Prediction of group IV-V hexagonal binary monolayers: electronic, optical, thermoelectric, and photocatalysis properties

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Group IV and V monolayers are very crucial 2D materials for their high carrier mobilities, tunable band gaps, and optical linear dichroism. Very recently, a novel group IV-V binary compound, Sn₂Bi, has been synthesized on silicon substrate, and has shown very interesting electronic and thermoelectric properties. Further investigations show that show that the monolayer would be stable in freestanding form by hydrogenation. Inspired by this, by means of ab-initio calculations, we systematically predict and investigate eight counterparts of Sn₂Bi, namely Si₂P, Si₂As, Si₂Sb, Si₂Bi, Ge₂P, Ge₂As, Ge₂Sb, and Ge₂Bi. The cohesive energies, phonon dispersions, and AIMD calculations show that, similar to Sn₂Bi, all of these freestanding monolayers are stable when they are hydrogenated. These hydrogenated monolayers are semiconductors with wide band gaps, which are favorable for opto-electronic purposes. The Si₂Y and Ge₂Y structures possess indirect and direct band gaps, respectively. They represent very interesting optical characteristics, such as good absorption in the visible region and linear dichroism, which are crucial for solar cell and beam-splitting devices, respectively. Moreover, the Ge₂P and Si₂Sb monolayers are promising for high-speed nano-electronic devices, because of their high carrier mobility, whereas Si₂Bi, Ge₂P, and Si₂As monolayers are suitable candidates for thermoelectricity. Finally, the Si₂Sb and Si₂Bi monolayers have suitable band gaps and band edge positions for photocatalytic water splitting. Summarily, our investigations offer very interesting and promising properties for this family of binary compounds.

We hope that our predictions open ways to new experimental studies and fabrication of suitable 2D materials for next generation opto-electronic, thermoelectric, and photocatalytic devices.

Keywords: 2D materials, First-principles, electronic properties, Optical properties, Thermoelectric

I. INTRODUCTION

The high tower of the contemporary technology is built by blocks of silicon and germanium. These elements have extensive applications such as filed-effect transistors,¹ ², computer chips,³ solar panels,⁴ ⁵, high-power lasers,⁶ and light-emitting diodes (LEDs)⁷, etc. Since the successful synthesize of the monolayer carbon (graphene)⁸ and discovery of its remarkable characteristics, such as high carrier mobility,⁹ strong mechanical parameters,¹⁰ and optical transparency,¹¹ a great inquiry for other elemental monolayers is in the agenda of many scientists around the world. The monolayers of carbons neighbors in group-IV, silicon and germanium (silicene and germanene) are among the most important predicted and synthesized monolayers beyond graphene¹² ¹³.

Unlike graphene, which is completely flat with an sp² bonding characteristics, the larger interatomic distance in silicene and germanene weakens the π – π overlaps, which leads to buckled structures with sp² – sp³ hybrid orbitals. Despite their buckled geometry, silicene and germanene share most of the important electronic features of graphene, such as Dirac cone, high Fermi velocity and carrier mobility¹⁴ ¹⁵, with some advantages including better tunability of the band gaps,¹⁶ stronger spin-orbit coupling¹⁷, and easier valley polarization,¹⁸ which are very important for electronics, spintronics, and valleytronics.

On the other hand, monolayers of group-V elements, known as pnictogens, including phosphorene, arsenene, antimonene, and bismuthene, recently have gained much attention for their topological aspects, as well as inherent, wide, and tunable band gaps¹⁹ ²². Generally, several allotropes are considered for these monolayers, including α (puckered; washboard) and β (buckled honeycomb; graphene-like), as the most important and stable phases.²³ For arsenene, antimonene, and bismuthene, the β-phase, and for phosphorene, the α-phase is more stable in aspects of energetics and phonon dispersions.²⁴ The α-phase phosphorene and arsenene possess direct band gaps, while their β counterparts have indirect ones. On the other hand, antimonene and bismuthene respectively have indirect and direct band gaps in both phases. These band gaps are within a wide range of 0.36 (for α-bismuthene) to 2.62 eV (for β-phosphorene).²⁵ ²⁷ Moreover, phosphorene, arsenene, and bismuthene possess carrier mobilities as high as several thousand cm² V⁻¹ s⁻¹.²⁴ These exciting properties makes group-V monolayers very favorable candidates for optoelectronics, thermoelectric, and photocatalytic devices.

Because of high ratio between the surface and thickness of 2D structures, effects of chemical functionalization play an important role in tuning their properties²⁸ ²⁹. Hence, in addition to pure elemental monolayers, 2D materials with functionalized structures gained attention for expanding the scope of realized physical aspects and enhancing potential applications. These efforts include designing and applying various types of heterostructures,° defecções,³¹ ³², vacancies,³³,
adsorptions\textsuperscript{34}, and compounds\textsuperscript{35}. Among these, binary compounds have the advantage of relatively easier fine control of the growth dynamics and more feasible fabrication. They could represent unusual atomic configuration and chemical stoichiometry\textsuperscript{36} which leads to extraordinary physical properties for future applications and opening ways to new researches.

As an example of group IV-V binary compound, Barreteau et al. have succeed to synthesize the bulk single crystals of layered SiP, SiAs, GeP, and GeAs by melt-growth method. They showed that these layered materials all exhibit semiconducting behavior, and suggest that they can be further exfoliated into 2D structures\textsuperscript{37}.

Very recently, Gou et al. have synthesized a unique hexagonal 2D binary compound, Sn\textsubscript{2}Bi, on a silicon (111) substrate which exhibits strong spin-orbit coupling and high electron-hole asymmetry\textsuperscript{38}. In the band structure of this semiconducting monolayer, electron flat bands and free hole bands are seen which are indicative of nearly free and strongly localized charge carriers. Moreover, this monolayer is very stable because all the Si, Bi, and Sn atoms satisfy the octet rule. These features make Sn\textsubscript{2}Bi a good candidate for nano-electronics and may result in nontrivial properties like ferromagnetism\textsuperscript{38} and superconductivity\textsuperscript{39}. Furthermore, the synthesis of other counterparts of Sn\textsubscript{2}Bi was proposed by Gou et al\textsuperscript{36}.

Generally, experimental synthesis of yet unknown systems can be guided by predictive theoretical first principles calculations which distinguish stable and unstable structures correctly\textsuperscript{40}. In other words, theoretical predictions play an important role in progress of materials science and technology, by means of justifying the cost and effort of potential experiments. Many advances in materials science have been conducted and inspired by earlier theoretical investigations. Most of the presently well-known synthesized 2D materials, such as graphene\textsuperscript{41}, borophene\textsuperscript{12}, stanene, germanene, silicene\textsuperscript{14}, bismuthene\textsuperscript{30}, antimonene\textsuperscript{43}, arsenene\textsuperscript{44}, etc. were firstly predicted by theoretical studies which brought sufficient motivations for experimental work.

Herein, inspired by the successful deposition of Sn\textsubscript{2}Bi monolayer, as well as the importance of group IV and V monolayers, we predicted a new family of binary compound monolayers with a hexagonal structure and an empirical formula of X\textsubscript{2}Y, where X and Y are respectively chosen from group-IV (Si and Ge) and V (P, As, Sb, and Bi), namely Si\textsubscript{2}P, Si\textsubscript{2}As, Si\textsubscript{2}Sb, Si\textsubscript{2}Bi, Ge\textsubscript{2}P, Ge\textsubscript{2}As, Ge\textsubscript{2}Sb, and Ge\textsubscript{2}Bi. We firstly stabilize the mentioned monolayers by hydrogenation, and further check their stability by cohesive energy, molecular dynamics, and phonon dispersion analysis, and interpret their phonon modes and thermodynamical properties. Furthermore, we analyze their electronic, optical, and thermoelectric properties and discuss their potential strengths.

