Structural, electrical and optical properties of bilayer SiX (X = N, P, As and Sb)

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Abstract

In this work, the structural, electrical, and optical properties of bilayer SiX (X = N, P, As, and Sb) are studied using density functional theory. Five different stacking orders are considered for every compound and their structural properties are presented. The band structure of these materials demonstrates that they are indirect semiconductors. The out-of-plane strain has been applied to tune the bandgap and its electrical properties. The bandgap increases with tensile strain, whereas, compressive strain leads to semiconductor-to-metal transition. The sensitivity of the bandgap to the pressure is investigated and bilayer SiSb demonstrates the highest bandgap sensitivity to the pressure. These structures exhibit Mexican hat-like valence band dispersion that can be approved by a singularity in the density of states (DOS). The Mexican-hat coefficient can be tuned by out-of-plane strain. Optical absorption of these compounds shows that the second and lower valence bands due to the high DOS display a higher contribution to optical transitions.

Keywords: DFT, bilayer, optical properties, electrical properties, out-of-plane strain

(Some figures may appear in colour only in the online journal)

1. Introduction

Two-dimensional (2D) materials have become an important research topic since exfoliation of graphene was realized [1]. The 2D structures of the other members of the group-IV atoms such as silicene, germanene, stanene, and plumbene have been reported theoretically and experimentally [2–6]. All these monolayers demonstrate a Dirac cone with a near to zero bandgap. On the other hand, group-V monolayers have been extensively studied in both theoretical and experimental works [7–11]. Among them, phosphorene attracts huge research interest in 2D materials due to its proper bandgap, high carrier mobility, and excellent transport properties [7]. After that, antimonene was introduced as an interesting 2D material with air stability [10, 12]. Theoretical studies predicted a range of exciting properties, including a tunable bandgap for application in optoelectronics and low thermal conductance with low electrical resistivity proposing thermoelectricity as a source of energy [13].

The combinations of group-IV and V atoms can undertake superior electrical properties of both groups. Barreteau et al [14] have built the bulk structure of layered SiP, SiAs, GeP, and GeAs. The layered configurations of these materials demonstrate that these materials can be exfoliated into 2D structures. The easy exfoliation of these materials has been approved experimentally [15–20]. The monoclinic crystal of GeAs and SiAs has a layered structure with C2/m space group [19]. Monolayers of GeAs and SiAs can be exfoliated from the bulk counterparts due to low interlayer energy [21]. Both monolayers demonstrate a bandgap around 2 eV [22]. The group IV and V monolayer compounds demonstrate a hexagonal lattice (V and IV and IV and V) with P6m2 space group [23–26]. These hexagonal compounds are semiconductors except CBi and PbN with metallic phases. The structural stabilities and electronic properties of IV and V monolayers with A2B2 formula (A = C, Si, Ge, Sn, Pb; B = N, P, As, Sb, Bi)
have been analyzed theoretically [23, 25]. Single-layer group IV and V compounds demonstrate fascinating photocatalytic activity [27–29], thermoelectric [30], mechanical [31], and IV and V compounds demonstrate fascinating photocatalytic activity [37–29], thermoelectric [30], mechanical [31], and IV and V compounds demonstrate fascinating photocatalytic activity [30], thermoelectric [31], and IV and V compounds demonstrate fascinating photocatalytic activity [32]. The electrical properties of SiX (X = N, P, As, and Sb) monolayers demonstrate that these materials are semiconductors with an indirect band gap [30]. These compounds have been reported as promising candidates for efficient thermoelectric applications.

Li et al [18] for the first time have exfoliated 2D GeP from the bulk monoclinic structure. Cheng et al [19] have reported the exfoliation energy of SiP, SiAs, GeP and GeAs which are of about 0.26 J m⁻², 0.27 J m⁻², 0.34 J m⁻² and 0.37 J m⁻², respectively. The exfoliation energy of SiP and SiAs are lower than graphite (0.32 J m⁻²), which confirms the experimental feasibility of their monolayers.

Field-effect transistors (FET) based on IV and V have been introduced as a candidate for nano-electronic applications, however, their performance is limited by their low mobility. Guo et al [33] have reported that the hole mobility of GeAs based FET at room temperature can reach 100 cm²V⁻¹ s⁻¹. The exfoliation energy of SiP and SiAs are lower than graphene (0.32 J m⁻²), which confirms the experimental feasibility of their monolayers.

