The electronic and optical properties of 3d transition metals doped silicene sheet: A DFT study

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Abstract
Based on density functional theory calculations, we study the structural, electronic and optical properties of doped Silicene with 3d-transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. Optical properties such as dielectric function, refractive index, reflectivity, absorption, electron loss function, and optical conductivity are investigated in both cases of in-plane (⊥) and out of the plane (||) light polarization. Due to the doping of pristine silicene, the intensity of absorption peaks decreases and the maximum absorption peaks become visible in pristine silicene for out of the plane light polarization. Due to the doping of pristine silicene, the intensity of absorption peaks decreases and the maximum absorption peaks become visible in pristine silicene for out of the plane light polarization (||). As light is polarized in-plane (⊥), the maximum absorption peak observed in Cu-doped silicene structure. Our computational results indicate that the refractive index is anisotropic in both directions for all structures. In order to doping of silicene by transition metals structural, electronic and optical properties of pristine silicene modified. We believe that our results provide a useful strategy for applications in the optoelectronic industries.

1. Introduction

After the discovery of graphene in 2004 [1] this material shades in all fields of science [2–4]. Silicene its similar 2D material [5] has been extensively investigated in the electronics industry [6–10]. Silicene has reported by Takeda and Shiraiash in 1994 [11]. The synthesis of silicene achieved successfully on Ag(100) [12], Ag(110) [13–15], Ag(111) [16], Ir(111) [17], CaSi2 [18], ZrB2(0001) [19], Au(110) [20], MoS2 [21], h-BN [22] and AlN [23] substrates. Due to the larger size of silicon compared to the carbon atom, the bond length of Si–Si is much larger than C–C and the bonding in silicene forms by mixed sp2 and sp3 hybridization [24–27]. Silicene has several main advantages than graphene such as an easier valley polarization, more fitness, much stronger spin–orbit coupling and better tunable band gap [28–32]. Theoretical and experimental studies on silicene introduced it as the best candidates for various applications include the electrode of ion batteries [33–37], solar cells, chips, medicine [38], super capacitors [39], spintronics [40, 41] and hydrogen storage [42].

Silicene has also many applications in the optoelectronic industries [43, 44]. Rita John et al. [45] researched silicene from IR to far UV and they found silicene in the IR and visible regions. In the previous researchers, optical properties of silicene have been studied that two maximum peaks at 1.74 eV and 4–10 eV observed because of the π → π* and σ → σ* transitions, respectively [46]. DFT calculations showed that mono-vacancy silicene has two wider peaks than the pristine silicene because of the shifted peaks to the lower energies [47]. Electronic and optical properties of silicene under mechanical strains have theoretically considered the strain engineering in tuning the properties of single-layer silicene. The tensile and asymmetric strain shifted the structure peaks in εz towards lower energy and the π plasmons in silicene vanished with asymmetric and tensile strains [48]. Compared to the pristine silicene, the absorption coefficient of the P and Al-doped silicene are higher and no main changes in values of conductivity with doping concentration for in-plane (⊥) light polarization [49]. For the graphene, electronic and optical properties of 3d-transition metals checked theoretically. Excellent improvement of static dielectric constant and great value of reflectivity in the low optical energy seen for all of them [50]. Intensity of reflection, refraction, and absorption improved in the visible light.
region for ten transition metals doped SnO₂ nanosheets and the absorption shows red shift for Ni, Fe, Mn and Cr doped silicene [51].

In this paper, we investigate the structural and electronic properties of pristine silicene and doped silicene with nine transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. With this type of doping, we calculate the values of the dielectric function and refractive index in both cases of in-plane (⊥) and out of the plane (||) light polarization to calculate some optical items like reflectivity, electron loss function, absorption, optical conductivity, and reflection.

2. Computational method

The calculations were performed within the framework of density functional theory (DFT) as accomplished by the VASP Package [52]. The generalized gradient approximation (GGA) [53] and GGA + U [54] performed with the parameterization scheme of Perdew-Burke-Ernzerhof (PBE) [53] for the applied exchange-correlation functional. Calculations done with different values of U (Uₜₐ = 3 [55], Uᵥ = 3.2, Uₖₐ = 3.6, Uₘ₃ = 3.9, U₉₄ = 4, U₉₃ = 3.35, U₉₅ = 6, Uₘ₄ = 4 [56], U₉₅ = 5 [57]). The energy of the self-consistent field (SCF) converged to 10⁻⁶ eV. The density functional theory calculations carried out with the plane wave cutoff energy of 400 eV on a 5 × 5 × 1 K-point mesh Monkhorst-pack scheme [58]. We studied silicene with a size of 3 × 3 supercell that includes 18 silicon atoms. As usual for avoiding interactions of the silicene sheet with its periodic images, a vacuum gap of 25 Å in the z-direction used.

3. Results

3.1. Structural and electronic properties of doped silicene

At first, the optimization process is done in each system to reach the minimum energy for determining the most stable state. According to our calculation, the optimized Si-Si bond length, Si–Si–Si bond angle, lattice constant and buckling height for pristine silicene obtained 2.26 ˚Å, 115.71°, 3.83 ˚Å, and 0.47 ˚Å, respectively. Our calculation for pristine silicene is in good agreement with previous findings based on DFT calculations [59]. The optimized structures of pristine and doped silicene are shown in figure 1.

