluorination of silicene shows a direct bandgap of 0.3 eV. Hydrogenation assumes a significant part in getting the enormous bandgap, and fluorination changes the bandgap from indirect to direct.

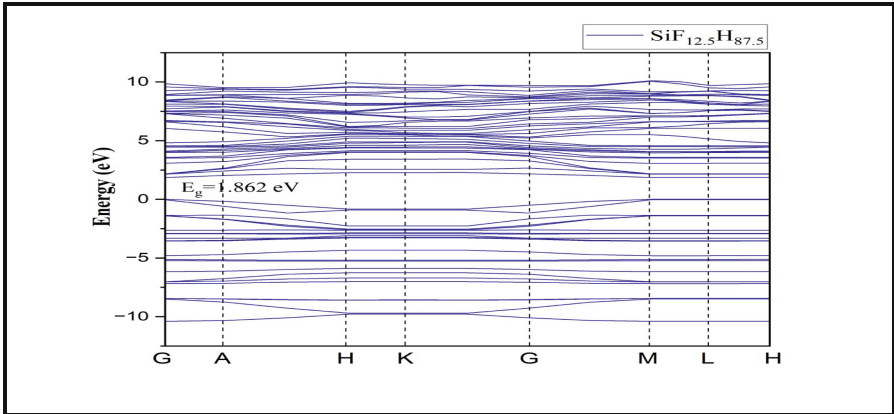


(a)

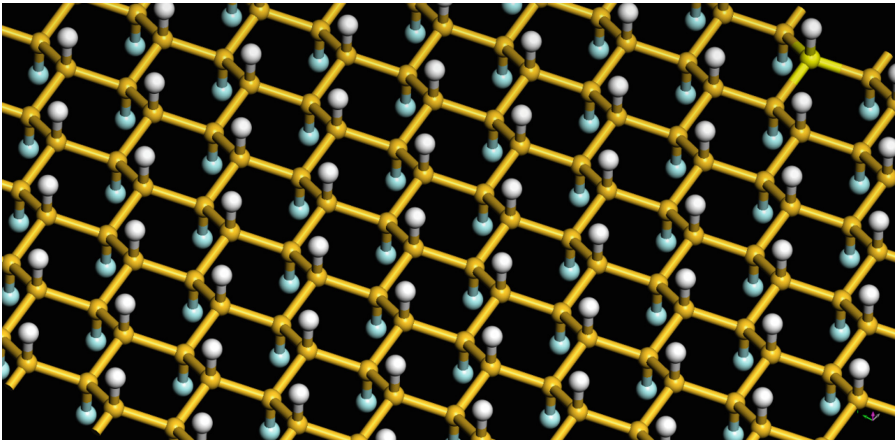


(b)

**Fig. 3.** Density of states of (a) silicene and (b) hydrogenated silicene



**Fig. 4.** Band structure for 12.5% occupancy of fluorine in hydro fluorinated silicene



**Fig. 5.** The perspective view of hydro fluorinated silicene ( $\text{SiH}_{0.5}\text{F}_{0.5}$ ), white balls indicate hydrogen, blue balls indicate fluorine and yellow circles indicate silicon, respectively

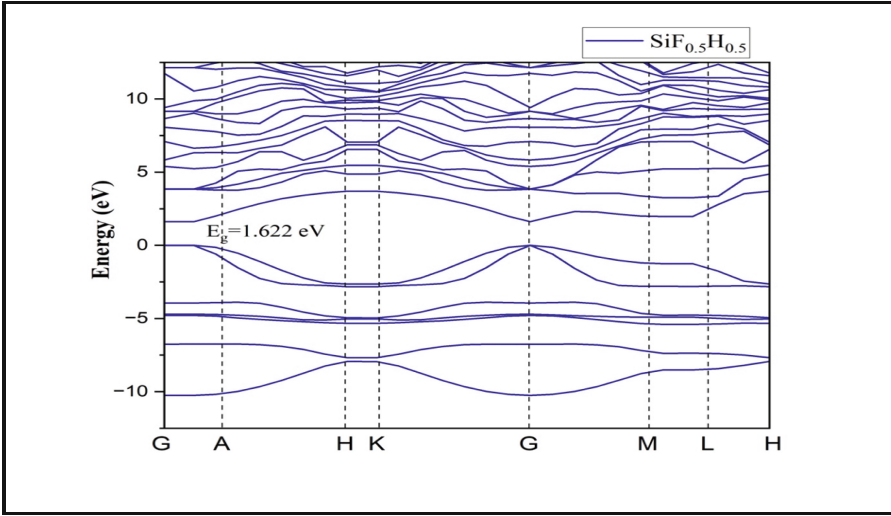


Fig. 6. Band structure calculated for 50% fluorine occupancy in hydro fluorinated silicene