Eventually, we consider these semiconductors for photocatalytic purposes and check their potential applications in water-splitting. Our results suggest that these monolayers are strongly applicable in a very vast array such as valleytronics, opto-electronics, optical detectors, beam-splitters, thermoelectric devices and water-splitters. Moreover, the structural similarity with the synthesized Sn\textsubscript{2}Bi monolayer, promises the possibility of their deposition on proper substrates and brings hopes for advances in technological devices.

II. COMPUTATIONAL DETAILS

The first-principles calculations were performed based on the density functional theory (DFT), as implemented in the Quantum Espresso package\textsuperscript{45}. During the entire calculations, the norm-conserving (NC) pseudo-potentials with a plain wave basis set were employed to describe the electron wave functions. The generalized gradient approximation (GGA) was used with the formulation of Perdew-Burke-Ernzerhof (PBE) to describe the electron exchange-correlation potential\textsuperscript{46}. Because the GGA usually underestimates the band gaps, the HSE06 hybrid functional was also used to obtain more accurate band gaps. The density mesh cut-off energy was set 300 Ry and the Γ-centered Monkhorst-pack scheme was used to sample the Brillouin zone with a 21×21×1 k-points. A vacuum space of 20 Å was chosen along with the z-direction to prevent spurious interactions between layers in the periodic boundary condition. All the monolayers were fully relaxed with a force and stress tolerance of 10\textsuperscript{-3} eV/Å and 10\textsuperscript{-4} GPa, respectively. To calculate the phonon dispersion, the finite displacement method was adopted, in which a 3×3×1 supercell with a 5×5×1 k-point sampling was built.

To investigate the optical properties, the frequency-dependent dielectric function was calculated using the time-dependent DFT within independent particle approximation (IPA) which describes single-particle excitations. The calculation was performed at the first-order perturbation theory by means of self-consistent ground-state energies.

To determine the structural stability of the monolayers, their cohesive energies (E\textsubscript{c}) were calculated using the equation below:

\[ E_c = \frac{E_{\text{sheet}} - \sum_i n_i E_{\text{atom-}i}}{N} \quad (1) \]

where \( E_{\text{sheet}} \) and \( E_{\text{atom-}i} \) stand for total energy of the sheet and the isolated atom-i with considerations of the spin polarization, respectively. \( N \) and \( n_i \) are the numbers of total atoms and atom-i in the unit cell, respectively.

To check the thermal stability of the monolayers, the ab-initio molecular dynamics (AIMD) simulations were performed using NVT canonical ensemble at room temperature (300 K). The initial model was constructed by a 3×3×1 supercell for minimizing the constraint caused by periodicity. Here, the total simulation time was set to be 4.0 ps with time steps of 2.0 fs.
III. RESULTS AND DISCUSSION

A. Structural Stability and Phonon Calculations

The graphene-like structure was used to construct eight new binary monolayers, with a threefold-coordinated X (Si and Ge) and Y (P, As, Sb, and Bi) atoms in a hexagonal unit cell containing six atoms, as shown in FIG. 1. Through the structural optimization with the GGA-PBE exchange-correlation, the relaxed lattice constants and bond lengths were calculated in the range of 6.33 to 7.23 Å and 2.26 to 2.75 Å, respectively. All the relaxed monolayers have buckled structures with buckling heights in the range of 0.86 to 1.24 Å in which the longer atomic radius creates larger buckling heights. The calculated structural parameters are available in the Supporting Information, TABLE S1.

The X and Y atoms have ns² np² (n = 3, 4) and ns² np³ (n = 3 – 6) outer shell electron configurations, respectively. Therefore, when they form a threefold configuration, the octet rule only fulfills for the Y, not X atoms. Thus, these pure structures are predicted to be unstable in a freestanding configuration. Phonon dispersion analyses confirm that these monolayers are dynamically unstable (FIG. S1). The same instability has also been reported for freestanding Sn₂Bi monolayer while it can be greatly stabilized by hydrogenation. However, there are two pre-investigated options left to stabilize the X₂Y binary compound monolayers: to deposit them on a suitable substrate such as ZnS (111), and to passivate them with hydrogen atoms which we discuss in the following.

For passivation, we investigated both single and double side hydrogenated structures, where hydrogen make bonds with X (Si and Ge) atoms, so the octet rule would be fulfilled. According to the cohesive energies, the double side hydrogenated model, having the lowest ground state energy, is predicted to be the most stable structure. Therefore, we denote the rest of the investigations to this model which is described in FIG. 1c. In the following, we further confirm their structural, thermal and dynamical stability by means of cohesive energy, molecular dynamics, and vibrational phonon analysis.

TABLE I lists the structural and electronic parameters for these monolayers. Lattice constants, bond lengths, and buckling heights are in the range of 6.26 to 7.18 Å, 2.27 to 2.75 Å, and 1.08 to 1.38 Å, respectively. As can be seen, hydrogenation causes an increase in buckling heights and a decrease in lattice constants for all the monolayers, which is due to the strong bonds between H and X atoms. Similar behaviors have also been reported for hydrogenation and fluorination of penta-graphene, silicone, germanene, and stanene. According to Eq. (1), the more negative values for cohesive energies suggest more structural stability for the monolayers. As shown in TABLE I, the cohesive energies vary from -3.88 for Si₂P to -3.08 for Ge₂Bi which indicates that all of the monolayers are stable. In fact, the structures represent more stability when the atoms are lighter. By comparison, one can easily realize that all the predicted monolayers are more stable than the hydrogenated Sn₂Bi monolayer ($E_c = -2.95$ eV/atom). Also, the Si₂Sb, Si₅Bi, Ge₂Sb, and Ge₂Bi monolayers are more stable than SiSb (-3.50), SiBi (-3.31), GeSb (-3.12), and GeBi (-2.98) binary compounds, respectively. The rest have appreciable cohesive energies comparable to SiP (-4.19), SiAs (-3.85), GeP (-3.60), and GeAs (-3.36). For a better comparison between cohesive energies of the predicted binary compounds, please pay attention to FIG. 2.

We have also performed the ab-initio molecular dynamics (AIMD) simulations to verify the thermal stability of the hydrogenated X₂Y binary compounds. FIG. 3 exhibits the fluctuations of potential energy and evolution of geometric structure of the hydrogenated Ge₂Bi monolayer during the simulations at 300 K. As can be seen, the potential energy oscillates with an extent of less than 0.4 eV/atom, and no obvious structural distortions are found, indicating that the hydrogenated Ge₂Bi is thermally stable at 300 K. The thermal stability of the hydrogenated Ge₂Bi guarantees stability of all the predicted structures because it has the highest cohesive energy among them (see FIG. 2). Indeed, this suggests that the hydrogenated X₂Y binary compounds can be realized experimentally at room temperature.

