

Effects of Sodium and Chlorine Doping on Optical Properties of Germanene: Density Functional Theory Calculation

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Abstract. Germanene is a two-dimensional material which is derived from germanium elements and arranged in a honeycomb-like hexagonal. This study aims to determine the optical properties of pristine germanene and effect of doping Sodium (Na) and Chlorine (Cl) atom on germanene. These elements are chosen owing to their ability to create strong bonds with germanene and easily available in nature. This research uses Density Functional Theory approach to measure the effects of sodium and chlorine doping on germanene's optical properties. The results showed that pristine germanene had higher optical and energy than the doped with sodium and chlorine. Cl-doped germanene had similar graphical shape with pristine germanene

1. Introduction

Since the discovery of graphene, interest on two dimension materials are continuously increasing. Germanene and silicene attracted special interest due to their similarities with graphene[1]. Even, compared to graphene, germanene and silicene are more likely to be implemented in current silicon based semiconductor technology. Today, applications of germanene are not restricted as electronic materials anymore but become more widely such as gas sensors[2], [3] and photo-catalyst supports[4].

Band structure is one of features of electronic structure which has close relation with optical properties. Electronic structure, including band structure of pristine germanene have been intensively studied. Similar to graphene, pristine germanene has zero band gap[5]. This semimetalic property hinder germanene to be applied in semiconductor industry.

Controlable band gap is the key for an electronic material like germanene to widen its applications. There are several ways to engineering band gap, these include hydrogenation[6][7], halogenation[8], adsorption of gas [2], metal elements[9], alkali and alkali earth [10] and organic molecules[11], applying an external electrical field[12], [13] and applying uniaxial[14] and biaxial strain[12]. Band Structure of a material has close relation [15].

Comparison of optical properties of pristine graphene, silicene, and germanene have been investigated previously using density functional theory. Refractive index of germanene is relatively larger than that of graphene. While, reflectivity of germanene is lower than that of graphene [16], [17]. Eventhough electronic structure and optical properties of pristine germanene have been studied insensively, electronic structure and optical properties of doped germanene is still very rare investigated. Therefore, this work is aimed to study the effects of Na and Cl adatoms on the optical properties of germanene.

2. Methods

In this work, we focus on the optical properties of Na-doped germanene and Cl-doped germanene using the *ab initio* pseudopotential density functional method. Pseudopotentials were expanded within a plane



wave basis set with an energy cutoff of 40 eV. Integrations in Brillouin zone were performed using special k points generated with a $12 \times 12 \times 1$ Monkhorst–Pack mesh parameters grid. Exchange and correlation effects were described by Perdew–Burke–Eruzerhof in generalized gradient approximation. Calculations of optical properties are based on norm-conserving pseudopotentials available in ABINIT. Na/Cl adatoms is placed on germanene with three possible sites i.e : 1) Bridge site (B-site), between two Ge/As atoms 2) Hollow site (H-site), in the centre of pentagon shape of silicene, and 3) Top site (T-site), above one Ge/As atom.

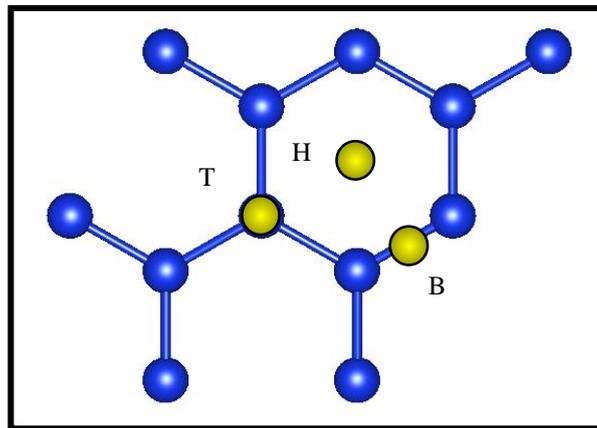


Figure 1. Three possible positions of Na/Cl adatom on germanene structure: Bridge (B), Hollow (H), and Top (T).

