Effect of As and Ga doping on the electronic structure and photoelectric properties of cubic Ca$_2$Ge

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Abstract

The electronic structure and optical properties of intrinsic and doped Ca$_2$Ge have been calculated by using the first-principles calculation method based on density functional theory. The doping content of As were 2.08% and 1.04%, respectively, and the doping concentrations of Ga were same with As. The band gap of intrinsic Ca$_2$Ge is 0.556 eV, and that decreased to 0.526 eV and 0.548 eV with respect of As doping amount of 2.08% and 1.04%. Meanwhile, the band gap is 0.25 eV when the doping amount of Ga was 1.04%, and the band gap is 0.23 eV for Ga was 2.08%. The band structures results shown that the Fermi levels of As-doped (2.08% and 1.04%) are moved into the bottom of conduction band. The electronic density of states shown that the electronic configurations at the top valence band and bottom conduction band were changed as As and Ga doped. The dielectric function results shown that the maximum number of 52.7 and 97.53 were respectively obtained at 0 eV for the 2.08% Ga-doped and the 1.04% As-doped. Moreover, the phenomenon of strong metallic reflection has been found in the energy range of 6.0 ~ 8.5 eV, and the metal reflection characteristics of intrinsic Ca$_2$Ge was greater than the doped Ca$_2$Ge. Analyzing the energy-loss function, it indicating that the energy region of appearing energy loss can be altered by doping As and Ga or changing their doped concentration.

1. Introduction

Ca$_2$Ge compound is a novel semiconductor material, which has high carries mobility, low dielectric constant, stable mechanical structure and thermodynamic properties [1–5]. Previous research results revealed that Ca$_2$Ge is a low-power and high-performance material, and used in the application field of photoelectric and thermoelectric. Meanwhile, there is no pollution in the process of producing and using. Therefore, Ca$_2$Ge compound is a potential semiconductor material and has a very important application prospect in future.

Ca$_2$Ge has been developed and proposed as a direct band gap material through the phase diagram of the Ca-Ge compounds system by Palenzona [1], in 2002. Research results indicated that liquid Ca$_2$Ge begins to solidify into crystals at 1310°C, and there are five compounds in Ca-Ge alloy, it includes CaGe, Ca$_2$Ge, CaGe$_2$, Ca$_3$Ge$_3$ and Ca$_4$Ge$_6$ compounds. However, only the Ca$_2$Ge compound has stable mechanical structure. Since then, many researchers have been attracted by the electronic structures and optical properties of Ca$_2$Ge. In 2003, Migas et al systematically studied the electric band structure and optical properties via the first-principles pseudo-potential plane wave method [2], the results discovered that the cubic Ca$_2$Ge compound is a direct band gap semiconductor with 0.6 eV at X point in Brillouin zone, and the crystal constant is 0.7197 nm. In addition, their studies also indicated the cubic Ca$_2$Ge has a great anti-radiation ability, and the optical properties were determined by the electron transformation between Ca and Ge atoms. In 2010, Yang et al have taken the first-principles pseudo-potential plane wave method to investigate the band structure, electric properties and formation heats to the Ca-X(X = Si, Ge, Sn, Pb) compounds [3]. In 2015, Tani et al have explored the geometric...
configuration, phonon spectrum and lattice dynamics of Ca$_2$Ge [6], their research results shown that the Ca$_2$Ge compound has a good development trend in the field of low energy consumption devices compared to the Ca$_2$Si compound, this was because it had higher photon frequencies when device was located at low voltage.

In the early stage, we have studied the electronic structure and structural stability of cubic Ca$_2$Ge under tensile and compressive stress. The results shown that the cubic Ca$_2$Ge has a good stable structure, and the band gap is decreased linearly with the stress increasing. In this paper, on the basis of our previous research, we have calculated the electronic structure and photoelectric properties of cubic Ca$_2$Ge, and studied the impact of As-doped and Ga-doped. This research will provide a theoretical basis for the preparation and industrial application of Ca$_2$Ge in future.