Tuning the electrical and optical properties of the multilayer structures for their potential application in electronic/mechanical devices, tunable photodetectors, and lasers is a challenge and can be done by changing stacking order, interlayer spacing, applying strain and electric field [34–35]. It has been shown that applying a vertical electric field can open a small bandgap even in bilayer graphene [38, 39]. Furthermore, it has been reported that a vertical electric field in the range of 0.2–0.3 V Â⁻¹ leads to a semiconductor-to-metal transition in bilayer TMDs [45]. While this method is promising, it has practical problems such as the necessity for a very large electric field. On the other hand, it has been shown that the band structure of bilayer TMDs can be effectively modified by the application of vertical strain [41].

To the best of our knowledge, there is not a comprehensive study on the electrical and optical properties of different stacking orders of bilayer SiX (X = N, P, As, and Sb). The bilayer SiX will surely enrich the family of the 2D materials with fascinating electrical properties and so it is necessary to investigate the electrical and optical properties in these materials. In addition, applying out-of-plane strain is a powerful method to tune the bandgap and electrical properties of 2D materials. Therefore, in this work, the effect of vertical strain on the electrical properties of bilayer SiX (X = N, P, As, and Sb) is studied using density functional theory. Five different stackings are investigated for every compound and their electrical properties are discussed. The band gaps of these materials decrease gradually with out-of-plane compressive strain and semiconductor-to-metal transition occurs at a specific pressure. This transition pressure depends on the stacking order of layers. This wide range (1.7–0.0 eV) bandgap tuning can be utilized in various applications.

2. Computational details

Density functional calculations are performed using the SIESTA package [42]. The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) [43] functional is utilized for the exchange–correlation term. A Monkhorst–Pack k-point grid of 21 × 21 × 1 is chosen for the unit-cell. The energy cutoff is set to be 200 Ry and a double-ζ plus polarization basis-set is used. The total energy is converged to better than 10⁻³ eV. The geometries are fully relaxed until the force on each atom is less than 0.01 eV Å⁻¹. A vacuum region of 30 Å is added to avoid interactions in the normal direction. The van der Waals interaction between layers is treated using Grimme’s correction to the PBE functional [44]. To visualize the atomic structures, XCrySDen package has been used [45]. The vertical strain is defined as, ε = (d – d₀)/d₀ where d₀ and d are the equilibrium and deformed interlayer distances, respectively. The applied pressure (P) is calculated from the energy cost per unit area for decreasing the interlayer distance by following equation [41],

\[ P = \frac{(E - E₀)}{(d₀ - d)A}, \]

where A is the area of the unit cell, and E₀ and E are the energies of the equilibrium and deformed structures. The effective mass of the carriers is calculated by using the following equation [46, 47],

\[ m^* = \frac{h^2}{(\partial^2 E/\partial k^2)}, \]

Here, h is the reduced Planck constant, k and ε are the energy and wave vector of conduction band minimum (CBM) and valence band maximum (VBM). The absorption coefficient is calculated using the energy dependent dielectric functions. The optical properties have been calculated from the complex frequency dependent dielectric function. Using the dipole approximation, the imaginary part of the dielectric function is calculated from the transition rate between conduction band states as follow [48, 49]

\[ \varepsilon_2(\omega) = \frac{4\pi^2 e^2 h}{m^* \omega^2} \sum_{ij} \frac{2}{(2\pi)^3} \int \frac{d\mathbf{k}}{A} |M_{ij}(\mathbf{k})|^2 \delta[\omega - \omega_j(\mathbf{k})], \]

where the integral is over all k-points in the Brillouin zone and the sum is over all combinations between the valence band state i and the conduction band state j. M_{ij}(\mathbf{k}) = \langle \varphi_j(\mathbf{k})|\mathbf{p}||\varphi_i(\mathbf{k})\rangle is the dipole transition matrix. E_i and \varphi_i are the energy and eigenfunction of the states i and j. \mathbf{p} is the polarization vector and \mathbf{p} is the momentum operator and \hbar \omega_j(\mathbf{k}) = E_j - E_i. The real part of the dielectric function \varepsilon_1(\omega) can be calculated using the Kramers–Kronig transformation, which is expressed as [50]