To further confirm the stability of the hydrogenated monolayers, the phonon dispersion spectra were calculated and displayed in FIG. 4. It is clear that there is no imaginary frequency in the whole Brillouin zone, which confirms that these freestanding monolayers are dynamically stable. The spoon-shaped curves near the Γ point do not mean instability, but they are signatures of the flexural acoustic modes, which are usually hard to converge in 2D sheets. These soft modes are also found in other analogous systems. All the phonon spectra have rather similar trends, which mean similar bonding. Also, it is clear that the maxima of acoustic modes decline with going down in group IV and V where SiP and Ge₂Bi display the highest (100 cm⁻¹) and lowest (38 cm⁻¹) peaks. Based on these maxima, the Debye temperatures are obtained by

$$\theta_D = \hbar \nu_m / K_B$$

where $\hbar$ and $K_B$ are the Planck and Boltzmann constants, respectively. The calculated temperatures are in the range of 143 to 54 K (listed in TABLE I) which are lower than graphene (2266 K), silicone (798 K), phosphorene (206 K), arsenene (170 K), and comparable to antimonene (101 K), bismuthene (50 K), and stanene (72 K). Such low Debye temperatures and large buckling heights, which are indicative of low lattice thermal conductivities, making these monolayers suitable candidates for thermoelectric applications.

Interestingly, the slope of the parabolic out-of-plane acoustic mode (ZA) near the Γ point (specified in FIG. 4) decreases with increasing of the average atomic mass of the monolayers. This will bring a slower phonon group velocity, subsequently lower lattice thermal conductivity,
FIG. 1. (Color on line) Structural configurations of the predicted binary compound monolayers. (a) Table of included elements. (b) Top and (c) side view of the pure and hydrogenated monolayers. The unit cell and the corresponding Brillouin zone have also been presented.

TABLE I. Structural parameters of the hydrogenated $X_2Y$ binary compound monolayers, including lattice constants ($a$), bond lengths ($R_{XX}$ and $R_{XY}$), buckling heights ($\Delta$), cohesive energies ($E_c$), band gaps ($E_g$), Debye temperatures ($\theta_D$), and constant volume heat capacity in room temperature ($C_{V}^{300K}$).

|          | $a$ (Å) | $R_{XX}$ (Å) | $R_{YY}$ (Å) | $\Delta$ (Å) | $E_c$ (eV/atom) | $E_g$: GGA, HSE (eV) | $\theta_D$ (K) | $C_{V}^{300K}$ (J mol$^{-1}$ K$^{-1}$) |
|----------|---------|--------------|--------------|--------------|----------------|---------------------|---------------|----------------------------------|
| Si$_2$P  | 6.26    | 2.35         | 2.27         | 1.08         | -3.88          | 2.39, 3.19 (ind)    | 143.7         | 15.45                            |
| Si$_2$As | 6.44    | 2.35         | 2.39         | 1.19         | -3.73          | 2.33, 3.04 (ind)    | 120.3         | 16.09                            |
| Si$_2$Sb | 6.79    | 2.35         | 2.60         | 1.30         | -3.58          | 2.04, 2.61 (ind)    | 97.9          | 16.57                            |
| Si$_2$Bi | 6.94    | 2.35         | 2.69         | 1.35         | -3.50          | 1.92, 2.43 (ind)    | 70.8          | 16.93                            |
| Ge$_2$P  | 6.52    | 2.46         | 2.36         | 1.15         | 3.34           | 2.21, 2.88 (dir)    | 94.7          | 17.18                            |
| Ge$_2$As | 6.69    | 2.47         | 2.47         | 1.23         | -3.24          | 1.80, 2.41 (dir)    | 83.5          | 17.71                            |
| Ge$_2$Sb | 7.03    | 2.47         | 2.67         | 1.33         | -3.13          | 1.57, 2.07 (dir)    | 69.3          | 18.03                            |
| Ge$_2$Bi | 7.18    | 2.48         | 2.75         | 1.38         | -3.08          | 1.17, 1.57 (dir)    | 54.9          | 18.22                            |

FIG. 2. Variation of cohesive energy with lattice constant of the hydrogenated $X_2Y$ binary compound monolayers.

FIG. 3. Potential energy fluctuations of the hydrogenated Ge$_2$Bi during the AIMD simulations at 300 K. The final geometric structure at the end of 4 ps has also been shown.
and stronger anharmonicity, especially for Si₂Bi, Ge₂As, Ge₂Sb, and Ge₂Bi. It is worth noting that the ZA mode has a high contribution to the phonon transport. On the other hand, the hybridization of the optical and acoustic phonon branches increases the phonon scattering which reveals low phonon transport. These behaviors represent the high potential of X₂Y monolayers in thermoelectricity.

The phonon dispersion spectrum is also a key to calculate the thermodynamic properties of a system. For example, the constant volume heat capacity, $C_V$ is defined as:

$$C_V = \sum_{s,q} K_B \left( \frac{\hbar \omega_s(q)}{K_B T} \right)^2 \frac{\exp(\hbar \omega_s(q)/K_B T)}{(\exp(\hbar \omega_s(q)/K_B T) - 1)^2}$$

where $\hbar$ is the reduced Planck’s constant, and $\omega_s(q)$ is the frequency of the $s$ phonon branch at the $q$ point. According to the Debye model, in the high-temperature limit, i.e. $K_B T \gg \hbar \omega$, the heat capacity simply approaches to the classical Dulong-Petit results, which is $3NKM_B$ where $N$ is the number of atoms in the unit cell and $M$ is the number of unit cells in a crystal ($\approx 24.94$ J mol⁻¹ K⁻¹ for one mole of a mono-atomic solid). FIG. 5 exhibits the $C_V$ calculated for the hydrogenated binary compounds as a function of temperature (one mole, divided by the number of atoms in the unit cell) which was calculated by use of the phonon dispersion spectra. As it is clear, the $C_V$ is converged to $\sim 24$ J mol⁻¹ K⁻¹ in high-temperature limit, which is in good agreement with the Debye model.

Moreover, the $C_V$ for Si₂P, Si₂As, Si₂Sb, Si₂Bi, Ge₂P, Ge₂As, Ge₂Sb, and Ge₂Bi, at room temperature (300 K) are $15.45$, $16.09$, $16.57$, $16.93$, $17.18$, $17.71$, $18.03$, and $18.22$ J mol⁻¹ K⁻¹, respectively (see TABLE I). Despite the importance of the $C_V$ in the understanding of thermal properties, it has not gained sufficient attention in 2D materials so far. To the best of our probe, some examples...
of similar calculations are: 23.1 (TiSeS), 22.7 (TiSeS), 22.5 (TiSeTe), 17.5 (CuTe₂O₃), 11.5 (borophene)⁶²,⁶⁵,⁶⁶, which are comparable with our results. It is provable that heavier materials have a greater $C_V$ at room temperature, i.e. they are more resistant to temperature increase. Therefore, one may conclude that compared with borophene, all of the predicted binary compounds, and compared with CuTe₂O₃, the Ge₂As, Ge₂Sb, and Ge₂Bi monolayers are better electronic devices in the aspects of not overheating. With confirming the structural stability and discussing the thermodynamical characteristics, now we turn our attention into the electronic properties of the predicted binary compounds.