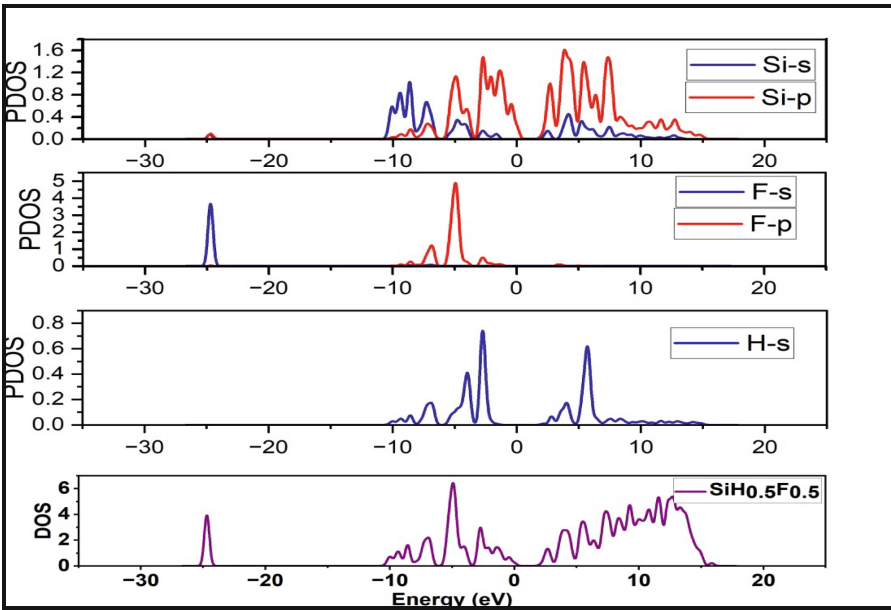


Fig. 7. The PDOS and TDOS of individual atoms of  $\text{SiH}_{0.5}\text{F}_{0.5}$

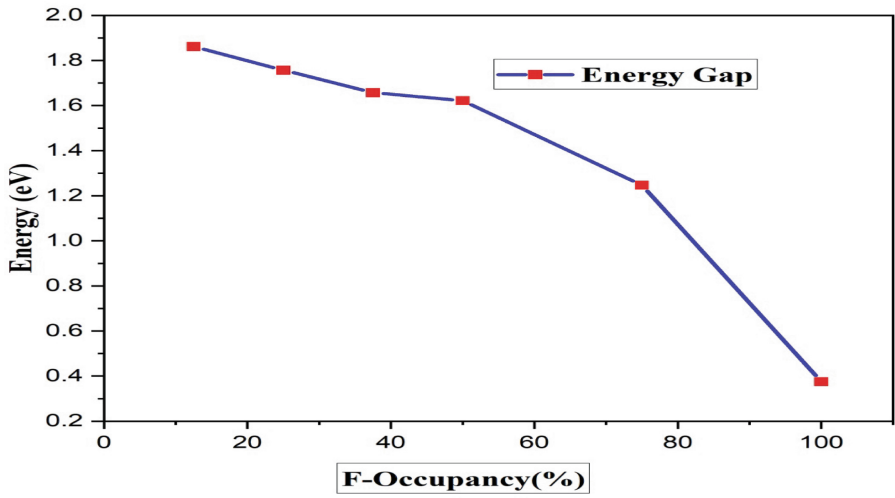


Fig. 8. Behavior of band gap with different occupancy of fluorine on hydrogenated silicene