Structural and electronic properties of doped silicene including binding energies (E₉), Si–X bond lengths, bond angle (Si–X–Si), lattice constant (a), local buckling (hₐ), Fermi level energy (E₉), total magnetic moment per supercell (total (μ₉₃)), magnetic moment contributed from 3d-transition metals (3d (μ₉₃)) and magnetic moment contributed from sum of all Si atoms (Si (μ₉₃)) are reported in table 1. Atomic radius reduces [60] from Ti to Zn but the bond length (Si–X) revealed in Ti (2.53 ˚Å) and lowest amount of 2.23 ˚Å revealed in the case of Fe, Ni-doped silicene. The bond length has a decreasing trend except for Co, Cu and Zn-doped silicene. For bond angle (Si–X–Si), the largest and lowest value of 92.64 ˚Å and 118.82 ˚Å are belonged to the Ti and Zn-doped silicene, respectively. On the base of our findings in table 1, local buckling increased in Ti, V, and Cr-doped silicene because of their angle nears to tetrahedral (sp³ hybridization) bond angle. In contrary to Cu and Zn, other atoms projected out of the silicene plane. The largest value of lattice constant (a) is for Zn-doped silicene 4 ˚Å and the lowest value is 3.47 ˚Å for Fe-doped silicene. According to the Fermi level energy (E₉) analysis, Cu-doped silicene (−3.58 eV) has a maximum amount in comparison with that other systems.

The density of states (DOS) and band structure plots for pristine and doped silicene with nine transition metals are shown in figure 2. The minimum of the conduction band (MCB) and the maximum of the valence band (MVB) touch at a single point known as the Dirac point. Although pristine silicene shows a semimetallic behavior, the doped silicene shows a metallic behavior with crossing bands at the Fermi level. According to the band structure behavior, the Fermi level of doped silicene shifted up toward the conduction band. In DOS plots of V, Cr, Mn, Fe, Co, Ni and Cu-doped silicene, an asymmetry observed near the Fermi level, resulted from the difference value of spin up and down. The largest value of difference observed in Mn-doped silicene 5μ₉₃. The major contribution of the magnetic moment comes from the difference between the majority and minority spin bands of coupled TM with Si atoms. Based on DOS results shown in the left-hand side of figure 2, observing an asymmetry in the spin up and spin down states near the Fermi level, gives rise to a net magnetic moment of values. An enhancement in the density of states implies that doping may lead to the formation of extended magnetic moments and enhance the tendency of the system towards ferro or anti ferromagnetism. The prediction of total magnetic moment for TM d orbitals by keeping together the ferromagnetic ordering between Si and TM atoms presented in table 1.

The TM atoms and three nearest-neighbor Si atoms are magnetically ordered in the cases of V, Cr, Mn, Fe, Co, Ni, and Cu. The results demonstrate that as the atomic number increases from Ti to Mn, the 3d orbitals become increasingly half-filled and total magnetic moment increased from zero to 5μ₉₃. After that from Mn to
Zn, spins are aligned antiparallel at the smallest volumes, owing to the Pauli’s exclusion principle equal spins prevent from occupying in the same spot. This reduces the magnetic moment of TM doped silicene from 5 \( \mu_B \) to zero. In the other hands, when the atoms are incorporated into a silicene, some of the electrons are forced into common spatial wave functions which forces their spins antiparallel and reduces the overall magnetic moment. This interaction changes its sign as soon as the wave functions cease to overlap strongly between TM and silicene surface in the case of V, and Cr doped. This produces antiferromagnetic coupling between V, Cr atoms and silicene surface. In the Zn atom, 3d orbitals are completely filled and no induced magnetism is expected, hence we also realize the nonmagnetic state in the case of Zn doped silicene, which agrees well with Zn-adsorbed graphene and germanene results [61]. As can see in table 1, total magnetic moment for Zn is zero and there is no charge redistribution between Zn atom and silicene surface. In the DOS structure of Zn-doped silicene, there is no difference between up and down electron spin, therefore Zn doped silicene is nonmagnetic. Additionally, we have calculated the binding energies of TM atoms onto silicene surface as defined in previous literature [61]:

\[
E_B = E_{\text{silicene}} + E_{\text{TM}} - E_{\text{TM+silicene}}
\]  

where \( E_{\text{TM+silicene}} \) and \( E_{\text{silicene}} \) are the energies of silicene containing the vacancy with and without an additional TM atom, respectively. \( E_{\text{TM}} \) is the total energy of the isolated atom in its ground state. The calculated values for

