Electron-photon interaction in monolayer antimonene

R Layton¹, A B Cahaya¹, A R T Nugraha² and M A Majidi¹

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok, Indonesia
²Research Center for Physics, Indonesian Institute of Sciences (LIPI), Tangerang Selatan, Indonesia

E-mail: aziz.majidi@sci.ui.ac.id

Abstract. Recent experimental and theoretical studies on two-dimensional (2D) antimonene revealed that this material is expected to be a potential semiconductor for optoelectronics applications. Using first-principle density functional theory (DFT) calculations, we verify that the so-called α-phase monolayer antimonene is a direct-gap semiconductor. Its optoelectronic properties are then described in terms of electron-photon interaction. Within the dipole approximation, the dipole vectors and the oscillator strength of the electron-photon interaction in monolayer antimonene were calculated. It has been found that the optical transition at a certain electronic wave vector can be analyzed according to the value and direction of the dipole vectors. This work will be important to further obtain the optical absorption spectra of monolayer antimonene for various light polarization.

1. Introduction

In this modern era, it cannot be denied that semiconducting materials support the rapid development of advanced technology. The use of semiconductors is widespread, especially in optoelectronics. The demands for flexible and tiny devices also have been significantly increasing. This condition triggers a lot of research on two-dimensional (2D) materials as the candidate for the next generation nano-optoelectronics.

Some monolayer materials in group IV of the periodic table such as graphene, silicene, and germanene showed extraordinary properties, e.g. direct bandgap and high carrier mobility [1]. Such properties can be exploited and applied for optoelectronic devices, although it is harder for graphene due to its zero bandgap [2]. Unlike group-IV materials that exhibit semimetal characteristics, group-V monolayer materials are expected to be semiconductors, thus they are potentially applied in optoelectronic devices.

A pioneering study on group-V monolayer materials was about phosphorene, which is also called the black phosphorus [3, 4], having a puckered lattice structure with many attractive properties such as a direct bandgap [3] and high carrier mobility [5, 6], thus making it a promising material for optoelectronics [7]. Since then, further studies have been devoted to exploring other monolayer group-V materials such as arsenene [8, 9], antimonene [9, 10, 11, 12], and bismuthene [12, 13]. However, to our knowledge, a fundamental study on the mechanism behind the possible optical transitions that determine the optical properties of these materials is still lacking.
In this paper, we focus on monolayer $\alpha$-Sb with puckered structure [9, 10] and perform the first-principle density functional theory (DFT) calculations to obtain and investigate the band structure. Then the dipole vectors which describe the interaction between electrons and photons in the material were calculated. In the rest of this paper, the computational details to obtain the band structure and the dipole vectors of monolayer $\alpha$-Sb will be shown, and discuss the calculated results. Finally, the conclusion and our perspectives for further development of this calculation.

2. Method

In order to obtain the band structure, we need to perform the first-principles calculation with density functional theory (DFT). We use the Quantum ESPRESSO package [14, 15] to calculate the band structure and, combined with an independent computer program, we calculate the dipole vector of electron-photon interaction. In figure 1, we show the unit cell of the $\alpha$-phase of monolayer antimonene ($\alpha$-Sb) that belongs to the orthorhombic Bravais lattice with puckered structure, with the lattice constants of 4.36 Å and 4.74 Å in two dimensions, and the puckered height of 2.93 Å. We set the $z$-axis large enough to 20 Å to prevent the interaction between atomic layers. In this work, we use projected-augmented-wave (PAW)-type pseudopotential with the kinetic energy cutoff of 70 Ry and 560 Ry for wavefunction and charge densities, respectively, and the energy convergence criterion was set to $10^{-6}$ a.u. We also take spin-orbit coupling (SOC) into account in the calculation and adopt Perdew-Burke-Ernzerhof (PBE) functional [16, 17]. We use a Brillouin zone grid of $15 \times 15 \times 1$ $k$-points for geometry optimization and self-consistent electronic structure calculations within the Monkhorst-Pack scheme.

Before proceeding to the band structure calculation, the atomic position is initially relaxed to get the optimized geometry structure. The ground-state density is then calculated using the self-consistent field (SCF) and non-self-consistent field (NSCF) approaches. For the NSCF calculation, we use a utility from Wannier90 packages to obtain a coarse grid of $k$-points as the input, so that the full Brillouin Zone can be obtained instead of the reduced Brillouin zone from the Monkhorst-Pack scheme mentioned before. Next, we perform the post-processing to generate the band structure data from the NSCF calculation.