\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega^2 - \omega'^2}, \]

where P denotes the Cauchy principal value. Then the absorption coefficient can be calculated by [51]

\[ \alpha(\omega) = \sqrt{2} \frac{\omega}{c} \sqrt{\varepsilon_2^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1^2(\omega)} \]
Figure 1. Bilayer SiX from (a) side, and (b) top view. The Si and X atoms are indicated by blue and yellow colors, respectively. The structural parameters are displayed for better insight.

where \( c \) is the speed of light.

3. Results and discussion

The schematic of five different stackings has been displayed in top and side views in figure 1. Two stacking categories are AA and AB which in AA stackings, the top layer is located exactly on the underlying layer, and in AB stackings, the top layer is shifted relative to the bottom layer. The structural properties of the bilayers are listed in table 1. The lattice constants are almost equal for the five stackings of each material which implies that stacking order has a negligible effect on the lattice constant. On the other hand, interlayer distance highly depends on the stacking configuration. The AA2 stacking of SiN has the lowest interlayer distance, whereas, the lowest one is for AB2 stacking in other compounds. The highest \( d_{\text{int}} \) is for AA1 and AB1 stackings and the interlayer distance is approximately the same in these two stackings. \( d_{\text{Si-Si}}, d_{\text{Si-X}} \) and \( d_{\text{X-X}} \) similar to lattice constant demonstrate a low dependency on the stacking configuration. Binding energy can be computed as [35],

\[
E_{\text{b}} = E_{\text{Bilayer}} - 2 \times E_{\text{Monolayer}},
\]

where \( E_{\text{Bilayer}} \) and \( E_{\text{Monolayer}} \) are the total energy of bilayer and monolayer SiX, respectively. The binding energy decreases with the atomic number of group-V elements and the heavier compounds display lower binding energy. The lowest binding energy which corresponds to the most stable structure is for AB2 configuration in all compounds except SiN, for which AA2 has the lowest binding energy. As one can observe, the binding energy highly depends on the interlayer distance. The lower interlayer distance results in the lowest binding energy. The elastic constants, \( C_{11}, C_{22} \) and \( C_{12} \) are also studied. \( C_{22} \) is the same as \( C_{11} \) and has not been written in the table. The stability of these configurations is confirmed by the Born stability criteria as: \( 0 < C_{11} \), \( 0 < C_{22} \) and \( C_{12} < C_{11}, C_{22} \) [52]. The values of \( C_{11} \) and \( C_{12} \) decrease with increasing the atomic number. Bilayer SiN demonstrates the highest elastic constants that are about 50\% and 300\% larger than bilayer graphene and MoS\(_2\), respectively [53, 54]. \( C_{11} \) shows a dependency with interlayer distance and binding energy in most cases and the highest \( C_{11} \) belongs to the stacking with the highest interlayer distance and largest binding energy.

The stability of bilayer compounds also is investigated with phonon dispersion and the results for AB2 stacking are shown in figure 2. The phonon dispersion for different stackings of materials is similar. So, we have plotted AB2 stacking as a sample. As one can observe, all materials demonstrate positive phonon frequencies that confirm their stability compatible with Born criteria.

The band structures of the bilayer SiX with AB2 configuration are depicted in figure 2. The AB2 stacking which is the most stable configuration is selected as a sample. All of them are indirect semiconductors where CBM is located at \( M \)-valley for four compounds whereas, the energy of \( K \)-valley is close to \( M \)-valley especially for bilayer SiN. On the other hand, the contour plot in figure 3 for SiN makes it clear that the actual VBM lies on a nearly circular line. This dispersion refers to Mexican hat dispersion. In the other materials, this same shape holds qualitatively but the energy band difference between the VBM circular line and the VBM at \( \Gamma \)-point are much smaller.