![Figure 1. Side and Top view of optimized structures of pristine silicene and doped silicene.](image)

| System   | Si-X(Å) | Si-X-Si (deg) | hza(Å) | \( E_f \)(eV) | total (\( \mu_B \)) | 3d (\( \mu_B \)) | Si (\( \mu_B \)) | \( E_B \)(eV) |
|----------|---------|---------------|--------|---------------|-------------------|----------------|---------------|--------------|
| Sil-Si   | 2.26    | 115.71        | 3.83   | 0.47          | -3.23             | 0              | 0             | 0            |
| Sil-Ti   | 2.53    | 92.64         | 3.65   | 0.97          | -3.07             | -0.01          | -0.01         | 0            | -6.45        |
| Sil-V    | 2.40    | 94.13         | 3.51   | 1.36          | -3.33             | 2.01           | 3.45          | -1.44        | -5.83        |
| Sil-Cr   | 2.38    | 97.60         | 3.58   | 1.01          | -3.35             | 2.99           | 4.51          | -1.52        | -4.38        |
| Sil-Mn   | 2.38    | 101.10        | 3.68   | 0.82          | -3.44             | 5              | 4.83          | 0.17         | -4.67        |
| Sil-Fe   | 2.23    | 101.85        | 3.47   | 0.90          | -3.39             | 4              | 3.47          | 0.53         | -5.67        |
| Sil-Co   | 2.26    | 106.43        | 3.61   | 0.56          | -3.53             | 2.98           | 1.87          | 1.11         | -6.05        |
| Sil-Ni   | 2.23    | 109.89        | 3.65   | 0.46          | -3.52             | 2.01           | 0.51          | 1.5          | -6.12        |
| Sil-Cu   | 2.28    | 113.78        | 3.82   | -0.73         | -3.58             | 1.01           | 0.05          | 0.96         | -4.39        |
| Sil-Zn   | 2.33    | 118.82        | 4.00   | -0.80         | -3.06             | 0              | 0             | 0            | -2.81        |
the $E_g$ show that substitutional doping is energetically more favorable for Ti, Ni and Co atoms, whereas it is less suitable for Zn atom. However, in the case of the Ti-doped silicene, the very large value of $E_g$ arise from the fact that this molecule is formed naturally as a diatomic molecule.

**Figure 2.** Density of states and Band Structures (a) pristine silicene, (b) Ti-doped silicene, (c) V-doped silicene, (d) Cr-doped silicene and (e) Mn-doped silicene (f) Fe-doped silicene (g) Co-doped silicene (h) Ni-doped silicene (i) Cu-doped silicene and (j) Zn-doped silicene (blue color is spin up and red color is spin down).
The PDOS analysis of all structures is shown in figure 3. The highest peak for 3d orbitals (V, Cr, Mn, Fe, Co, Ni and Cu-doped silicene) doesn’t locate around the Fermi level. According to our results, all structures showed the highest peak of d orbital in valence part in contrast to the d orbital of Ti-doped silicene which is located in the conduction part. The density of states and band structure plots for pristine silicene and Al, B, N, and P-doped silicene had been investigated by Mousavi-Khoshdel et al[37]. They reported an asymmetric for N-doped silicene with 0.75 $\mu_B$ as a net magnetic moment and asymmetric for Al, B and P atoms. Compared to N-doped silicene, V, Cr, Mn, Fe, Co, Ni, and Cu-doped silicene have more values in the present work.

3.2. Optical properties of doped silicene

In this work, the optical properties of pristine and doped silicene with nine transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn have calculated. The optical properties give us information about the dielectric function, refractive index, reflectivity, electron loss function, absorption, optical conductivity, and reflection. There is no doubt the main part of optical properties is dielectric function; it is calculated from $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ [62]. The real part of the dielectric function $\varepsilon_1(\omega)$ calculated from the imaginary part by using Kramers—Krong [63] transformation with this equation [64]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_{0}^{\infty} \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)}$$ (2)
The imaginary part of the dielectric function $\varepsilon_2(\omega)$ is calculated from [65]:

$$
\varepsilon_2(\omega) = \left( \frac{4\pi^2 e^2}{m\omega^2} \right) \sum \left( \langle iM | j \rangle^2 f_i (1 - f_j) \times \delta(E_f - E_i - \omega) \right) dk
$$

where $\omega$ is the photon frequency, $i$ and $j$ are the first and final states, $M$ is dipole matrix, $f_i$ is Fermi distribution function, $E_i$ and $E_f$ are electron energy for first and final states, respectively. Other optical constants like refractive index, reflectivity, electron loss function, absorption, optical conductivity and reflection calculated from the imaginary part and real part of the dielectric function. The real part of refractive index with dielectric function given by [66].

Figure 3. Partial Density of States reported on the p orbitals of the silicon atoms and the d orbitals of the substitutional atoms. The blue solid line refers to total DOS of each system. The Fermi levels are set to zero.
Nine transition metals Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn are shown in 3.2.3. A greater than it
materials means radiation photon scattered by materials and the imaginary part is related to the absorbed energy by the
Dielectric Function is a complex function that describes the optical properties. It has two parts; the real part
3.2.1. Dielectric function
The real part of dielectric function starts almost from zero energy when light is in-plane (\(|\rangle\)) light polarization.
The results of the real part of dielectric function in both cases of in-plane (\(|\rangle\)) and out of the plane (\(\perp\)) light
polarization reported in table 2. As shown in figure 4, the real part has isotropic behavior for pristine silicene above 13 eV and other doped silicene structures above 9 eV in both polarization directions. One can see, all structures were red-shifted. The refractive index of pristine silicene is in agreement with the previous reports in both polarization direction directions [45]. The results of imaginary parts of dielectric function in both cases of in-plane (\(|\rangle\)) and out of the plane (\(\perp\)) light polarization is presented in figures 4(c)–(d) and table 3. The imaginary part of dielectric function starts almost at zero energy when light is in-plane (\(\perp\)) polarization and is zero after 13 eV.