3. Result and discussion

In this calculations, the most favorable sites was determined by calculating the binding energy for adsorption. The system with the lowest binding energy is the most favorable one.

$$E_{\text{binding}} = E_{\text{system}} - (E_{\text{pristine germanene}} + E_{\text{adatom}})$$

Based on binding energy calculation, Na-adatom at B-site is the most favorable position. T-site is the most favorable position of Cl adatom in germanene. Therefore, next we focus on optical properties of germanene with Na-adatom in B-site and with Cl-adatom in T-site.

In order to observe the effect of Na adatom on the optical properties of germanene, here we compare optical properties of pristine germanene and germanene with Na-adatom in B-site. Figure 1, Figure 2, and Figure 3 show density of states and band structure of pristine germanene, Na-doped germanene, Cl-doped germanene respectively.

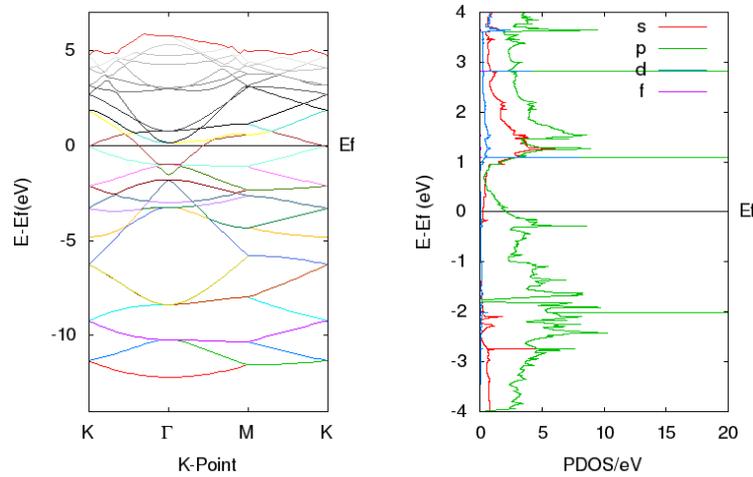


Figure 2. Band Structure and Density of State of pristine germanene

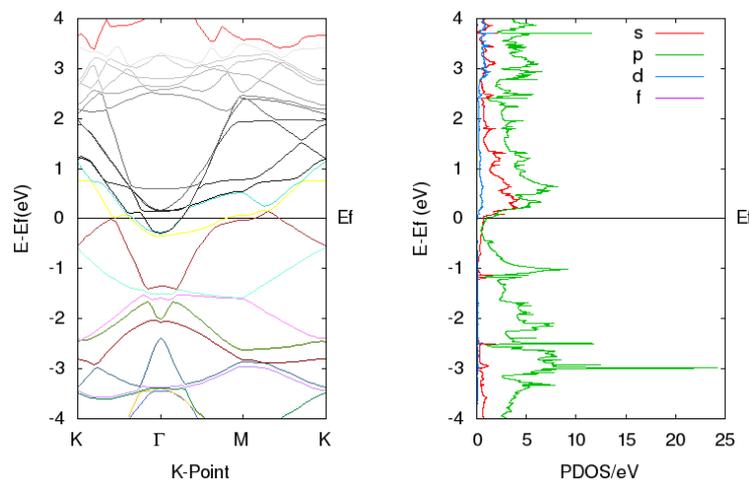


Figure 3. Band Structure and Density of State of Na-doped germanene

Eventhough band structure of pristine germanene, Na-doped germanene, and Cl-doped germanene have different shape, all of them are conducting materials due to overlap of their energy levels near fermi energy. The Density of states spectra of the three systems also have similarities in term of orbital contribution. For all three system, p orbitals are dominant.

One of the most important optical constants of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave, through a relationship called *dispersion*. In addition to dispersion, an electromagnetic wave propagating through a lossy medium experiences attenuation, which means it loses its energy, due to various loss mechanisms such as the generation of phonons (lattice waves), photogeneration, free carrier absorption, scattering, In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index, n , and the imaginary part is called the *extinction coefficient*, K . The refractive index of an optical or dielectric medium, n , is the ratio of the velocity of light c in vacuum to its velocity v in the medium; $n = c/v$.