2. Calculated methods and model

2.1. The theoretical methods of optical properties

The energy was absorbed when the electron of top valence band value was greater than band gap, the electrons of valence band were transited to the conduction band and become conductive carriers. The absorption energy formula can be defined as the follow [7]:

$$\alpha(h\nu) = B(h\nu - E_g)^m$$

(1)

Where $\alpha$ is the energy absorption coefficient, $\nu$ is the frequency of absorbed energy, $B$ is the characteristic length and $E_g$ is the band gap value, respectively. There are two values can be defined to the parameter $m$, if it took 0.5 which has direct band gap, and took 2 has indirect band gap.

The change of dielectric constant and refractive index can be described as the reflection of the macroscopic optical response, the dielectric function and refractive index are as the follows [8].

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

(2)

$$N(\omega) = n(\omega) + ik(\omega)$$

(3)

Where $\varepsilon_1(\omega)$ is the real part of the dielectric function, and $\varepsilon_2(\omega)$ is the imaginary part. The expression (3) describes the complex refractive coefficient of optical properties, which is expressed by the refractive index and extinction coefficient. The relationship between dielectric function and refractive index are as the follows:

$$\varepsilon_1(\omega) = n^2 - k^2$$

(4)

$$\varepsilon_2(\omega) = 2nk$$

(5)

The dielectric function and refractive coefficient can be deduced by the Kramers-Kronig relation in the first Brillouin zone [9], the real part and imaginary part in the complex dielectric function are defined as the following expression (6) and (7) respectively.

$$\varepsilon_2(\omega) = \frac{4\pi^2}{m^2\omega^2\varepsilon_0} \sum_{\gamma,V} \int_{BZ} \frac{dk}{2\pi} \frac{1}{2} |e \cdot M_{CV}(K)|^2 \delta(E_C(k) - E_V(K) - \hbar\omega)$$

(6)

$$\varepsilon_1(\omega) = 1 + \frac{8\pi^2\varepsilon_0^2}{m^2\omega^2\varepsilon_0} \sum_{\gamma,V} \int_{BZ} \frac{dk}{2\pi} \frac{1}{2} |e \cdot M_{CV}(K)|^2 \frac{\hbar^2}{[E_C(k) - E_V(k)]^2 - \hbar^2\omega^2}$$

(7)

In expression (6) and (7), the $|e \cdot M_{CV}(K)|^2$ is the matrix element of momentum for the electrons of the top valence band and the bottom conduction band. In addition, the absorption coefficient, reflection spectrum and energy-loss function are deduced as the expression (8) and (10) respectively.

$$I(\omega) = \sqrt{2} \omega \sqrt{\varepsilon_1^2(\omega) - \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}^{1/2}$$

(8)

$$R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

(9)

$$L(\omega) = \frac{1}{\varepsilon(\omega)} \left[ \varepsilon_2^2(\omega) \right]$$

(10)

2.2. Calculated method and theoretical model

The Cambridge Serial Total Energy Package (CSTEP) is used for all calculations, which is based on the first-principles pseudo potential method wave method [10]. Firstly, the geometry structures of the intrinsic and the doped in cubic Ca$_2$Ge were optimized by the BFGS algorithm (proposed by Broyden, Fletcher, Gold-farb and Shannon) [11, 12]. Secondly, the band structure, electronic density of states and optical properties of the intrinsic and the doped Ca$_2$Ge were calculated respectively using the optimized structure. The cutoff energy for the plane wave basis was set to 380 eV for all calculations, the convergence precision in total energy of the
supercell with this cutoff was set to $5 \times 10^{-5}$ eV/atom. The tolerance in the self-consistent field (SCF) calculation was $5 \times 10^{-7}$ eV/atom. The exchange correlation energy was calculated within the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof form [13–16]. The convergence precision of maximum force in atoms was set as 0.5 eV nm$^{-1}$, and the convergence precision of maximum displacement in atoms was set as 0.0002 nm. The k-point sampling was $4 \times 5 \times 3$ according to the Monkhorst-Pack method in the Brillouin Zone (BZ).

The cubic Ca$_2$Ge bulk belongs to the space group of Fm$\overline{3}$m (No.225), the lattice constant $a$ is 0.7148 nm. The molecular structure diagrams of As-doped and Ga-doped in cubic Ca$_2$Ge are shown in the figure 1. For the cubic Ca$_2$Ge, there is only one equivalent position of Ge atom, which indicates that doping As or Ga atom is not affected by different position of Ge atom. The band structures, electron density of states and optical properties in intrinsic and doped structures were calculated, the doped structures include the 2.08% As-doped, 2.08% Ga-doped, 1.04% As-doped and 1.04% Ga-doped.