B. Electronic Properties

The electronic band structures of X₂Y binary compound monolayers have been presented at the GGA and HSE06 levels in FIG. 6. As can be seen, all the monolayers are semiconductors. The Ge₂Y monolayers have direct band gaps at the $\Gamma$ point. In contrast, the Si₂Y monolayers have indirect band gaps where their valence band maxima (VBM) are located at the $\Gamma$ point and their conduction band minima (CBM) are located at the M (for Si₂P and Si₂As) and K (for Si₂Sb and Si₂Bi) points, which are identical at both GGA and HSE levels. The band gaps predicted at the HSE level are in the range of 1.57 to 3.19 eV, where Si₂P and Ge₂Bi exhibit the largest and smallest values, respectively (see TABLE I). It is obvious that the band gaps decrease regularly with increasing the average atomic mass, which is rather common in 2D semiconductors⁶³,⁶⁴. For example, in group V binary compound monolayers, studied by Zhang et al, the PAs and SbBi monolayers indicate the largest (2.55 eV) and smallest (1.41 eV) band gaps, respectively. In more details, the reported band gaps are in the order of PAs > PSb > PBI > AsBi > SbBi⁶⁵.

All the calculated band structures demonstrate parabolic valence bands centered at the $\Gamma$ point which provides high hole conductivity. Among these, the Ge₂Y structures have parabolic conduction bands centered at $\Gamma$ point, which indicate free electrons, while the Si₂Y structures have nearly flat conduction bands along with the K – M direction, which are signatures of localized electrons. In other words, the Si₂Y structures have both free and strongly localized charge carriers like the Sn₂Bi monolayer deposited on the silicon substrate.⁶⁶ This high electron-hole asymmetry enforces the materials to exhibit completely different optical and thermoelectric behavior in the n-type and p-type doping. In addition, all the monolayers have some conduction band extrema (CBE) near the CBM at high symmetry points M, $\Gamma$, and $K$ which are favorable for an n-type Seebeck coefficient.⁶⁸ These CBEs may approach each other by mechanical strain to achieve band convergence⁶⁹. The band convergence improves electrical conductivity without affecting other transport coefficients. These features will make the X₂Y monolayers promising candidates for optical, photocatalytic and thermoelectric applications.

We also took into account the spin-orbit coupling (SOC) interaction in the calculation of the GGA band structures (SOGGA) as presented in FIG. S2. It can be seen that consideration of the SOC, more or less, terminates the degeneracy between energy bands and narrows the band gaps. Due to the stronger spin-orbit interactions for heavier atoms, the band splitting increases as the compounds are heavier. Summarily, the effect of SOC on the band gaps is smaller than 0.3 eV for most of the monolayers, except for relatively heavy X₂Bi (Si₂Bi & Ge₂Bi) which have SOGGA band gaps approximately 0.5 eV smaller than that of GGA. Overall, for its small influence on most of the monolayers, the SOC was not considered for the rest of our calculations.

FIG. 7 shows the total and orbital projected density of states of the hydrogenated binary monolayers. It can be seen that in the whole energy range, the p orbitals are dominant and the s orbitals have negligible proportions in the electronic characteristics, which was predictable according to the electronic arrangement of the contained atoms. This domination have been reported for other group IV and V 2D structures.⁷¹,⁷² As it is clear, for all the monolayers, the Y-p orbitals are dominant in the valence bands, and major peaks around -2 eV are raised by them. These are attributed to the rather flat bands around -2 eV in the band structures (see FIG. 6). On the other hand, the conduction bands are slightly dominated by Si atom for the Si contained structures, while for the Ge contained ones, Ge-p and Y-p orbitals share rather equal proportions of the conduction band states.

Also, more or less, we see an overlapping of DOS of X-p and Y-p orbitals near the Fermi energy for all the monolayers, which are signatures of strong covalent bonds between the atoms, due to the orbitals hybridization. As can be seen, orbitals hybridization is rather similar for all the compounds in the valence bands, but in the conduction bands, it is not significant for Si₂P and Si₂As. More interestingly, in the Ge contained compounds, the Y-s orbitals also participate in the hybridization. Orbitals hybridization between different atoms was also reported for other structures such as Sn₂Bi, C₃N, C₃P, and C₃As compounds⁷⁲ and As/Sb, Sb/Ge, and Sb/Bi heterostructures⁷²,⁷₁,⁷₃.

Moreover, the H atoms have a very limited contribution in the DOS, which means that electrons are strongly bound to them and do not construct many states in the valence and conduction bands. Namely, a very small hybridization with Y-s orbitals, and no interfere with X orbitals is seen, which suggests ionic bonds between the H and X atoms.

To shed more light on the electronic properties and bonding mechanism of the compounds, electron density ($n(r)$), electron difference density ($\delta n(r)$), and electron localization function (ELF) were calculated at the GGA level. Our calculations display that all the monolayers have similar characteristics, therefore, we only present...
the analyses for Si₂Sb monolayer, as a representative, in FIG. 8. Analyses for the rest of the monolayers are available in FIG. S3 – S5. It is clear from FIG. 8a, that the lattice has a minimum uniform electron density of about 0.3 e Å⁻³ which exhibits an in-plane isotropic lattice in aspects of electronic characteristics. It is obvious from \( n(r) \) and \( \delta n(r) \) (FIG. 8b,c) that there is a gentle electron accumulation between Sb and Si atoms. Moreover, the ELF (FIG. 8d) indicates a high localization between these atoms. Therefore, one could conclude that the Sb and Si atoms share electrons mutually and make covalent bonds.

Meanwhile, there is a high electron density and accumulation on the H, with significant electron depletion around Si atoms. Besides, the ELF displays the highest localization on the H and a low localization around the Si atoms. Therefore, it is deducible that the H atoms make ionic bonds with Si atoms. This approves our discussion about the low contribution of H related electrons in the density of states. Also, the strong ionic bonds make sense about the stability of the monolayers after hydrogenation. In other words, the hydrogenation somehow plays the role of a substrate for the originally unstable pristine monolayers and stabilizes them.

C. Optical Properties

High optical absorption in 2D materials brings hopes for energy harvesting purposes such as solar cells. Moreover, linear dichroism is a phenomenon widely reported for 2D materials, which is the difference between optical absorption for light beams polarized parallel and perpendicular to an orientation axis, and is a key element for interesting optical applications such as beam splitters, LCDs, half-mirrors, etc.\(^{74–76}\). For instance, it is reported that Sb and As monolayers have optical absorption edges near \( \sim 2 \) and \( \sim 3 \) eV, for perpendicular and parallel polarizations, respectively\(^{75}\).

As mentioned in the previous section, the X₂Y binary compounds were predicted to have hopeful signs of optical potentials, such as wide band gaps in the range of visible light. In this section, we calculate and discuss the optical properties of these monolayers to extract more physical insights and possible applications.

The optical properties are associated with the interactions between light, electrons, and ions in the materials, which should be explained through the complex dielectric function, \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \). Based on Fermis golden rule, one can derive the imaginary part of the dielectric function as below\(^{77,78}\):

\[
\epsilon_2(\omega) = \frac{4\pi^2e^2}{m^2\omega^2} \sum_{C,V} |P_{C,V}|^2 \delta(E_C - E_V - \hbar\omega) \quad (3)
\]
FIG. 7. (Color on line) Total and partial density of states of the hydrogenated X$_2$Y binary compound monolayers at the GGA level. The Fermi levels were shifted to zero.