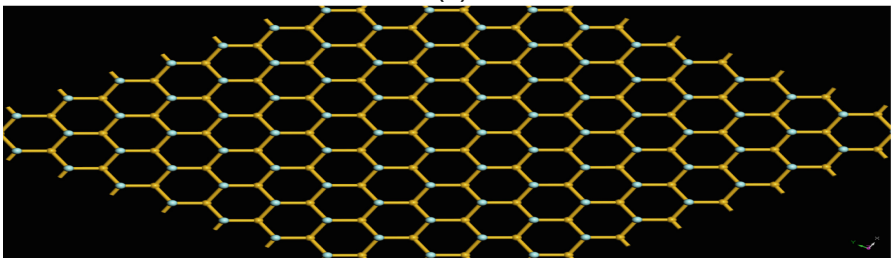
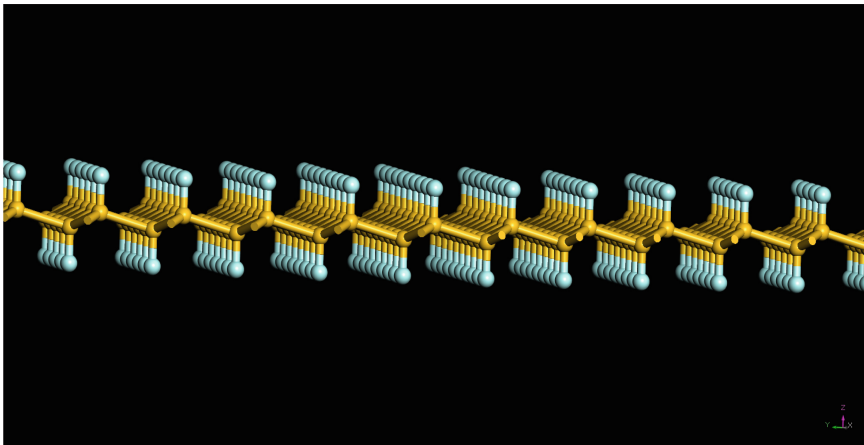
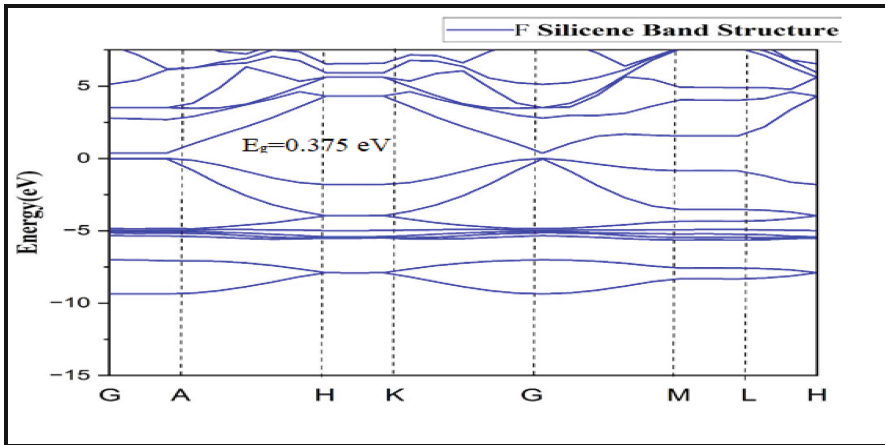
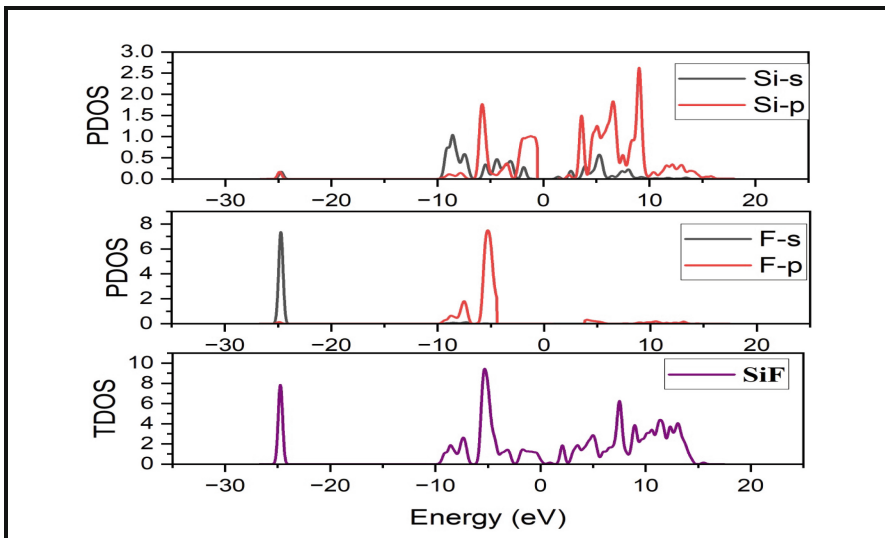


Fig. 9. (a) Side and (b) top views of fluorinated silicene





**Fig. 10.** The calculated band structure for fluorinated silicene



**Fig. 11.** The PDOS and TDOS of individual atoms of fluorinated silicene

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