The values of the band gaps for different stackings of SiX compounds are listed in table 2. The size of the band gaps of the bilayer SiN is distributed from 1.232 eV in AA2 to 1.434 eV in AB2 stacking. The bandgap of Bilayer SiN displays a low dependency on the stacking order. On the other hand, the bandgap of bilayer SiSb highly depends on the stacking orders. The bandgap of AB1 stacking of SiSb is 1.086 eV that is approximately two times as large as the
Table 1. The lattice constant (a), the interlayer distance (d_{int}), the distance between Si atoms (d_{Si-Si}), the distance between X atoms (d_{X-X}), Si-X (d_{Si-X}) bond length and elastic constants (C_{11} and C_{12}) of SiX bilayers with different stacking orders.

| Stacking order | a(Å) | d_{int}(Å) | d_{Si-Si}(Å) | d_{X-X}(Å) | d_{Si-X}(Å) | E_{g}(eV) | C_{11}(N m^{-1}) | C_{12}(N m^{-1}) |
|----------------|------|------------|--------------|------------|------------|----------|----------------|----------------|
| SiN AA1        | 2.908| 3.222      | 2.396        | 3.572      | 1.778      | −1.341   | 558.45         | 136.12         |
| AA2            | 2.909| 3.716      | 2.401        | 3.569      | 1.780      | −1.439   | 554.42         | 123.27         |
| AB1            | 2.907| 3.188      | 2.398        | 3.574      | 1.779      | −1.338   | 557.48         | 135.65         |
| AB2            | 2.907| 2.932      | 2.403        | 3.583      | 1.781      | −1.383   | 519.66         | 123.91         |
| AB3            | 2.909| 2.743      | 2.399        | 3.568      | 1.779      | −1.416   | 555.37         | 138.46         |
| SiP AA1        | 3.536| 3.596      | 2.357        | 4.416      | 2.287      | −1.51    | 288.98         | 57.09          |
| AA2            | 3.537| 3.039      | 2.357        | 4.415      | 2.287      | −1.609   | 287.86         | 56.79          |
| AB1            | 3.537| 3.587      | 2.356        | 4.412      | 2.287      | −1.509   | 288.72         | 56.01          |
| AB2            | 3.541| 2.998      | 2.361        | 4.417      | 2.289      | −1.639   | 279.62         | 55.97          |
| AB3            | 3.54  | 3.002      | 2.359        | 4.416      | 2.289      | −1.629   | 288.36         | 53.94          |
| SiAs AA1       | 3.683| 3.711      | 2.348        | 4.576      | 2.402      | −1.809   | 254.50         | 54.86          |
| AA2            | 3.686| 3.106      | 2.346        | 4.576      | 2.403      | −1.936   | 252.78         | 51.62          |
| AB1            | 3.683| 3.713      | 2.347        | 4.576      | 2.402      | −2.009   | 254.34         | 54.42          |
| AB2            | 3.693| 2.994      | 2.347        | 4.565      | 2.405      | −1.965   | 241.08         | 54.63          |
| AB3            | 3.688| 3.065      | 2.347        | 4.574      | 2.404      | −1.953   | 252.88         | 48.73          |
| SiSb AA1       | 3.978| 4.074      | 2.342        | 4.819      | 2.609      | −2.042   | 197.94         | 49             |
| AA2            | 3.982| 3.273      | 2.341        | 4.814      | 2.611      | −2.228   | 194.86         | 41.31          |
| AB1            | 3.978| 4.069      | 2.342        | 4.819      | 2.609      | −2.043   | 197.63         | 49.19          |
| AB2            | 3.994| 3.145      | 2.342        | 4.799      | 2.614      | −2.277   | 190.01         | 32.75          |
| AB3            | 3.987| 3.222      | 2.34         | 4.81       | 2.612      | −2.252   | 196.06         | 34.95          |