3.2.2. Refractive index
The refractive index of a material is a dimensionless number that describes how fast light propagates through the
material [67]. It consists of real and imaginary parts; the real part is the phase velocity and the imaginary part is the extinction coefficient. The extinction coefficient for a material refers to measures the light electromagnetic of material in the absorption event [66]. Real and imaginary parts of the refractive index curves of pristine and doped silicene are shown in figure 5. Because of decreasing the velocity of light when it polarizes along the direction of electrons in the lattice, the refractive index values are larger in (\(|\rangle\)) than (\(\perp\)) light polarization. According to our results, the refractive index is anisotropic in both directions for all structures (as shown in figure 5) and the real part has isotropic behavior for pristine silicene above 13 eV and other doped silicene structures above 9 eV in both polarization directions. One can see, all structures were red-shifted. The refractive index of pristine silicene is in agreement with the previous reports in both polarization direction directions [45]. Real and imaginary parts of the refractive index were greater in both cases of in-plane (\(\perp\)) and out of the plane (\(|\rangle\)) light polarization for pristine silicene, it was greater than nine transition metals in both parts. The real part of the refractive index for out of the plane (\(|\rangle\)) light polarization had been reported for silicene 3.25 that our result was greater than it [45].

3.2.3. Reflectivity
Reflectivity defined as the amplitude or intensity of the reflected wave relative to the wave of the event. It is an important idea in the fields of optics, solar thermal energy, physics, and electrical engineering. Reflectivity curves
of pristine and doped silicene in both cases of in-plane (⊥) and out of the plane (||) light polarization is shown in figure 6.

In-plane (⊥) light polarization reflection occurs in the UV region (0–10 eV) whiles in out of the plane (||) polarization of light, reflectivity is in the IR and visible regions (low frequency region, up 10 eV). Reflectivity curves start almost at zero energy when light is in both polarization directions. The maximum reflectivity peaks

Table 2. The real part of dielectric function peaks of pristine silicene and doped silicene in both cases of in-plane (⊥) and out of the plane (||) light polarization.

| System | ⊥   | ||  |
|--------|-----|----|
| Sil    | 1.205 | 1192.40 |
| SiTi   | 1.293 | 9.52  |
| SiV    | 1.231 | 7.27  |
| SiCr   | 1.249 | 9.21  |
| SiMn   | 1.280 | 9.15  |
| SiFe   | 1.234 | 7.11  |
| SiCo   | 1.225 | 7.27  |
| SiNi   | 1.235 | 7.74  |
| SiCu   | 1.214 | 9.51  |
| SiZn   | 1.254 | 19.82 |
are shown in table 4 for pristine silicene and other doped systems in both cases of in-plane (⊥) and out of the plane (||) light polarization. These results indicate that Cu- doped silicene has more value in comparison with other doped systems.

According to our results, peaks formed to be red-shifted in both polarization directions. For pristine silicene, the value of reflectivity was higher than the doped silicene with nine transition metals for out of plane (||) light
polarization and Cr-doped silicene has the highest peak for in-plane (⊥) light polarization. The peak position of pristine silicene reported by Rita john et al [45] exhibited between 0–12 eV using DFT calculations. The Reflectivity of Al and P-doped silicene was limited in low energy (less than 4 eV) and high energy (more than 8 eV) in both cases of in-plane (⊥) and out of the plane (||) light polarization, respectively [49]. 3d-transition metals reflectivity doped SnO2 nanosheets increased in the visible light region (0–3 eV [45]). According to our findings, the peak position of pristine silicene and doped silicene are between 0–15 eV in both light polarization directions.

3.2.4. Electron loss function
The electron energy loss function (L(ω)) is a probability of passing electrons through the material loss of their energy. The observed peaks in the loss function diagram are descriptive of the parameters related to the plasma response. The most prominent peaks in loss function known as plasmon peak that describes collective excitation of the electron charge density. The electron energy loss function plots of pristine and doped silicene in both cases of in-plane (⊥) and out of the plane (||) light polarization is shown in figure 7. According to our calculation, obvious peaks in both polarization directions are found to be red-shifted. The most significant peaks in the energy loss function are seen at 0–10 eV for in-plane polarization of light (⊥) and 5–7 eV and 9–11 eV for out of the plane (||) light polarization, respectively.

The energy values of loss function peaks of pristine silicene and doped silicene in both polarization directions mentioned in table 5 show that pristine silicene has the most value (9.91 eV) and Ti-doped silicene least value (5.02 eV) for out of the plane (||) light polarization. The energy values of Loss Function 15, 9.68, 9.1 and 7.6 eV for in-plane (⊥) light polarization and 15.4, 6.89, 6.67 and 5.98 eV for out of the plane (||) light
polarization reported by Rita John et al [45] for graphene, silicene, germanene, and stanine, respectively. The electron energy loss spectra of pristine silicene and Al and P-doped silicene examined by Das et al with the expand of doping concentration, the peaks were red-shifted [49].