Having information about the electronic structure, we can calculate the dipole vector. The polarized light applied to the material induces interaction between electron and photon. The interaction gives a small perturbation that can be written in the Hamiltonian as

$$H = H_0 + H_{\text{opt}} = \left[ \frac{p^2}{2m} + U(r) \right] + \left[ i\hbar e \mathbf{A} \cdot \nabla \right],$$

(1)

where $H_0$ is the Hamiltonian of one electron, $H_{\text{opt}}$ is the perturbed Hamiltonian, $e$ is the fundamental electron charge, $p$ is the momentum, $m$ is the electron mass, $U$ is the potential, $i$ is the imaginary number, $\hbar$ is the reduced Planck constant, $\mathbf{A}$ is the vector potential, and $\nabla$ is the nabla operator. We can define the dipole vector using part of the perturbed Hamiltonian as

$$\mathbf{D}(k_f, k_i) = \langle \Psi(k_f, \mathbf{r}) | \nabla | \Psi(k_i, \mathbf{r}) \rangle,$$

(2)

where $\Psi$ is the electron wave function and $k_i$ ($k_f$) is the initial (final) electron wave vector. To calculate the dipole vector numerically according to equation (2), we use a computer program from Tatsumi et al. [18,19] and modify it to be easily integrated with Quantum ESPRESSO. In this program, we need the wave function data in XML format that can also be obtained from the Quantum ESPRESSO post-processing step.

We have described the method and how to calculate the band structure and the dipole vector. In the next section, we will show the results and explain the meaning of the dipole vector for describing the electron-photon interaction in $\alpha$-Sb.
3. Results and Discussion

Figure 2 displays the band structure of the 2D monolayer $\alpha$-Sb and the density of state (DOS) obtained from the first-principle DFT calculation. We find that $\alpha$-Sb is a direct-gap semiconductor, consistent with previous studies [9, 10, 12]. The other details of the band structure obtained from our calculation also quite agree with other theoretical calculations with the same geometrical structure of $\alpha$-Sb [9, 10, 12].

It can be seen that the band structure of $\alpha$-Sb does not have an overlap between valence and conduction bands, with the minimum conduction band (CBM) at the $\Gamma$ point and the maximum valence band (VBM) at a $k$ point along the Y-$\Gamma$ path, and there are at least two direct bandgaps. The first (second) one is located at a $k$ point along the Y-$\Gamma$ (S-Y) path with an energy gap of about 0.18 eV (0.89 eV). Compared with previous studies [9, 12], there is a slight discrepancy for the direct bandgaps at the Y-$\Gamma$ path that could be caused by the different considerations of exchange-correlation energy functional. We used the PBE functional while Ref. [9,12] used Heyd-Scuseria-Ernzerhof (HSE06) functional, which is the mixing of PBE and Hartree-Fock correction. For semiconducting materials, it is often said that the HSE06 functional could give a better bandgap than the PBE functional when compared with the experiments [21, 22]. However, using the HSE06 functional is computationally more expensive than the PBE functional, while the shapes of the wave functions obtained from the two different functionals are essentially not changed. Therefore, for our purpose of calculating the dipole vectors, where the shape of the wave function plays an important role, using the PBE functional is acceptable.

Using equation (2), we calculate the dipole vector as shown in figure 3. The blue (red) arrows represent the real (imaginary) part of the dipole vector. In figure 3, we can see that there are imaginary parts that are perpendicular to the real parts at the horizontal and vertical lines from the center. There is also one imaginary arrow at the top edge and at the bottom edge, although it is parallel with the real part.

If we look at the Brillouin zone in figure 1(b), we could imagine it to be comparable with the Brillouin zone for plotting the dipole vectors in figure 3, with the center as the $\Gamma$ point, left (right) edge from the $\Gamma$ point as the X point, top (bottom) edge from the $\Gamma$ point as the Y point, and the left (right) edge from the Y point as the S point. So, we could say that the imaginary parts that are perpendicular to the real parts are located at the $k$ points along the $\Gamma$-X and $\Gamma$-Y paths. The $\Gamma$-Y path is the location for the direct bandgap. However, in the S-Y direction where the second smallest direct gap exists, there is an imaginary part that is parallel with the real part of the dipole vector. Furthermore, when we look at the $\Gamma$-X path, there is another direct bandgap although the gap is bigger than the other two direct gaps mentioned earlier.
Figure 2. (a) Band Structure of $\alpha$-Sb. (b) Density of states of $\alpha$-Sb.

Figure 3. Dipole vector of $\alpha$-Sb.