The bandgap of the AA2 stacking. The bandgap of heavier compounds has a higher dependency on the stacking order. We also observed a high dependency of the bandgap on the stacking order in bilayer antimonene [37]. The highest bandgap in Bilayer SiN is 1.434 eV for AB2 stacking. After AB2 stacking, AB1 and AA1 stackings have the highest bandgap. In three other materials, SiP, SiAs and SiSb, AA1 and AB1 stackings approximately have the same bandgap and demonstrate the highest bandgap. The lowest bandgap is one of the AA2, AB2 or AB3 stackings that is different for various compounds. For example, the lowest bandgap in SiN is 1.232 eV in AA2 stacking, whereas, in SiAs the lowest gap occurs for AB2 stacking. PBE is known to underestimate band gaps. In order to have a prediction of the precise bandgap of bilayer SiX, HSE06 functional implemented in Quantum ESPRESSO [55, 56] package is used and the calculated values of the band gaps are listed in table 2. However, PBE provides reasonable bond lengths and angles and predicts the band structure precisely. Therefore, except the value of the band gaps $E_{g}^{HSE06}$ in table 2, the other results have been obtained at the PBE level. Our calculated band gaps at HSE level ($E_{g}^{HSE06}$) for monolayer SiX structures are 2.65, 2.28, 2.37, and 1.78 eV for SiN, SiP, SiAs, and SiSb, respectively. These values are in good agreement with previously reported band gap values for monolayer SiX [23] which confirms the accuracy of our results.

All structures exhibit the Mexican-hat dispersion in the top of the valence band that is more noticeable in bilayer SiN. The value of the Mexican-hat coefficient can be obtained with [57]: $M = \Delta E / \Delta K$, where $\Delta E$ and $\Delta K$ are the energy and momentum difference between the $\Gamma$-point and the VBM. The values of the Mexican-hat energies and coefficients for different stackings of SiX compounds are listed in table 2. Bilayer SiN demonstrates the highest Mexican-hat coefficient of 0.696 eV at AA1 stacking. The different stackings display different Mexican-hat coefficients. Mexican-hat energies for bilayer SiN are distributed from 0.206 to 0.324 eV. On the other hand, despite the negligible $E_{M}$ of other compounds, some stackings demonstrate a relatively high Mexican-hat coefficient.
Conduction and valence band energies in the first Brillouin zone of four compounds with AB2 stacking. First Brillouin zone is indicated with dashed line. The top and bottom rows are for conduction and valence bands, respectively.

![Conduction and Valence Band Energies](image)

**Figure 3.** Conduction and valence band energies in the first Brillouin zone of four compounds with AB2 stacking. First Brillouin zone is indicated with dashed line. The top and bottom rows are for conduction and valence bands, respectively.

Table 2. The electrical properties of the different stacking orders of bilayer SiX. The band gap calculated with PBE ($E_g^{\text{PBE}}$) and HSE06 ($E_g^{\text{HSE06}}$) functionals in eV unit. The strain ($\epsilon_{\text{strain}}$) and pressure ($P_{\text{strain}}$) required for semiconductor-to-metal transition are in percent and GPa, respectively. The effective masses at $\Gamma$-point of valence band, and $K$- and $M$-valleys of the conduction band are in $m_0$ unit. The Mexican-hat energy ($E_{\text{M}}$) and coefficient ($M_1$) at $\Gamma$-point of the valence band are in eV and eV\*a unit, respectively.