FIG. 8. (Color on line) Iso-surface and cut plain of the hydrogenated Si$_2$Sb monolayer: (a) Iso-surface of electron density with an iso-value of 0.3 eÅ$^{-3}$. (b) Cross-section cut plain of electron density, (c) electron difference density, and (e) electron localization function (ELF) along with the black dashed line in (a). The color bar next to the sub-figures denotes the scope of each quantity. In (c), the red and blue colors show electron accumulation and depletion, respectively.
where $e$ is the electron charge, $m$ is the electron effective mass, $P$ is the momentum transition matrix, and $E$ is the electron energy level. Moreover, $C$ and $V$ indices stand for conduction and valance bands, respectively. No need to explain, $\delta(x - x_0)$ is the Dirac delta function, which ensures conversion of energy during electron transitions from band to band. This means that every excited state has an infinite lifetime, i.e. is stationary$^{79}$. Subsequently, the real part can be calculated through Kramer-Kronig relation$^{74,80}$:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega$$

(4)

Moreover, based on the real and imaginary parts, the optical absorption coefficient, $\alpha(\omega)$, is calculated through:

$$\alpha(\omega) = \frac{2}{c} \sqrt{\frac{\epsilon_1 + \epsilon_2 - \epsilon_1}{2}} \omega$$

(5)

where $c$ is the speed of light.

For the isotropy of the monolayers in the $xy$ plane, there is no significant difference between $xx$ and $yy$ polarizations, therefore the calculations were performed for polarized radiations, parallel ($E^\parallel$) and perpendicular ($E^\perp$) to the incidence direction ($z$-direction). FIG. 9 shows the calculated optical properties of the hydrogenated $X_2Y$ binary compounds, including real and imaginary parts of the dielectric function ($\epsilon_1$ and $\epsilon_2$), and the absorption coefficient ($\alpha$), for both polarizations. Interestingly, the predicted monolayers can be separated into two groups, group-A, including $Si_2P$, $Si_2As$, $Si_2Sb$, and $Ge_2P$, and group-B including $Si_2Bi$, $Ge_2As$, $Ge_2Sb$, and $Ge_2Bi$. The materials in each group exhibit similar properties, which will be discussed in detail.

As we know, negative values in the real part of the dielectric function stand for metallic reflectivity$^{27}$. As it is clear in FIG. 9 (left panel), group-A monolayers have significant negative values in the real part of the dielectric function within $\sim 3.6$ to 8 eV ($\sim 345$ to 155 nm) in the UV region, for perpendicular polarized radiation ($E^\perp$). On the contrary, group-B monolayers have significant negative values within $\sim 6.8$ to 9.5 eV ($\sim 180$ to 130 nm), for parallel polarized radiation ($E^\parallel$). In other words, group-A and group-B materials are metallic for $E^\perp$ and $E^\parallel$ UV radiation, within the mentioned ranges, respectively. This means that group-A and group-B monolayers have a good complement in blocking the UV radiation, within the mentioned ranges, respectively.

The imaginary part of the dielectric function and the absorption coefficient are bound to each other and should be analyzed together. Based on the band to band transition theory, the peaks in the imaginary part of the dielectric function are concerned with energy absorption and direct transitions of electrons between bands below and above the Fermi level. As can be seen in FIG. 9 (middle panel), all the monolayers have major peaks around $\sim 3.5$ and $\sim 7$ eV for $E^\perp$ and $E^\parallel$ polarizations, respectively.

Moreover, in group-A monolayers, the $E^\pm$ peaks are much stronger than the $E^\parallel$ peaks, whereas, in group-B monolayers, they are relatively equal. This would be representative of the difference, and equality of significant absorption ranges ($\alpha \geq 10^7 m^{-1}$) between $E^\pm$ and $E^\parallel$ polarizations, for group-A and group-B monolayers, respectively. In other words, as it is shown in FIG. 9 (right panel), group-B monolayers have relatively wider significant absorption ranges for $E^\parallel$ polarizations, which is due to the stronger $E^\parallel$ peaks in the imaginary part of the dielectric function.

The widest significant absorption range belongs to $Si_2Bi$, which is in the range of 2.36 to 12.4 eV (525 to 100 nm). For comparison, it should be noted that the Si and Ge monolayers have significant optical absorption in the range of $\sim 3.5$ to 5 eV (354 to 248 nm) and $\sim 3$ to 6 eV (413 to 206.6 nm), respectively$^{52,81}$. Our calculations show that most of the predicted compounds have greatly wider significant absorption ranges. For more details about the optical properties, please note to TABLE II.

Summarily, one can conclude that group-A monolayers, having stronger linear dichroism, have more potential applications in beam splitting, and group-B monolayers, having a wider absorption range for both polarizations, are more favorable for energy harvesting systems and solar cells. It should be added that three of group-B monolayers, namely $Ge_2As$, $Ge_2Sb$, and $Ge_2Bi$ have direct and wide band gaps, which makes them even more ideal for this purpose.

D. Thermoelectric Properties

Approximately two-thirds of the energy produced in the globe is spoiled as waste heat which has a major contribution to the global warming$^{82}$. Hopefully, thermoelectric (TE) materials have been offered as a solution for this crisis, which can convert heat to electricity, autonomously. The efficiency of a TE material is calculated by the dimensionless figure of merit given by, $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$. In which $S$, $\sigma$, $T$, and $\kappa$ stand for the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivities, respectively. As it turns out, a promising TE material must have a large power factor ($S^2\sigma$) and low thermal conductivity. But due to dependency of these quantities together, finding the proper material for thermoelectricity is still an important challenge. In this section, we present thermoelectric properties of the eight hydrogenated binary compounds, in order to find a suitable candidate for thermoelectric devices.
FIG. 9. Optical properties of the hydrogenated X₂Y binary compound monolayers, including the real and imaginary parts of the dielectric function (ε₁ and ε₂), and absorption coefficient (α), for the perpendicular (E⁺) and parallel (E∥) polarizations.
The electrical conductivity \( \sigma \) is related to the group velocity \( v_k \), which is given by:

\[
\nu_k = \frac{1}{h} \frac{\partial \varepsilon(k)}{\partial k}
\]

Once calculated, the transport distribution function is expressed as:

\[
\Xi(\varepsilon) = \sum_k \nu_k \times v_k \tau_k
\]

The electrical conductivity \( \sigma \) and Seebeck coefficient \( S \) are found by:

\[
\sigma(\mu, T) = e^2 \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon),
\]

\[
S(\mu, T) = \frac{eK_B}{\sigma} \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{K_BT},
\]

where \( f_0(\varepsilon) = \frac{1}{\exp \left( \frac{\varepsilon - \mu}{k_B T} \right) + 1} \)

in the linear response regime, where \( f_0(\varepsilon) \) is the Fermi-Dirac distribution function and \( \mu \) is the chemical potential. Correspondingly, the electronic thermal conductivity is determined by the Wiedemann-Franz law \( \kappa_e = L\sigma T \), where \( L \) is the Lorenz number \( (1.510^{-8} \text{ W} \Omega^{-1} \text{K}^{-2}) \).

In the constant relaxation time approximation (CRTA), the Seebeck coefficient is independent of relaxation time while the electrical conductivity and thermal conductivity are obtained with respect to the relaxation time \( (\sigma/\tau, \kappa_e/\tau) \). Hence, we adopt the Bardeen-Shockley deformation potential (DP) theory based on the basis of effective mass approximation to estimate the relaxation time from the carrier mobility \( \mu \).