The formation energies were calculated by expression (11) [11, 12]. The $E_f$ represents the formation energy, the $E_{doping}$ is the total energy of Ca$_2$Ge after doping As or Ga atoms, the $E_{Ca_2Ge}$ is on behalf of the energy of intrinsic cubic Ca$_2$Ge, and the $E_{Ge}$ and $E_{As or Ga}$ are the chemical potential of Ge and doping atom (As or Ga), respectively. The $n_1$ is the number of atoms which being replaced, $n_2$ is the number of doped atoms. The calculated results of formation energy are shown in table 1. The calculated results indicated that the structures of the doped 2.08%, 1.04% As atoms and 1.04% Ga atoms are more stable.

$$E_f = E_{doping} - n_1 E_{Ge} - n_2 E_{As or Ga}$$ (11)

### 3. Calculation results and discussion

#### 3.1. The energy band structures and Electronic density of states

The band structures of intrinsic Ca$_2$Ge, doped 2.08% As/Ga and doped 1.04% As/Ga are shown in the figure 2. From figure 2 can be seen that the intrinsic and all doped Ca$_2$Ge are the direct band gap semiconductor, and obtained the minimum band gap value at $\Gamma$ point in the Brillouin Zone. For the intrinsic Ca$_2$Ge, the band gap if 0.556 eV is obtained which agrees well with Ref.1. For the doped 2.08% and 1.04% As atoms, the band gap values are 0.526 eV and 0.548 eV, respectively, and both of the Fermi planes are moved into the bottom of conduction band. In theoretically, Ca$_2$Ge has been transformed from semiconductor to conductor as As-doped. But the Fermi level was closed to the bottom of conduction band, therefore, there are few electrons in the conduction band at 0 K. As a result, the Ca$_2$Ge doped with 2.08% and 1.04% As atoms maintained the same semiconductor...
properties with the intrinsic Ca$_2$Ge. The band gap values are only 0.23 eV and 0.25 eV when the doping concentration were 2.08% and 1.04% Ga atoms, respectively.

The electronic density of states of the intrinsic and all doped Ca$_2$Ge have been calculated and the results are shown in figure 3. It can be seen that the electrons nearing the top valence band are mainly consisted of the Ge 3p to the intrinsic Ca$_2$Ge compound, and the conduction band composed of the Ca 3d. Moreover, there are quite a lot of the Ge 3s in the bottom of conduction band. When doped 2.08% and 1.04% As atoms, the biggest difference compared to the intrinsic Ca$_2$Ge is the s state of As atoms which offers a lot of electrons in the bottom conduction band. In the system of doped 2.08% and 1.04% Ga atoms, the top valence bands have been influenced greatly by the p state electrons of Ga atoms. In the figure 3, it clearly shows that there are d state electrons of Ca atoms in intrinsic and all doped Ca$_2$Ge compounds, this is because of the 4 s electrons of Ca atoms are moved to the 3d orbital when Ca$_2$Ge compounds were formed. Therefore, it made the electron configure that was transformed from $3s^23p^64s^2$ to $3s^23p^63d^14s^1$.

Figure 2. The band structure. (a) intrinsic Ca$_2$Ge, (b) 2.08% As-doped, (c) 2.08% Ga-doped, (d) 1.04% As-doped, (e) 1.04% Ga-doped.

Figure 3. Electronic density of states. (a) intrinsic Ca$_2$Ge, (b) 2.08% As-doped, (c) 2.08% Ga-doped, (d) 1.04% As-doped, (e) 1.04% Ga-doped.
3.2. The optical properties