| Stacking order | $E_g^{\text{PBE}}$ | $E_g^{\text{HSE06}}$ | $\epsilon_{\text{strain}}$ | $P_{\text{strain}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $m_{\text{M,\Gamma}}$ | $E_{\text{M}}$ | $M_1$ |
|----------------|-------------------|----------------------|--------------------------|-----------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| SiN AA1        | 1.401             | 2.408                | -18                      | 16.14           | 0.585             | 0.553             | 1.081             | 0.383             | 1.091             | 0.989             | 0.331             | 0.696             |
| SiN AA2        | 1.232             | 2.215                | -36                      | 42.47           | 0.538             | 0.535             | 1.045             | 0.371             | 1.143             | 1.051             | 0.206             | 0.506             |
| SiP AA1        | 1.064             | 1.921                | -9                       | 4.04            | 0.434             | 0.461             | 2.321             | 0.141             | 1.729             | 1.402             | 0.021             | 0.134             |
| SiP AA2        | 0.768             | 1.529                | -6                       | 2.50            | 0.382             | 0.423             | 2.839             | 0.142             | 1.436             | 1.289             | 0.002             | 0.025             |
| SiP AB1        | 1.05              | 1.919                | -8                       | 3.42            | 0.434             | 0.467             | 2.144             | 0.14             | 1.683             | 1.364             | 0.021             | 0.138             |
| SiP AB2        | 0.742             | 1.538                | -6                       | 1.14            | 0.501             | 0.496             | 2.412             | 0.134             | 1.577             | 1.318             | 0.001             | 0.017             |
| SiP AB3        | 0.731             | 1.53                 | -6                       | 1.96            | 0.484             | 0.52              | 2.338             | 0.138             | 1.459             | 1.282             | 0.001             | 0.019             |
| SiAs AA1       | 1.258             | 2.03                 | -10                      | 4.47            | 0.428             | 0.46              | 6.237             | 0.133             | 1.848             | 1.461             | 0.009             | 0.096             |
| SiAs AA2       | 0.92              | 1.609                | -9                       | 4.1             | 0.379             | 0.427             | 2.804             | 0.136             | 1.004             | 0.884             | 0.008             | 0.101             |
| SiAs AB1       | 1.263             | 2.029                | -10                      | 4.36            | 0.427             | 0.463             | 5.468             | 0.134             | 1.829             | 1.451             | 0.01             | 0.097             |
| SiAs AB2       | 0.773             | 1.532                | -6                       | 1.65            | 0.503             | 0.518             | 2.953             | 0.125             | 0.978             | 0.822             | 0.005             | 0.068             |
| SiAs AB3       | 0.879             | 1.558                | -8                       | 2.87            | 0.47              | 0.506             | 5.621             | 0.132             | 0.999             | 0.86              | 0.007             | 0.089             |
| SiSb AA1       | 0.995             | 1.553                | -10                      | 3.99            | 0.411             | 0.446             | 0.411             | 0.2              | 0.445             | 0.459             | 0.0              | 0.0               |
| SiSb AA2       | 0.476             | 1.141                | -4                       | 1.36            | 0.351             | 0.408             | 0.38              | 0.176            | 0.782             | 0.685             | 0.019             | 0.225             |
| SiSb AB1       | 1.086             | 1.647                | -11                      | 4.54            | 0.419             | 0.451             | 0.443             | 0.243             | 0.444             | 0.459             | 0.0              | 0.0               |
| SiSb AB2       | 0.524             | 1.185                | -4                       | 0.92            | 0.392             | 0.653             | 0.875             | 0.131             | 0.707             | 0.59              | 0.012             | 0.155             |
| SiSb AB3       | 0.568             | 1.224                | -5                       | 1.51            | 0.415             | 0.445             | 0.626             | 0.166             | 0.748             | 0.644             | 0.016             | 0.188             |

For a better understanding of the contribution of the atoms and orbitals on the band structure, partial density of states (PDOS) for AB2 stackings are plotted along with the band structures in figure 4. The singularity in the valence band especially in SiN is obvious. There also exists the singularity in the valence band of the other compounds but their values are small. These singularities come from the Mexican-hat in the VBM. As one can observe, the p orbitals of two atoms have the main contribution to both conduction and valence band edges.

While the CBM is located at M-valley, the energy of the K-valley in some of the configurations is close to M-valley and K-valley contributes to the CBM. On the contrary, the VBM is located at $\Gamma$-point, and the energy of the M- and K-points are much lower. The effective masses for the M- and K-valleys of the conduction band and $\Gamma$-point of the valence band are listed in table 2. Two effective masses at K-valley in the conduction band ($m_{\text{K,\Gamma}}$ and $m_{\text{M,\Gamma}}$) demonstrate almost the same values in most configurations. On the other hand, M-valley presents two different effective masses, $m_{\text{M,\Gamma}}$ and $m_{\text{M,\Gamma}}$, which are approximately three times as large as $m_{\text{K,\Gamma}}$ in bilayer SiN. Their ratio reaches more than one order of magnitude in SiP, and SiAs show the highest difference between these two effective masses. On the other hand, SiSb behaves differently and the difference between these two effective masses highly depends on the stacking order. Two effective masses are also calculated at $\Gamma$-point of the valence band that is approximately the same.
These materials exhibit a high hole effective mass. SiP displays the highest hole effective mass, whereas, SiSb has the lowest one close to its electron effective mass.