3.2.5. Absorption

As we know, another major optical property is absorption and its calculations closely depend on the light of polarization direction and the imaginary part of the dielectric function. In this paper, we studied the absorption of the pristine and doped silicene with nine transition metals in both cases of in-plane (⊥) and out of the plane (||) light polarization (figure 8). The energy interval was presented from 0 to 15 eV.

When light polarized, the peaks appear from 0–13 eV in both directions. The value of first and the second maximum absorption peaks that occurred for in-plane (⊥) and out of the plane (||) light polarization (in figure 8). The energy interval was presented from 0 to 15 eV.

As light is polarized out of the plane (||), the maximum absorption peaks become visible: 1.18, 4.05, 4.12, 4.13, 4.15, 4.16, 4.17 and 4.19 eV in pristine silicene, Ti, Cr and Ni, Fe, Mn and Co, V, Zn and Cu-doped silicene, respectively. Another peak appears at 4.41, 2.12, 2.07, 1.98 and 1.94 eV in pristine silicene, Cr and Fe, V, Mn and Cu, and Zn-doped silicene, respectively. All nine transition metals doped silicene sheets have red-shifted to lower energies in both cases of in-plane (⊥) and out of the plane (||) light polarization. The intensity of peaks was less than pristine silicene for out of the plane (||) light polarization. The highest peaks 14.5, 8.34, 8.31 and 6.7 eV in graphene, silicene, germanene and stanine that peaks were due to the existence of saddle points along M to K.

Table 5. The photon energy at Loss Function peaks of pristine silicene and doped silicene in both cases of in-plane (⊥) and out of the plane (||) light polarization.

| System | E (ev) | E (ev) |
|--------|--------|--------|
| ⊥       |        |        |
| Sil     | 8.23   | 9.91   |
| SilTi   | 7.93   | 5.02   |
| SilV    | 8.18   | 6.08   |
| SilCr   | 8.14   | 6.11   |
| SilMn   | 8.15   | 6.01   |
| SilFe   | 8.26   | 6.04   |
| SilCo   | 8.22   | 6.08   |
| SilNi   | 8.25   | 6.10   |
| SilCu   | 8.31   | 6.12   |
| SilZn   | 8.16   | 6.04   |

Figure 7. Electron Loss Function curves of pristine silicene and doped silicene (a) in-plane (⊥) polarization (b) out of the plane (||) polarization.
direction and the highest peaks in 4.17, 3.69, and 3.27 eV for them in both cases of in-plane (⊥) and out of the plane (||) light polarization, respectively [45]. Absorption spectrum for pristine graphene and F, O, N, and B-doped graphene in both cases of in-plane (⊥) and out of the plane (||) light polarization, studied by Goudarzi et al and their results showed two main peaks at 4.3 and 14.2 eV and two main peaks at 11.6 and at 14.67 eV in both cases of in-plane (⊥) and out of the plane (||) light polarization, respectively. For doped graphene, all absorption peaks have blue-shifted to high energy [70]. Yong Feng et al [51] studied ten transition metals doped SnO$_2$ nano sheets and all TM doped SnO$_2$ nano sheets have shifted to the low energies (red-shift). The absorption peaks of Cr, Fe, and Ni were below 1.5 eV but Mn located around 2.20 eV. Zakerian et al [47] determined absorption spectrum of pristine silicene and mono-vacancy defect ed and reported main peaks around 1.2 and 4 eV for pristine silicene and 0.9 and 3.7 eV for mono-vacancy defected silicene within a many-body green function and Bethe-Salpeter equation formal. Absorption coefficients for pristine silicene and Al and P-doped silicene were done by Das et al [49] with DFT calculation (GGA/PBE). Their results showed an absorption coefficient of 4.07 eV for pristine silicene for E$\perp$ and 9.11 eV for E$\perp$ which are in the ultraviolet range. In the case of doped silicene, the value of absorption coefficient was higher than the pristine silicene through the ultraviolet range. Optical absorption spectra had been reported for silicene by Wei et al and the $\pi \rightarrow \pi^*$ resonant excitation in silicene appeared at 1.23 eV [71].

### 3.2.6. Conductivity

Optical conductivity is conductivity in the presence of an alternating electric field. In order to study the optical conductivity for pristine silicene and doped silicene, we performed optical conductivity calculations in both cases of in-plane (⊥) and out of the plane (||) light polarization that are shown in figure 9. According to the computational results, we can find a real part of optical conductivity starts at 1.5 eV in Figure 9. Absorption curves of pristine silicene and doped silicene (a) in-plane (⊥) polarization (b) out of the plane (||) polarization.

| System | The first maximum peak (eV) | The second maximum peak (eV) |
|--------|-----------------------------|------------------------------|
| Sil    | 7.85                        | 5.60                         |
| SilTi  | 7.62                        | 4.80                         |
| SilV   | 7.83                        | 5.52                         |
| SilCr  | 7.75                        | 5.45                         |
| SilMn  | 7.78                        | 5.33                         |
| SilFe  | 7.88                        | —                            |
| SilCo  | 7.84                        | —                            |
| SilNi  | 7.86                        | 4.24                         |
| SilCu  | 7.95                        | —                            |
| SilZn  | 7.76                        | —                            |
conductivity starts at 0 eV for out of the plane (||). Compared to the real part, more attractively the energy at which the imaginary part of optical conductivity is zero in both polarization directions. As light polarized (⊥), the optical conductivity plot is in agreement with the loss function plot in the same direction. The real and imaginary parts of the optical conductivity of pristine silicene reported by Rita John et al were in good agreement with the present work in (⊥) direction [45].