To investigate the thermoelectric properties, the electronic band structure \( \varepsilon(k) \) is required, which is used to calculate the group velocity \( v_k \). Group velocity is defined as the gradient of energy bands in the reciprocal space as below:

\[
\nu_k = \frac{1}{h} \frac{\partial \varepsilon(k)}{\partial k}
\]

Once it is calculated, the transport distribution function is determined from:

\[
\Xi(\varepsilon) = \sum_k \nu_k \times v_k \tau_k
\]

where \( \tau_k \) is the relaxation time at state \( k \). Subsequently, the electrical conductivity \( \sigma \) and Seebeck coefficient \( S \) are obtained directly by:

\[
\sigma(\mu, T) = e^2 \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon),
\]

\[
S(\mu, T) = \frac{eK_B}{\sigma} \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{K_BT},
\]

\[
f_0(\varepsilon) = \frac{1}{\exp \left( \frac{\varepsilon - \mu}{k_B T} \right) + 1}
\]

The calculated elastic constant, deformation potentials, effective masses, carrier mobilities, and relaxation times at room temperature have been tabulated in TABLE III. As can be seen, the elastic constant decreases as the average atomic mass of the monolayers increase. In other words, the \( \text{Si}_2\text{P} \) and \( \text{Ge}_2\text{Bi} \) monolayers exhibit the largest \( 144.88 \text{ Jm}^{-2} \) and smallest \( 79.94 \text{ Jm}^{-2} \) values.

### Table II: Optical parameters of the hydrogenated \( X_2Y \) binary compounds, for perpendicular and parallel polarizations.

| Group-A | \( X \) | \( E_{\text{r}}^\perp \) | \( E_{\text{r}}^\parallel \) | \( \Xi(\varepsilon) \) |
|---------|----|-----------------|-----------------|-----------------|
| \( \text{Si}_2\text{P} \) | \( 800 - 155 \) | \( 3.74 \) | \( 375 - 150 \) | 
| \( \text{Si}_2\text{As} \) | \( 310 - 165 \) | \( 3.53 \) | \( 395 - 155 \) | 
| \( \text{Si}_2\text{Sb} \) | \( 340 - 200 \) | \( 3.05 \) | \( 465 - 170 \) | 
| \( \text{Ge}_2\text{P} \) | \( 290 - 195 \) | \( 3.4 \) | \( 430 - 155 \) | 
| \( \text{Si}_2\text{Bi} \) | \( 270 - 130 \) | \( 2.72 \) | \( 525 - 100 \) | 
| \( \text{Si}_2\text{As} \) | \( 170 - 140 \) | \( 3.38 \) | \( 450 - 135 \) | 
| \( \text{Si}_2\text{Sb} \) | \( 175 - 135 \) | \( 3.05 \) | \( 495 - 120 \) | 
| \( \text{Ge}_2\text{Bi} \) | \( 180 - 140 \) | \( 2.72 \) | \( 530 - 120 \) | 

To investigate the thermoelectric properties, the electronic band structure \( \varepsilon(k) \) is required, which is used to calculate the group velocity \( v_k \). The group velocity is defined as the gradient of energy bands in the reciprocal space as shown below:

\[
\nu_k = \frac{1}{h} \frac{\partial \varepsilon(k)}{\partial k}\]

Once it is calculated, the transport distribution function is determined from:

\[
\Xi(\varepsilon) = \sum_k \nu_k \times v_k \tau_k\]

where \( \tau_k \) is the relaxation time at state \( k \). Subsequently, the electrical conductivity \( \sigma \) and Seebeck coefficient \( S \) are obtained directly by:

\[
\sigma(\mu, T) = e^2 \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon),
\]

\[
S(\mu, T) = \frac{eK_B}{\sigma} \int d\varepsilon \left( \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{K_BT},
\]

\[
f_0(\varepsilon) = \frac{1}{\exp \left( \frac{\varepsilon - \mu}{k_B T} \right) + 1}
\]

in the linear response regime, where \( f_0(\varepsilon) \) is the Fermi-Dirac distribution function and \( \mu \) is the chemical potential. Correspondingly, the electronic thermal conductivity is calculated by the Wiedemann-Franz law \( \kappa_e = L\sigma T \), where \( L \) is the Lorenz number \( (1.510^{-8} \text{ W} \Omega^{-1} \text{K}^{-2}) \).

In the constant relaxation time approximation (CRTA), the Seebeck coefficient is independent of the relaxation time while the electrical conductivity and thermal conductivity are obtained with respect to the relaxation time \( (\sigma/\tau, \kappa_e/\tau) \). Hence, we adopted the Bardeen-Shockley deformation potential (DP) theory based on the basis of effective mass approximation to estimate the relaxation time from the carrier mobility \( \mu \).
FIG. 10. Variations of (a) total energies, energies of (b) CBM and (c) VBM of hydrogenated GeSb monolayer under strain.

TABLE III. 2D elastic constant ($C^{2D}$), deformation potential ($E_I$), effective mass ($m^*$), carrier mobility ($\mu$), and the relaxation time ($\tau$) for holes and electrons of the hydrogenated X$_2$Y binary compound monolayers. The mobility was calculated at room temperature in the zigzag and armchair directions.

| Carriers | $C^{2D}$ (Jm$^{-2}$) | $E_I$ (eV) | $m^*$ ($m_0$) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $\tau$ (fs) |
|----------|-----------------------|------------|---------------|----------------|-------------|
|          |                       |            | zig | arm | zig | arm | zig | arm | zig | arm |
| Si$_2$P  | hole                  | 146.88     | 9.21 | 0.19 | 0.28 | 838.56 | 569.03 | 90.71 |
|          | electron              | 146.88     | 6.95 | 2.32 | 0.11 | 55.06  | 1161.4 | 72.74 |
| Si$_2$As | hole                  | 126.98     | 8.44 | 0.19 | 0.27 | 891.24 | 627.17 | 96.41 |
|          | electron              | 126.98     | 7.28 | 2.95 | 0.12 | 29.37  | 722.02 | 49.33 |
| Si$_2$Sb | hole                  | 108.49     | 8.03 | 0.17 | 0.20 | 1154.9 | 981.63 | 111.8 |
|          | electron              | 108.49     | 4.75 | 3.04 | 0.11 | 58.85  | 1626.4 | 101.8 |
| Si$_2$Bi | hole                  | 91.43      | 10.79 | 0.25 | 0.13 | 374.91 | 720.97 | 53.36 |
|          | electron              | 91.43      | 5.45 | 3.11 | 0.11 | 36.41  | 1029.4 | 64.48 |
| Ge$_2$P  | hole                  | 122.42     | 7.58 | 0.46 | 0.11 | 443.04 | 1852.7 | 116.1 |
|          | electron              | 122.42     | 23.01 | 0.13 | 0.12 | 306.38 | 331.92 | 22.67 |
| Ge$_2$As | hole                  | 110.11     | 11.75 | 0.5  | 0.1  | 153.48 | 767.4  | 43.69 |
|          | electron              | 110.11     | 21.01 | 0.1  | 0.1  | 536.7  | 536.7  | 30.55 |
| Ge$_2$Sb | hole                  | 93.33      | 11.22 | 0.49 | 0.09 | 155.02 | 843.98 | 43.24 |
|          | electron              | 93.33      | 20.06 | 0.08 | 0.07 | 833.55 | 952.64 | 37.96 |
| Ge$_2$Bi | hole                  | 79.94      | 9.4   | 0.52 | 0.08 | 183.53 | 1193.1 | 54.34 |
|          | electron              | 79.94      | 16.97 | 0.07 | 0.07 | 1218.9 | 1218.9 | 48.58 |

respectively. This reveals a smoother variation of total energy under strain for the heavier structures which is reasonable. It can also be seen that the lowest deformation potential belongs to the monolayers with strongly localized CBM, i.e. Si$_2$Y. The rest of them exhibit very high tunability under strain. It should be pointed out that the deformation potential controls the scattering rate caused by electron-phonon interaction, and smaller values of this constant can generate large carrier mobility.