3.2.1. The analysis of the dielectric function

The calculated dielectric function of intrinsic and doped Ca$_2$Ge are shown in figure 4. From figure 4, the real part of dielectric function of intrinsic, doped 2.08% As/Ga, and 1.04% As/Ga are 12.67, 12.42, 52.7, 25.86 and 36.9, respectively at 0 eV ($\varepsilon_1(0)$), and the $\varepsilon_1(0)$ have been secured the maximum value with the doped concentration 2.08% Ga atoms. In addition, it can be seen from figure 4b that the real part of the dielectric function has an obvious peak at 0 eV on the effect of Ga doped, this is due to the polarization intensity of the electronic structure system is increased by Ga doped. Analyzing the changes of dielectric function $\varepsilon_1$ with the energy increasing, the intrinsic and doping 2.08% As atoms obtained the maximum values of 37.89 and 32.53 at around 2 eV, doping 1.04% As and Ga atoms reached the maximum value of 97.53 and 51.02 respectively near the energy of 0.5 eV. And it was obtained the maximum value at 0 eV with the doped concentration of 2.08% Ga atoms.

The imaginary part of the dielectric function can be expressed as the phase difference between the turning-direction polarization in the structure system and the applied high-frequency electric field, the polarization results in various relaxation, which represents the loss degree of the material. The imaginary parts of the dielectric function are showed in figure 5, combining with the band structure and electronic density of states, it can be analyzed that there are a strong energy absorption phenomenon for the intrinsic Ca$_2$Ge at 0.9 eV, 2 eV, 2.4 eV, 3 eV, 3.2 eV, 3.6 eV and 4.2 eV, which make the electrons in the valence band transition to the conduction band, which corresponding to the peaks of the $\varepsilon_2$. For the doping 2.08% As and Ga atoms, the peak positions are basically the same as that in the intrinsic Ca$_2$Ge, but the peak positions of doping 1.04% As and Ga atoms were moved to the low energy area, and appeared stronger energy absorption peak value at 0.6 eV, 1.4 eV, 1.7 eV, 2.5 eV and 3 eV. Besides, the peak value of doping 1.04% As and Ga atoms are larger than others, and the doping 1.04% As atoms obtains the maximum value of 165 at 1.6 eV, indicates that the light absorption is the strongest for the doping 1.04% As and Ga atoms. In addition, since Ga doping belongs to the P-type parameter, Ga atoms provided electron holes on the impurity band of the electronic system, and these electron holes will accept electrons from near the top of the valence band, and produce recombination, they were dynamic. Nevertheless, there is still a strong absorption peak without energy absorption, the reason is attributed to the recombination.

Figure 4. The dielectric function $\varepsilon_1$ of the intrinsic and doped Ca$_2$Ge. (a) As-doped, (b) Ga-doped

Figure 5. The dielectric function $\varepsilon_2$ of the intrinsic and doped Ca$_2$Ge. (a) As-doped, (b) Ga-doped
probability which was increased with the number of electron holes increasing. This explains that the 2.08% Ga doping peak is higher than 1.04% Ga doping as well.

3.2.2. The analysis of the refractive index

The refractive index and extinction coefficient can be deduced by the expression (4) and (5). The change of the refractive indexes and extinction coefficients in the intrinsic and all doped Ca$_2$Ge are calculated and shown in figures 6 and 7, respectively. As shown in figure 6, the refractive indexes of the intrinsic, doped 2.08% As/Ga and doped 1.04% As/Ga are 3.56, 3.52, 7.56, 5.08 and 6.09 respectively at 0 eV point, and reached the maximum value of 5.56 in the effect of doped 2.08% Ga atoms. The doped 2.08% As atoms has the same variation trend with the intrinsic Ca$_2$Ge, which obtained the maximum peak value of 6.48 and 6.01 respectively at 2 eV, and the 1.04% doped As and Ga atoms obtained the respective maximum peak values of 10.56 and 7.57 at 0.5 eV. for the doping 2.08% Ga atoms, the refractive indexes of other energies are less than 0 eV point. In addition, we can also analyze the refractive index of doping 1.04% As and Ga atoms are more intense.

Form the figure 7, the main changes of the extinction coefficient in the intrinsic and all doping Ca$_2$Ge are in the range of 0.2 ~ 4.5 eV. The doping 2.08% As and Ga atoms have the same variation trend with the intrinsic Ca$_2$Ge, as well as the energy positions of peaks. Additionally, the peak values of intrinsic Ca$_2$Ge are larger than the doping 2.08% As and Ga atoms. For the doping 1.04% As and Ga atoms, the energy positions are moved to the low energy region, and the peak values larger than the intrinsic and 2.08% doping Ca$_2$Ge. According to the expression (4) and (5), the refractive index and extinction coefficient also presented the peak values at 0 eV on the effect of Ga doping in the figures 6b and 7b.