4. Conclusion

The electronic and optical properties for pristine silicene and Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn-doped silicene were studied using DFT calculations. The imaginary part of dielectric function decreases from 441.42 until 0.76 for out of the plane (||) light polarization and the oscillatory behavior of all the materials exists only up to 0.85 eV along the (||) polarization direction. The maximum intensity absorption peak occurs for Cu-doped silicene when light is in-plane (⊥) and the maximum absorption highest peaks become visible in pristine silicene in polarizing (||) direction. The optical conductivity plot when light is polarized (⊥) is in good agreement with the loss function plot in the same direction and according to our information, obvious peaks are in both polarization directions that they are found to be red-shifted. The most significant peaks in the energy loss function are seen at 0–10 eV in (⊥) polarization direction and 5–7 and 9–11 eV, respectively in (||) polarization direction. Reflectivity curves start almost at zero energy when light is in both polarization directions and the highest peak of reflectivity occurs in Cr-doped silicene and pristine silicene in both cases of in-plane (⊥) and out of the plane (||) polarization of light, respectively. Real and imaginary parts of the refractive index were greater in (||) than (⊥) polarization direction for pristine silicene and corresponding to our findings, the refractive index is anisotropic in both directions for all structures. The present paper will help for further understanding that nine
transition metals doped silicene can be change electronic and optical properties of pristine silicene and more importantly, they may be useful for interesting application such as designing optoelectronic industries.