The imaginary part of the dielectric function ($\varepsilon_2$) determines the optical absorption [50, 58]. For this reason, $\varepsilon_2$ as a function of energy for four compounds are depicted in figure 5. The first peak of $\varepsilon_2$ which corresponds to the lowest direct gap occurs at 2.8, 2.18, 2.15, and 1.7 eV for SiN, SiP, SiAs, and SiSb, respectively. Three compounds, SiP, SiAs, and SiSb, have a single band in the valence band edge that limits the bandgap. SiSb with a lower bandgap demonstrates $\varepsilon_2$ at lower energy whereas in SiN with the highest bandgap, $\varepsilon_2$ starts at higher energy. The peaks in the joint density of states (DOS) corresponding to the vertical transitions determine the peaks in $\varepsilon_2$ and hence the absorption coefficient. Bilayer SiP, SiAs, and SiSb demonstrate the same maximum value of $\varepsilon_2$ with a shift in energy, whereas, SiN shows a much lower value. The optical absorption as a function of energy for all bilayers is shown in figure 5. It is clear that all features of $\varepsilon_2$ and absorption coefficient are very similar up to 4 eV. While $\varepsilon_2$ decreases at energies higher than 4 eV, the absorption coefficient exhibits peaks around 4–6 eV. To clarify this effect, the real part of the dielectric functions ($\varepsilon_1$) are also plotted in figure 5. The negative values are seen in the range of 4–6 eV. These negative values indicate the plasmonic excitations.

The out-of-plane strain has been proposed as a powerful method to modify the electrical properties of bilayers or hetero-structures [35, 36, 41]. The tuning of the properties of 2D materials with vertical pressure had been carried out in several experimental works [59–63]. The pressure up to 35 GPa had been applied via a high-pressure diamond anvil cell (DAC), as a controllable and reversible degree of freedom to modulate the properties of multilayer structures [60]. The DAC technique along with a hydrostatic pressure medium has been confirmed to be effective in clarifying the structural, electrical, vibrational, and optical properties of a large number of materials [59–63]. We have applied the out-of-plane strain to all stacking and their electrical properties are studied. The variation of the bandgap of the compounds as a function of vertical strain is plotted in figure 6. The band gaps are enhanced with tensile strain. On the other hand, vertical compressive strain decreases the bandgap values and semiconductor-to-metal transition occurs at a specific strain in a compressive regime. The reduction of the bandgap under vertical strain is caused by enhanced interlayer (X–X) interaction. As the interlayer distance decreases due to a rise in strain, the overlap of p orbitals between two layers increases, and the layers start to interact chemically. The VBM moves toward the Fermi level at the $\Gamma$ point. Moreover, the CBM also moves toward the Fermi level with increasing strain. The semiconductor to metal transition occurs when the VBM crosses CBM after a transition strain. The required strain for phase transition ($\varepsilon_{\text{trans}}$) and its counterpart pressure ($P_{\text{trans}}$) are listed in table 2. $\varepsilon_{\text{trans}}$ is too high for bilayer SiN, for example, it reaches to $-36\%$ for AA2 stacking that needs 42.47 GPa of pressure. $\varepsilon_{\text{trans}}$ depends on the value of the bandgap and a larger bandgap results in a higher $\varepsilon_{\text{trans}}$. Only AA2 stacking of SiN does not obey this theorem. $P_{\text{trans}}$ of bilayer SiN are distributed between 10 and 20 GPa, except AA2 stacking. SiP, SiAs and SiSb demonstrate a lower $\varepsilon_{\text{trans}}$ and $P_{\text{trans}}$. One can observe, the bandgap of all stackings of bilayer SiN are close to each other under different strains and just AB3 stacking exhibits a lower bandgap at the compressive strain. In SiP, SiAs, and SiSb, the bandgap of AA1 and AB1 configurations vary close to each other. Furthermore, the
three structures with more stability (AA2, AB2, and AB3) vary similarly with strain. The difference between these two groups increases for the heavier compounds. As one can observe, SiSb demonstrates a large difference between these two groups.