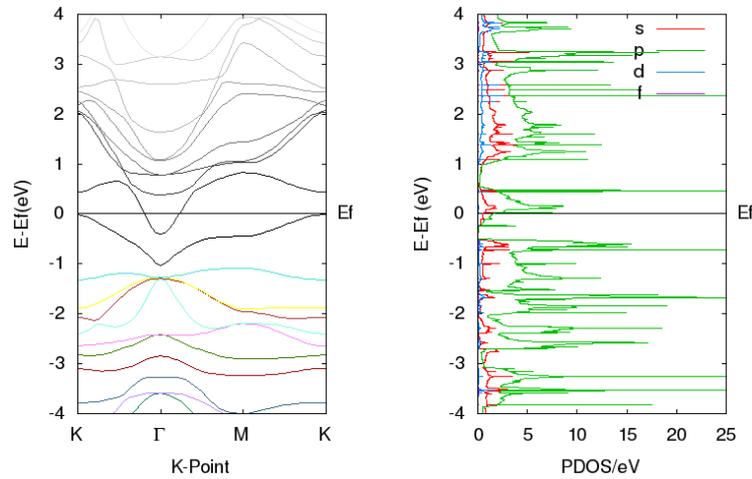


Figure 4. Band Structure and Desity of State of Cl-doped germanene

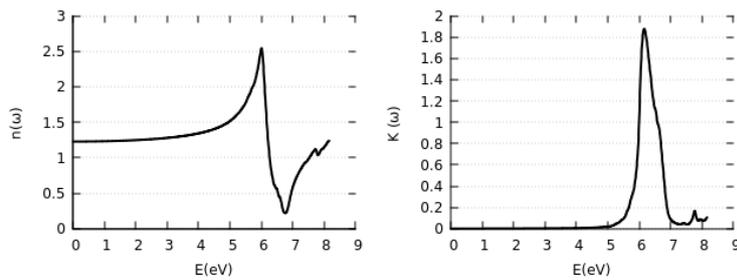


Figure 5. Real and imaginary part of refractive index of pristine germanene

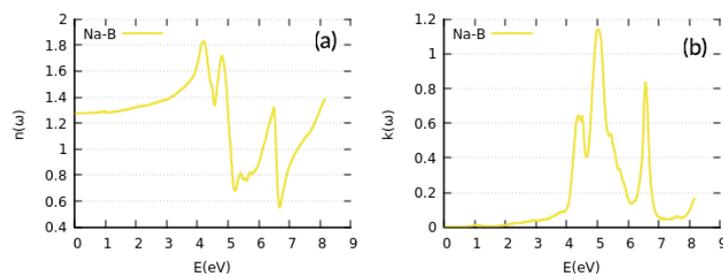


Figure 6 Real and imaginary part of refractive index of germanene with Na-atom

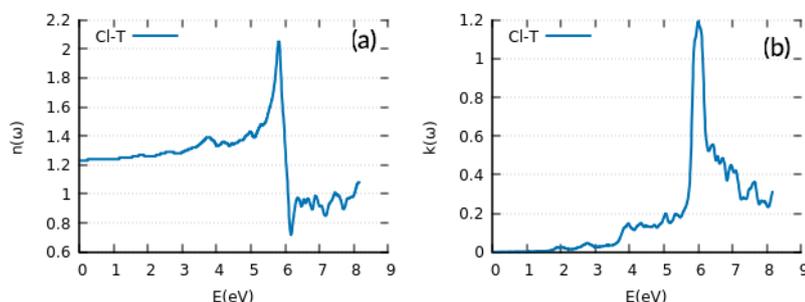


Figure 7. Real and imaginary part of refractive index of germanene with Cl-adatom

By adding Na adatom (Figure 6), both real part and imaginary part of refractive index decrease. The decrease of real part of refractive index indicates normal dispersion, while decrease of imaginary part of refractive index which represents extinction coefficient, indicates decrease of absorption. Peaks of real part and imaginary are observed at lower energy compared to pristine germanene. It indicates that Na adatom induces a new state such that it requires lower energy to absorb. While, Cl adatom (Figure 7) hardly does not change refractive index of germanene.

4. Conclusion

The all three systems i.e pristine germanene, Na-doped germanene, and Cl-doped have different shapes but are the same in terms of having no band gap. Their Density of States shows that for all systems, p-orbitals are dominant. Na adatom shifts refractive index, while Cl adatom seems to have no effect on refractive index. There is a split of reflection and absorption index of Na-doped germanene.

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