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References

[1] Hauser A W and Schwerdtfeger P 2012 Methane-selective nanoporous graphene membranes for gas purification Phys. Chem. Chem. Phys. 14 13292–8
[2] Ponomarenko L A, Schedin F, Katsnelson M I, Yang R, Hill E W, Novoselov K S and Geim A K 2008 Chaotic dirac billiard in graphene quantum dots Science 320 356–8
[3] Zhou Q, Coh S, Cohen M L, Louie S G and Zettl A 2013 Imprint of transition metal d orbitals on a graphene Dirac cone Physical Review B 88 235431
[4] Nieszporek K and Drach M 2015 Alkane separation using nanoporous graphene membranes Phys. Chem. Chem. Phys. 17 1018–24
[5] Houssa M, Dimoulas A and Molle A 2015 Silicene: a review of recent experimental and theoretical investigations J. Phys. Condens. Matter 27 223502
[6] Yu X, Ni Z, Liu Y, Ruan Z, Xu M and Yang D 2015 Density functional theory study on boron-and phosphorus-doped hydrogen-passivated silicene Phys. Chem. Chem. Phys. 17 4146–51
[7] Zhao T, Zhang S, Wang Q, Kawazoe Y and Jena P 2014 Tuning electronic and magnetic properties of silicene with magnetic superhalogens Phys. Chem. Chem. Phys. 16 22979–86
[8] Osborn T H, Farajian A A, Pupysheva O V, Aga R S and Voon L C Y 2011 Ab initio simulations of silicene hydrogenation Chem. Phys. Lett. 511 101–5
[9] Le Lay G 2015 2D materials: silicene transistors Nat. Nanotechnol. 10 202
[10] Pamungkas M A, Setyowati D A and Abdurrahman 2018 2018 AIP Conference Proceedings 2021 Optical Properties of Ga-doped Silicene and As-doped Silicene: First Principle Calculations pp 050014
[11] Vogl P, De Padova P, Quaresima C, Avila I, Franzesekakis E, Asensio M C, Resta A, Elet E and Le Lay G 2012 Silicene: compelling experimental evidence for graphene-like two-dimensional silicon Phys. Rev. Lett. 108 135501
[12] Le Lay G, Aufray B, Léandri C, Oughaddou H, Biberian J P, De Padova P, Dávila M E, Elet E and Kara A 2009 Physics and chemistry of silicene nano-ribbons Appl. Surf. Sci. 256 524–9
[13] Kara A, Enríquez H, Seitzonson A P, Voon L C Y, Vizzini S, Aufray B and Oughaddou H 2012 A review on silicene—new candidate for electronics Surf. Sci. Rep. 67 1–18
[14] Aufray B, Kara A, Vizzini S, Oughaddou H, Léandri C, Elet E and Le Lay G 2010 Graphene-like silicon nanoribbons on Ag (110): a possible formation of silicene Appl. Phys. Lett. 96 183102
[15] Enríquez H, Vizzini S, Kara A, Lalmi B and Oughaddou H 2012 Silicene structures on silver surfaces J. Phys. Condens. Matter 24 314211
[16] Tao L, Cinquanta E, Chiappe D, Grazianetti C, Fanciulli M, Dubey M, Molle A and Akinwande D 2015 Silicene field-effect transistors operating at room temperature Nat. Nanotechnol. 10 227
[17] Meng L, Wang Y, Zhang L, Du S, Wu R, Li L, Zhang Y, Li G, Zhou H and Hofer W A 2013 Buckled silicene formation on Ir (111) Nano Lett. 13 685–90
[18] Ali M A and Tchalala M R 2014 Chemical synthesis of silicon nanosheets from layered calcium diclride Journal of Physics: Conference Series 491 012009
[19] Fleurence A, Friedlein R, Ozaki T, Kawai H, Wang Y and Yamada-Takamura Y 2012 Experimental evidence for epitaxial silicene on diboride thin films Phys. Rev. Lett. 108 245501
[20] Rachid Tchalala M, Enríquez H, Mayne A J, Kara A, Orth S, Silly M G, Bendounan A, Sirotti F, Greber T and Aufray B 2013 Formation of one-dimensional self-assembled silicon nanoribbons on Au (110) (2 × 1) Appl. Phys. Lett. 102 083107
[21] Chiappe D, Scalise E, Cinquanta E, Grazianetti C, van den Broek B, Fanciulli M, Houssa M and Molle A 2014 Two-dimensional silicene nanosheets with local hexagonal structure on a MoS2 surface Adv. Mater. 26 2096–101
[22] Liu H, Gao J and Zhao J 2013 Silicene on substrates: a way to preserve or tune its electronic properties The Journal of Physical Chemistry C 117 10533–9
[23] Houssa M, Fourtois G, Afanasiev V V and Stesmans A 2010 Can silicon behave like graphene? A first-principles study Appl. Phys. Lett. 97 112106
[24] Liu C-C, Feng W and Yao Y 2011 Quantum spin Hall effect in silicene and two-dimensional germanium Phys. Rev. Lett. 107 076802
[25] Shao Z-G, Ye X-S, Yang L and Wang C-L 2013 First-principles calculation of intrinsic carrier mobility of silicene J. Appl. Phys. 114 093712
[26] Pizzochero M, Bonfanti M and Martinazzo R 2016 Hydrogen on silicene: like or unlike graphene? Phys. Chem. Chem. Phys. 18 15654–66
[27] Pizzochero M, Bonfanti M and Martinazzo R 2019 To bend or not to bend, the dilemma of multiple bonds Phys. Chem. Chem. Phys. 21 26342–50
[28] Li S, Wu Y, Tu Y, Wang Y, Jiang T, Liu W and Zhao Y 2015 Defects in silicene: vacancy clusters, extended line defects, and di-adatoms Sci. Rep. 5 7881
[29] Quhe R, Fei R, Liu Q, Zheng J, Li H, Xu C, Ni Z, Wang Y, Yu D and Gao Z 2012 Tunable and sizeable band gap in silicene by surface adsorption Sci. Rep. 2 853
[30] Jose D and Datta A 2013 Properties of graphene: unlike graphite Acc. Chem. Res. 47 593–602
[31] Jia T-T, Fan X-Y, Zheng M-M and Chen G 2016 Silicene nanomeshes: bandgap opening by bond symmetry breaking and uniaxial strain Sci. Rep. 6 20971
[32] Lew Yan Voon L C, Zhu J and Schwingenschlögl U 2016 Silicene: recent theoretical advances Applied Physics Reviews 3 040802
[33] Liu S, Li H, He Y, Li X, Li Y and Wang X 2015 Pathway into the silicene nucleation on silicene substrate at nanoscale Mater. Des. 85 60–6
[34] Guo G, Yao Y, Zheng J, Yuan J and Zhao H 2017 Design lithium storage materials by lithium adatoms adsorption at the edges of zigzag silicene nanoribbon: a first-principle study Appl. Surf. Sci. 406 161–9