These structures can be introduced as pressure sensors. In order to investigate the feasibility of semiconductor to metal transition and possible application of the structures as a pressure sensor in experiments, the applied pressure ($P$) is calculated, and the sensitivity of the bandgap on the applied pressure is studied. The bandgap variation versus the applied pressure is plotted in figure 7 for AB3 stacking. The plot is almost linear for all of the structures and the pressure range is easily achievable experimentally. Furthermore, the bandgap change is reversible and in the absence of pressure the bandgap is completely recovered and the structure relaxes back to the equilibrium structure. This is very important for pressure switches and sensor applications. SiSb displays the highest sensitivity to the pressure and the bandgap closes at low pressure. The bandgap of SiSb closes at a pressure lower than 2 GPa. The sensitivity of the bandgap decreases with the decrement of the X atomic number. SiN demonstrates the lowest bandgap sensitivity but remains a semiconductor until the pressure of 10 GPa. The transition pressure decreases as the atomic number of the X atom increases. This is due to the increased delocalization of the atomic orbitals, which leads to reduced interaction between Si and X atoms and a lower transition pressure. This trend is also observable in the bandgap variation with X atomic number (see table 2).

The energy of the effective valleys in the conduction and valence bands for various strains are plotted in figure 8. The behavior of all stackings is the same and AB2 stacking is plotted as a sample. The figures demonstrate the CBM and VBM are located at $M$- and $\Gamma$-points, respectively. The energies of
Figure 8. The energy of the valleys in the conduction and valence bands for various strain in AB2 stacking of bilayer SiX.

Figure 9. The Mexican-hat energy and coefficient of SiX bilayers as a function of out-of-plane strain. The top and bottom rows stand for energy and coefficient of the Mexican-hat, respectively.

\[ K \]-valleys in the conduction band \( (E_{CK}) \) become closer to \( E_{CM} \) under tensile strain. However, the energy of \( \Gamma \)-valley in the conduction band and \( K \)-point in the valence band are far from the CBM and VBM, respectively. Therefore, these two valleys do not contribute to electrical properties. \( E_{CM} \) decreases with applying compressive strain and at the same time, \( E_{VT} \) rises. These two bands intersect at \( \varepsilon_{\text{trans}} \). Therefore, the CBM and VBM get closer to Fermi level, and electron and hole density increase exponentially which results in the increment of the current.

The compounds demonstrate Mexican-hat dispersion at the valence band that can be affected by the strain. Mexican-hat energy and coefficient as a function of strain are plotted in figure 9. SiSb, SiAs, and SiSb display a comparable Mexican-hat coefficient with SiN, whereas, their Mexican-hat energies are much lower than SiN. One can observe that the value of the Mexican-hat energy in SiN is approximately one order of magnitude larger than the others that is compatible with table 2. Mexican-hat energy and coefficient behave similarly in a compound. For example, in the bilayer SiN Mexican-hat energy and coefficient increase with the tensile strain and decrease in the compressive regime. However, Mexican-hat properties in other compounds show a minimum at equilibrium and increase with applying both compressive and tensile strains. Mexican-hat vanishes at tensile strain for SiAs and SiSb bilayers. AA1 and AB1 stackings demonstrate a larger Mexican-hat property than the other stackings in the SiN and SiP and their differences rise at the compressive strain.
4. Conclusion

The structural, electrical, and optical properties of five different stacking orders of bilayer SiX (X = N, P, As, and Sb) are studied. All these materials are indirect semiconductors where the CBM and VBM are located at M- and Γ’-points, respectively. The Mexican-hat is obvious from the band structures and the singularity in the DOS confirms the existence of the Mexican-hat. SiN stackings demonstrate a considerable Mexican-hat dispersion, whereas, it is negligible for other compounds. In the following, the out-of-plane strain has been applied to tune the electrical properties. The bandgap increases with a rise in the tensile strain and a semiconductor-to-metal transition occurs at compressive strains. SiSb demonstrates the highest bandgap sensitivity to the pressure, whereas, SiN has the lowest bandgap sensitivity and closes at a higher level of pressure. At high tensile strain, the energy of the K-valley gets closer to the M-valley and contributes to the CBM. SiN displays a high Mexican-hat coefficient that increases with tensile strain and decreases with compressive strain. Other compounds also indicate a high Mexican-hat coefficient but the energy of the Mexican-hat is small for them. The optical absorption is also studied where the peaks in the conduction and valence bands of DOS determine optical absorption. The single band in the valence band edge of SiP, SiAs, and SiSb has a low DOS and a little contribution to the optical absorption.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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