In the Si$_2$Y monolayers, the effective mass of electrons along with the zigzag direction is relatively large, with a range of 2.32 to 3.11 $m_0$ due to the flat CBM along the K – M direction, while the effective mass of electrons along with the armchair direction is relatively small and equals to 0.11 $m_0$. In the Ge$_2$Y monolayers, due to the parabolic CBMs, the effective mass of electrons along with the zigzag and armchair directions stay very low with a range of 0.07 to 0.13 $m_0$ which leads to high mobility. Meanwhile, the effective mass of heavy holes in the armchair direction experiences a decreasing trend with increasing the atomic mass, whereas in the zigzag direction there is no specific order.

Using all these quantities, we calculated the carrier mobility for each monolayer along with the zigzag and arm-
chair directions as presented in TABLE III. Obviously, the carrier mobilities exhibit strong anisotropy which is dominated by the corresponding anisotropy of the carrier effective masses. For the electrons, the mobility along with the armchair direction is larger than that of along with the zigzag direction, while for holes there is no specific order. Regardless of the direction, the highest mobility for holes (1852 cm²V⁻¹s⁻¹) and electrons (1626 cm²V⁻¹s⁻¹) belong to Ge₂P and Si₂Sb monolayers, respectively. Comparing with the highest reported mobility for SnS (623), SnSe (1035), GeS (1045), GeSe (541), PbSe (152), Te (1345), ZrS₂ (1045), PbTe₂ (2066), SnSe₂ (4563), and MoS₂ (200), monolayers, makes Ge₂P and Si₂Sb monolayers competitive candidates for high-speed nano-electronic devices. Also, one can conclude that the Si₂Sb, Si₂Bi, and Ge₂Bi monolayers are favorable for application in field-effect transistors due to their high mobility for both holes and electrons.

The thermoelectric transport coefficients of hydrogenated X₂Y binary compound monolayers are calculated as a function of the carrier concentration at room temperature and plotted in FIG. 11. Within the framework of the rigid band approach, all the results are investigated for both p-type and n-type carriers where the doping effects are mimicked by shifting the Fermi level to the valence and conduction bands, respectively. As can be seen, all the monolayers have nearly identical Seebeck coefficients in the p-type doping. However, at a specific doping level, the Ge₂P and Ge₂Bi monolayers exhibit the highest (2767 μV/K) and the lowest (1673 μV/K) peaks, respectively. In contrast, in the n-type doping, Si₂Bi and Ge₂Bi have the highest and the lowest Seebeck coefficients, and the obtained maximum values for these monolayers are 2837 and 1629 μV/K, respectively. All the peaks are tabulated in TABLE IV. For each material except Ge₂As and Ge₂Bi, the peak of the n-type Seebeck coefficient is larger than that of the p-type. The high Seebeck coefficient of Si₂Bi can be attributed to the flat CBM especially along with K – M direction. The obtained peaks for the Si₂Bi and Ge₂P monolayers are bigger than that of SnS (2380), SnSe (1750), GeS (2810), GeSe (1900), MoS₂ (2688), WS₂ (2728), BiAs (1735), and BiSb (1579) monolayers, which indicates the potential of Si₂Bi and Ge₂P monolayers for producing voltage at a temperature difference. Moreover, the maximum Seebeck coefficients for MX (M=Ga, In and X=S, Se, Te) metal monochalcogenides are approximately 1600 and 1400 μV/K for both p-type and n-type doping, respectively, which are also lower than that of X₂Y binary compounds showing their capability in the thermoelectric applications.

No considerable difference is seen in the p-type electrical conductivity of all the monolayers which may be probably due to the semi-identical valence bands (FIG. 6). On the other hand, in the n-type doping, the highest and the lowest electrical conductivity belong to Si₂P and Si₂Sb monolayers, respectively. It can also be seen that the n-type conductivity is higher than that of p-type which is attributed to the presence of several extrema in the conduction band that facilitates the electrons participation in the electrical transport.

No need to mention, the Seebeck coefficient reaches its maximum value at the low level of doping as the electrical conductivity tends to zero. Hence, to obtain the optimal carrier concentration for a high figure of merit, we calculated an important parameter called power factor from $PF=S^2\sigma/\tau$, as presented in FIG. 11 (right panel). By comparing the power factors, one can understand that the n-type doping exhibits much better thermoelectric performance than the p-type doping for all the monolayers which is due to the higher density of states near the Fermi level in the conduction band than that in the valence band. This electron-hole asymmetry can also be due to the existence of several extrema in the conduction bands. Such similar superiorities have been reported for As, Bi, Sb, Sn, Ge, and PbSe, and SnSe, and PbTe₂. However, the Si₂P monolayer produces the largest power factor (6.47×10¹⁰ W/K²ms) in the n-type doping (~ 910² cm⁻²) resulting from the moderate thermopower and electrical conductivity. Its worth noting that in a higher level of n-type doping (~ 2.3×10¹⁵ cm⁻²), the power factor of Si₂P reaches to 16.94×10¹⁰ W/K²ms, but because of the direct proportion between doping level and thermal conductivity, it may not lead to higher thermoelectric performance. In contrast, Si₂Bi and Ge₂P monolayers have the largest power factor (~ 24.31×10¹⁰ W/K²ms) in the n-type doping (~ 2.6×10¹³ cm⁻²) which can be attributed to the convergence of their CBMs and CBEs. Moreover, the Si₂As monolayer shows acceptable thermoelectric performance due to its high power factor (22.37×10¹⁰ W/K²ms). It should be pointed out that in a higher level of n-type doping (~ 1.41×10¹⁵ cm⁻²), the power factor of Si₂Bi reaches to 26.29×10¹⁰ W/K²ms. It can also be seen that for these monolayers, the n-type power factors are nearly four times higher than that of the p-type ones. All the peaks are tabulated in TABLE IV. Compared with MoS₂ (12×10¹⁰), SnSe₂ (1610), and Sb₂Te₂ (15.5×10¹⁰), the Si₂Bi, Ge₂P, and Si₂As monolayers are potential candidates for thermoelectricity. The peaks of power factor also state that the Ge₂As, Ge₂Sb, and Ge₂Bi monolayers are not appropriate for thermoelectric applications despite their ideal Seebeck coefficients.

To further insight into the thermoelectric properties, the variation of both the Seebeck coefficient and power factor with temperature have also been explored. As it is clear, by increasing the temperature, the Seebeck coefficients reduce with different proportions. At temperatures of 600 and 800 K, the highest Seebeck coefficient for n-type and p-type belongs to Si₂P monolayer. On the other hand, a higher temperature generates a higher power factor. At 600 and 800 K, the highest power factor for n-type is 37.61×10¹⁰ and 45.25×10¹⁰ W/K²ms, respectively, which belong to the Si₂Bi monolayer. By comparing the power factors in high temperatures, it is concluded that the Si₂Bi monolayer is the most appro-
FIG. 11. (Color on line) Electronic transport properties of the hydrogenated X$_2$Y binary compound monolayers including the Seebeck coefficient (left panel), electrical conductivity (middle panel), and the power factor (right panel) as a function of doping level ($N$) at room temperature (300 K) and GGA level. The doping level implies the numbers of electrons or holes per the surface of the unit cell which has two forms n- and p-types.