For the rest of the $k$ points in the Brillouin zone of $\alpha$-Sb, the components of the dipole vectors are all real with no imaginary part. The disappearance of the imaginary part of the dipole vector, in this case, is the same as that in monolayer graphene. However, graphene is a semimetal that has no bandgap because it possesses the inversion symmetry [23, 24, 25]. As a result, the optical transition by, for example, circularly polarized light at two distinct $k$ points with the inversion symmetry, is not allowed because the dot product of the dipole vectors with the polarization vector of the circularly polarized light is zero [23, 24]. This is also the same case for the parallel one since the dot product is also zero.

On the other hand, at the $\Gamma$-X and the $\Gamma$-Y bandgap point there exist imaginary parts. Thus, we expect that the optical transition by circularly polarized light at two distinct $k$ points are allowed because the inner product of the dipole vectors with the polarization vector of the circularly polarized light is nonzero [18, 19, 23, 24], hence beneficial for valleytronics [26, 27], i.e. optoelectronics using the optical transitions at parabolic valleys that constitute the bandgaps. The calculated results for such a hypothesis will be presented elsewhere. It should be noted that, although we only mentioned the circular polarization, the results of dipole vectors are general for any other light polarization (e.g. linear polarization with any angle) because equation (2) is independent of the polarization vector.

In addition to the dipole vector, we calculate the oscillator strength [28, 29] of the optical transition by the absolute square of the dipole vector. This quantity shows how strong the light absorption can occur for a given optical transition. The black color refers to the $k$ points where the optical transitions...
are completely forbidden [29]. We see some bright spots corresponding to the probable optical transitions, which are scattered at certain $k$ points on the Brillouin zone, making a unique pattern. If we compare the plot of oscillator strength with the dipole vector, we can see that the value of oscillator strength is nonzero mostly at the $k$ points where the real parts of the dipole vectors tend to rotate. The oscillator strength is also enhanced when the imaginary parts appear near the center of the Brillouin zone although exactly at the center itself the oscillator strength is zero.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{Oscillator strength of $\alpha$-Sb. The black color corresponds to the completely forbidden transition, while the brighter colors indicate the possible optical transitions with some probabilities. Note that the largest value of oscillator strength in this plot is normalized to unity.}
\end{figure}

4. Conclusions
We have shown the electronic structure of monolayer $\alpha$-Sb by using the first principle calculations and found it to be a direct-gap semiconductor with possible exploitation for valleytronics, especially at the $\Gamma$-X and $\Gamma$-Y bandgap points. The dipole vectors with the real parts parallel to the imaginary parts are located at the S-Y point, while those with the real parts perpendicular to the imaginary parts are located at the $\Gamma$-X and $\Gamma$-Y points. The dot product of the dipole vectors with the polarization vector of the circularly polarized light for the parallel case (S-Y point) is zero, while for the perpendicular case is nonzero ($\Gamma$-X and $\Gamma$-Y points), thus the optical transitions for monolayer $\alpha$-Sb are allowed mostly around the $\Gamma$-X and $\Gamma$-Y points. Further works are suggested to clarify the optical selection rule for various light polarization in the monolayer $\alpha$-Sb, for example, by calculating the optical matrix elements explicitly under the different light polarization.

Acknowledgments
We acknowledge financial support from the Ministry of Research and Technology of the Republic of Indonesia through PDUPT Research Grant No. NKB-217/UN2.RST/HKP.05.00/2020. A.R.T.N. acknowledges Mahameru Grid LIPI for their high-performance computing facilities.

References
[1] Roome N J and Carey J D 2014 Beyond Graphene: Stable Elemental Monolayers of Silicene and Germanene *ACS Applied Materials & Interfaces* **6**(10) 7743-7750
[2] Partoens B and Peeters F M 2006 From Graphene to Graphite: Electronic Structure around K point *Physical Review B* **74**(075404)
[3] Takao Y, Asahina H and Morita A 1981 Electronic Structure of Black Phosphorus in Tight Binding Approach J. Phys. Soc. Jpn. **50** 3362-3369

[4] Li L, Yu Y, Ye G J, Ge Q, Ou X, Wu H, Feng D, Chen X H and Zhang Y 2014 Black Phosphorus Field-Effect Transistors Nature Nanotechnology **9**(5) 372-377

[5] Liu H, Neal A T, Zhu Z, Luo Z, Xu X, Tomanek D and Ye P D Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility ACS Nano **8** 4033-4041

[6] Qiao J, Kong Z, Hu Z, Yang F and Ji Wei 2014 High-Mobility Transport Anisotropy and Linear Dichroism in Few-Layer Black Phosphorus Nature Communications **5**(4475)