[35] Shi L, Zhao T S, Xu A and Xu J B 2016 Ab initio study of a silicene and graphene heterostructure as an anode material for Li-and Na-ion Journal of Materials Chemistry A 4 16377–82
[36] Seyed-Talebi S M, Kazeminezhad I and Behesthian J 2015 Theoretical prediction of silicene as a new candidate for the anode of lithium-ion batteries Phys. Chem. Chem. Phys. 17 29869–96
[37] Momeni M J, Mousavi-Khosheil M and Targhobi E 2017 First-principles investigation of adsorption and diffusion of Li on doped silicenes: prospective materials for lithium-ion batteries Mater. Chem. Phys. 192 125–30
[38] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films science 306 666–9
[39] Yang G M, Xu Q, Fan X and Zheng W T 2018 Quantum capacitance of silicene-based electrodes from first-principles calculations The Journal of Physical Chemistry C 122 1903–12
[40] Johl H, Lee M-D, Ng S-P N, Kang H-C and Tok E S 2014 Influence of interconfigurational electronic states on Fe, Co, Ni-silicene materials selection for spintronics Sci. Rep. 4 7594
[41] Li S, Ren J-C, Ao Z and Liu W 2018 Enhanced stability and induced magnetic moments of silicene by substitutional doping of nickel Chem. Phys. Lett. 706 202–7
[42] Qiu J, Fu H, Xu Y, Oreshkin A I, Shao T, Li H, Meng S, Chen L and Wu K 2015 Ordered and reversible hydrogenation of silicene Phys. Rev. Lett. 114 126101
[43] Lu-Gang C, Fa-Min L and Wen-Wu Z 2010 Structural, electronic and optical properties of orthorhombic distorted perovskite TbMnO3 Chin. Phys. B 19 097101
[44] Kooji E S and Poelsema B 2006 Shape and size effects in the optical properties of metallic nanorods Phys. Chem. Chem. Phys. 8 3349–57
[45] John R and Merlin B 2017 Optical properties of graphene, silicene, germanene, and stanene from IR to far UV—a first principles study J. Phys. Chem. Solids 110 307–15
[46] Chinnathambi K, Chakrabarti A, Banerjee A and Deb S K 2012 Optical properties of graphene-like two dimensional silicene preprint arXiv:1205.3009
[47] Zakerian F and Berahman M 2016 Optical properties of defected silicene: the many-body approach Opt. Quantum Electron. 48 370
[48] Mohan B, Kumar A and Ahiwulavia P K 2014 Electronic and optical properties of silicene under uni-axial and bi-axial mechanical strains: a first principle study Physica E 61 40–7
[49] Das R, Chowdhury S, Majumdar A and Jana D 2015 Optical properties of P and Al doped silicene: a first principles study RSC Adv. 5 41–50
[50] Nath P, Sanyal D and Jana D 2013 2015 Optical properties of transition metal atom adsorbed graphene: a density functional theoretical calculation Physica E 69 306–15
[51] Feng Y, Ji W-X, Huang B-J, Chen X-L, Li F, Li P, Zhang C-W and Wang P-J 2015 The magnetic and optical properties of 3d transition metal doped SnO2 nanosheets RSC Adv. 5 24306–12
[52] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas Phys. Rev. 136 B864
[53] Perdew J, Burke K and Ernzerhof M 1998 Perdew, Burke, and ernzherof reply Phys. Rev. Lett. 80 891
[54] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA + U method J. Phys. Condens. Matter 9 767
[55] Hu Z and Metiu H 2011 Choice of U for DFT + U calculations for titanium oxides The Journal of Physical Chemistry C 115 5841–5
[56] Jain A, Hautier G, Ong S F, Moore C J, Fischer C C, Persson K A and Ceder G 2011 Formation enthalpies by mixing GGA and GGA + U calculations Phys. Chem. Chem. Phys. 13 45115
[57] Harto K, Manson N, Ahmad Z A and Mohamad A A 2016 Electronic properties of ZnO nanoparticles synthesized by Sol–gel method: a LDA + U calculation and experimental study Procedia Chemistry 19 125–32
[58] Monkhorst H J and Pack D J 1976 Special points for Brillouin-zone integrations Physical Review B 13 5188
[59] Sivek J, Sahin H, Partoens B and Peeters F M 2013 Adsorption and absorption of boron, nitrogen, aluminum, and phosphorus on silicene: stability and electronic and phonon properties Physical Review B 87 085444
[60] Clementi E, Raimondi D L and Reinhardt W P 1967 Atomic screening constants from SCF functions: II. Atoms in 37 to 86 electrons J. Chem. Phys. 47 1300–7
[61] Kalam T P 2014 Tuning the structural, electronic, and magnetic properties of germanium by the adsorption of 3d transition metal atoms The Journal of Physical Chemistry C 118 25200–8
[62] Xu B and Yi L 2008 Optical properties of the intermetallic compound Fe3TiSn J. Phys. D: Appl. Phys. 41 095404
[63] Mahan G D 2013 Many-Particle Physics (Springer Science & Business Media)
[64] Hecht E 2003 Optics Fourth Edition, Hardcover 4th edition (Addison-Wesley) (August 12, 2001) 680
[65] Naem M, Hasanain S K and Mumtaz A 2007 Electrical transport and optical studies of ferromagnetic cobalt doped ZnO nanoparticles exhibiting a metal–insulator transition J. Phys. Condens. Matter 20 025210
[66] Guo G Y, Chu K C, Wang D S and Duan C-G 2004 Linear and nonlinear optical properties of carbon nanotubes from first-principles calculations Physical Review B 69 205416
[67] Rani P, Dubey G S and Jindal V K 2014 DFT study of optical properties of pure and doped graphene Physica E 62 28–35
[68] Saha S, Sinha T P and Mookerjee A 2000 Electronic structure, chemical bonding, and optical properties of paraelectric BaTiO3 Applied Physics Reviews 7 085444
[69] Schulz L G and Tanganelli R F 1954 Optical constants of silver, gold, copper, and aluminum: II. The Index of Refraction n JOSA 44 362–8
[70] Goudarzi M, Parhizgar S S and Behesthian J 2019 Electronic and optical properties of vacancy and B, N, O and F doped graphene: DFT study Opto-Electron. Rev. 27 130–6
[71] Wei W, Dai Y, Huang B and Jacob T 2013 Many-body effects in silicene, silicene, germanene and germanene RSC Adv. 3 15879–94