TABLE IV. The n- and p-type Seebeck coefficients ($S$) and power factors ($PF$) of the hydrogenated X$_2$Y binary compound monolayers at different temperatures.

| Doping | 300K | 600K | 800K | 300K | 600K | 800K |
|--------|------|------|------|------|------|------|
|        | $|S| \, (\mu V/K)$ | $PF \, (10^{10} W/K^{2}ms)$ |        | $|S| \, (\mu V/K)$ | $PF \, (10^{10} W/K^{2}ms)$ |        |
| Si$_2$P | n | 2779 | 1957 | 1460 | 19.12 | 27.32 | 32.23 |
|         | p | 2757 | 1858 | 1368 | 6.47 | 10.4 | 12.89 |
| Si$_2$As | n | 2831 | 1870 | 1398 | 22.37 | 29.69 | 35.26 |
|         | p | 2748 | 1748 | 1284 | 5.89 | 9.81 | 12.15 |
| Si$_2$Sb | n | 2814 | 1589 | 1188 | 17.49 | 25.44 | 30.25 |
|         | p | 2758 | 1501 | 1105 | 5.97 | 10.41 | 12.15 |
| Si$_2$Bi | n | 2837 | 1505 | 1132 | 24.39 | 37.61 | 45.25 |
|         | p | 2749 | 1355 | 989 | 5.34 | 9.59 | 11.76 |
| Ge$_2$P | n | 2832 | 1746 | 1298 | 24.25 | 29.56 | 31.83 |
|         | p | 2767 | 1642 | 1210 | 5.47 | 10.16 | 12.37 |
| Ge$_2$As | n | 2512 | 1396 | 1062 | 12.7 | 17.78 | 21.82 |
|         | p | 2752 | 1389 | 1033 | 5.3 | 9.85 | 12.06 |
| Ge$_2$Sb | n | 2387 | 1203 | 904 | 8.56 | 19.25 | 23.4 |
|         | p | 2335 | 1147 | 846 | 5.29 | 9.76 | 11.95 |
| Ge$_2$Bi | n | 1629 | 821 | 617 | 7.35 | 9.38 | 10.99 |
|         | p | 1673 | 847 | 636 | 5.22 | 9.55 | 11.73 |

appropriate candidate for thermoelectricity, and after that, the Ge$_2$P monolayer has the second-best performance. Also, it is seen that the Ge$_2$As, Ge$_2$Sb, and Ge$_2$Bi monolayers are not suitable for thermoelectric purposes. All the results state that a better thermoelectric performance can be achieved in n-type doping.

To complete this section, the electronic thermal conductivity of the predicted binary compounds with respect to the scattering time $\kappa_e/\tau$, is shown in FIG. 12. As can be seen, the p-type thermal conductivities are lower than
the n-type ones, which are due to the lower DOS in the valence bands near the Fermi level. These outcomes are similar to that of the electronic conductivity in FIG. 11 (middle panel) since they are connected together by the Wiedemann-Franz law.

E. Photocatalytic Properties

Water splitting is a chemical reaction in which the water molecule is broken down into oxygen and hydrogen\textsuperscript{100}. This process has attracted much attention because of clean, inexpensive, and environment friendly production of hydrogen. One of the well-known methods for water splitting is photocatalysis by use of a semiconductor sheet and solar energy. The general chemical formula for this reaction is presented as\textsuperscript{101}:

\[
2\text{H}_2\text{O}_{(\text{liquid})} + 4\text{H}^+ \rightarrow 4\text{H}^+ + \text{O}_2_{(\text{gas})}
\]

\[
4\text{H}^+ + e^- \rightarrow 2\text{H}_2\text{O}_{(\text{gas})}
\] (16)

The first half reaction shows the water oxidation at the anode and the second one indicates the water reduction at the cathode. The overall process results in production of hydrogen and oxygen gases as illustrated in FIG. 13. A semiconductor could be a potential photocatalyst for water splitting if the CBM energy is higher than the reduction potential of H\textsuperscript{+}/H\textsubscript{2} and the VBM energy is lower than the oxidation potential of O\textsubscript{2}/H\textsubscript{2}O\textsuperscript{102}. It should be noted that there are not many photocatalysts that meet all of the requirements, so far. Therefore, finding a suitable candidate semiconductor for this purpose is a crucial challenge, that we are going to face in this section.

Due to dependency of the reduction/oxidation (known as redox) potentials to the pH, these potentials were adopted at pH=0, 7, and 12, similar to the previous studies\textsuperscript{103,104}. In FIG. 14, the HSE06 band edges of the hydrogenated X\textsubscript{2}Y monolayers have been presented with respect to the vacuum level. As can be seen, at pH=0, the X\textsubscript{2}P and X\textsubscript{2}As monolayers have suitable band edge for water splitting reaction while at pH=12, all the monolayers are eligible. However, this reaction usually occurs in a neutral environment (pH=7). At this pH, all the monolayers except Ge\textsubscript{2}Bi satisfy the condition of the band edge position.

As suggested by Zhang et al, the materials with indirect band gaps are more desirable for photocatalytic activity\textsuperscript{105}, therefore Si\textsubscript{2}Y monolayers will react better than Ge\textsubscript{2}Y ones. On the other hand, the band gap value should be smaller than 3 eV for enhancing the visible light absorption\textsuperscript{106,107}, therefore the Si\textsubscript{2}P and Si\textsubscript{2}As monolayers, having large band gaps for visible light, cannot produce high efficiency for electron-hole generation and accordingly for water splitting. Summarily, the Si\textsubscript{2}Sb and Si\textsubscript{2}Bi monolayers are very promising candidates for water splitting.
IV. CONCLUSION

In summary, using first-principles calculations, for the first time, we have proposed a new family of two-dimensional binary compounds with an empirical formula of $X_2Y$, where $X$ and $Y$ belong to groups IV (Si and Ge) and V (P, As, Sb, and Bi), respectively. Different from their pure structures, the hydrogenated $X_2Y$ monolayers exhibit a very high stability according to cohesive energy, phonon dispersion analysis, and AIMD simulations. We have obtained many interesting physical properties by computing the electrical, optical, thermal and photocatalytic behavior of these monolayers. Our calculations disclose that all of the monolayers are semiconductors with band gaps in the range of 1.57 to 3.19 eV. The optical results reveal that Si$_2$P, Si$_2$As, Si$_2$Sb, and Ge$_2$P monolayers have potential applications in beam splitting, and Si$_2$Bi, Ge$_2$As, Ge$_2$Sb, and Ge$_2$Bi monolayers are more favorable for energy harvesting systems and solar cells. Moreover, the extremely high electron mobilities suggest that Ge$_2$P and Si$_2$Sb monolayers are promising for high-speed nano-electronic devices whereas Si$_2$Bi, Ge$_2$P, and Si$_2$As monolayers are competitive candidates for thermoelectricity. Besides, the Si$_2$Sb and Si$_2$Bi monolayers were found to have suitable band gaps and band edge positions for photocatalytic water splitting. Our results suggest the binary monolayers of group IV-V for uses in nano-electronic and optoelectronic applications, and propose them for further experimental works.

SUPPORTING INFORMATION

See the Supporting Information for details about the structural and electronic properties.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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See the Supporting Information for details about the structural and electronic properties.
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