[7] Xia F, Wang H, and Jia Y, 2014 Rediscovering Black Phosphorus as an Anisotropic Layered Material for Optoelectronics and Electronics Nature Communications **5**(4458)

[8] Kamal C and Ezawa E 2015 Arsenene: Two Dimensional Buckled and Puckered Honeycomb Arsenic Systems Physical Review B: Condens. Matter Phys. **91**(085423)

[9] Xu Y, Peng B, Zhang H, Shao H, Zhang R, Lu H, Zhang D W and Zhu H 2016 First Principle Calculation of Photonic, Electronic and Optical Properties of Monolayer Arsenene and Antimonene Allotropes Ann. Phys. **529**(1600152)

[10] Wang G, Pandey R and Karn S P 2015 Atomically Thin Group-V Elemental Films: Theoretical Investigations of Antimonene Allotropes ACS Appl. Mater. Interface. **7** 11490-11496

[11] Ji J, Song X, Liu J, Yan Z, Huo C, Zhang S, Su M, Liao L, Wang W, Ni Z, Hao Y and Zeng H. 2016 Two-Dimensional Antimonene Single Crystals Grown by Van der Walls Epitaxy. Nature Communications **7**(13352)

[12] Kecik D, Ozcelik V O, Durgun E and Ciraci S 2019 Structure Dependent Optoelectronic Properties of Monolayer Antimonene, Bismuthene, and their Binary Compound J. Chem. Phys. **21**(7907)

[13] Akturk E, Akturk O U and Ciraci S 2016 Single Layer and Bilayer Bismuthene: Stability at High Temperature and Mechanical and Electronic Properties Physical Review B **94**(014115)

[14] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys. Condens. Matter. **21**(395502)

[15] Giannozzi P et al 2017 Advanced capabilities for materials modelling with Quantum ESPRESSO J. Phys. Condens. Matter. **29**(465901)

[16] Perdew J P, Burke K, Ernzerhof M 1996 Generalized Gradient Approximation Made Simple. Physical Review Letters **77** 3865-3868

[17] Ernzerhof M and Scuseria G E 1999 Assessment of the Perdew–Burke–Ernzerhof Exchange-Correlation Functional J. Chem. Phys. **110**(5029)

[18] Tatsumi, Y, Ghalamkari K and Saito R 2016 Laser Energy Dependence of Valley Polarization in Transition-Metal Dichalcogenides Physical Review B **94**(235408)

[19] Tatsumi Y 2017 Polarization Dependence of Optical Absorption and Raman Spectra for Atomic Layer Materials Ph.D.’s Thesis

[20] Kokalj A, Mol J 1999 Graphics Modelling **17** 176-179

[21] Heyd J, Scuseria G E and Ernzerhof M 2003 Hybrid Functionals Based on Screened Coulomb Potential J. Chem. Phys. **118** 8207-8215

[22] Garza A J and Scuseria G E 2016 Predicting Band Gaps with Hybrid Density Functional J. Phys. Chem. Lett. **7**(20) 4165-4170

[23] GhalamkariK, Tatsumi Y and Saito R 2018 Energy Band Gap Dependences of Valley Polarization of Hexagonal Lattice J. Phys. Soc. Jpn. **87**(024710)

[24] Ghalamkari K 2017 Valley polarization in optical absorption of atomic layer materials. Master’s Thesis

[25] Dini K., Iorsh I V, Bogdanov A and Shelykh I A 2018 Optical valleytronics in gapped grapheme ArXiv 1807 01228

[26] Ang Y S, Yang S, Zhang C, Ma Z and Ang L K 2017 Valleytronics in merging Dirac cones: All-electric-controlled valley filter, valve, and universal reversible logic gate Physical
Review B 96(24)

[27] Zang Y, Ma Y, Peng R, Wang H, Huang B and Dai Y 2020 Large valley-polarized state in single-layer NbX$_2$ (X = S, Se): Theoretical prediction Nano Res. 12(1)

[28] Grüneis A, Saito R, Samsonidze G, Kimura T, Pimenta M A, Jorio A, Souza Filho, A.G., Dresselhaus, G., and Dresselhaus, M.S. 2003. Inhomogeneous optical absorption around the K point in graphite and carbon nanotubes. Physical Review B. 67(165402).

[29] Chowdhury, M.T., Saito, R., and Dresselhaus, M.S. 2012. Polarization Dependence of X-Ray Absorption Spectra in Graphene. Physical Review B. 85(115410).