3.2.3. The analysis of the reflection spectrum

The relationship between reflection spectrum and refractive index can be described by the expression (9), the reflection spectrum of intrinsic and all doped Ca$_2$Ge are shown in figure 8. The intrinsic and all doped Ca$_2$Ge have presented stronger metal reflection characteristics in the energy range of 6.0 ~ 8.5 eV, the energy width of presenting metal reflection characteristics in intrinsic Ca$_2$Ge is greater than doped Ca$_2$Ge. When the energy is less than 3 eV, the doping 1.04% As and Ga atoms have stronger reflectivity.
3.2.4. The analysis of the absorption coefficient

The absorption coefficient can describe the attenuation of light intensity with the propagation distance increasing in crystal. The absorption coefficient of the intrinsic and all doping Ca$_2$Ge have been calculated by the expression (8), and the calculated results are shown in figure 9. When the energy is less than 0.5 eV, the absorption coefficient is dropped to zero, it indicates that photons are not absorbed in this energy range, and thus, the absorption coefficient increases and reaches the maximum value at around 6.09 eV. At the energy range of 6.2 ~ 7.5 eV, the absorption coefficients of intrinsic and doping 2.08% As atoms decrease to zero, corresponding to the metal reflection characteristics in figure 8.

3.2.5. The analysis of the energy-loss function

The energy-loss function is revealed the electrons energy dissipation in crystal, when electrons undergo inelastic scattering, and its relation to the plasma oscillation of crystals in low energy region. The energy-loss functions of intrinsic and all doping Ca$_2$Ge have been calculated by the expression (10) and the calculated results are shown in figure 10. Analyzing the energy-loss function, indicates that the intrinsic and doping 2.08% Ga atoms obtained the max value of 28.54 and 50.73 respectively at around 8.5 eV. Nearly 8.8 eV, the doping 2.08 Ga atoms occurred the second peak, and the doping 2.08% As atoms gets the largest peak value of 88.44. For the doping 1.04% As and Ga, got the max values of 42.01 and 43.27 at 9.3 eV, and the second peak values of 32.53 and 27.25 respectively at 9.9 eV. The results show that the energy region with the largest energy loss can be changed by doping As and Ga or changing their doping concentration.
4. Conclusions

The electronic structure and optical properties of intrinsic and doped Ca$_2$Ge were calculated by the GGA of the pseudo-potential plane wave method. The calculated band structures indicated that the intrinsic and all doped Ca$_2$Ge belonged to the direct band gap semiconductor at $\Gamma$ point, and the band gaps of the intrinsic, 2.08% doped As and Ga atoms, 1.04% doped As and Ga atoms were 0.556 eV, 0.526 eV, 0.23 eV, 0.548 eV and 0.25 eV, respectively. But the Fermi levels of the doped 2.08% and 1.04% As atoms were moved in the bottom of conduction band. The electrons nearing the top valence band were mainly consisted of the p state electrons of Ge atoms, and the conduction band composed by the d state electrons of Ca atoms. For the doping 2.08% and 1.04% of As atoms, the s state of As atoms offered a lot of electrons in the bottom conduction band. With doped 2.08% and 1.04% Ga atoms, the top valence band have been influenced greatly by the p state electrons of Ga atoms. The dielectric function results showed the doping 2.08% Ga atoms obtained a maximum value of 52.7 at 0 eV, the intrinsic and doping 2.08% As atoms got the maximum value of 37.89 and 32.53 at around 2 eV, doping 1.04% As and Ga atoms reached the maximum value of 97.53 and 51.02 respectively at about 0.5 eV, and obtained the maximum value at 0eV with the doping concentration of 2.08% Ga atoms. In addition, according to the diagrams of refractive index, extinction coefficient, reflectivity and absorption, the phenomenon of strong metallic reflection was found in the energy range of 6.0 $\sim$ 8.5 eV, and the energy width of presenting metal reflection characteristics in intrinsic Ca$_2$Ge was greater than doped Ca$_2$Ge. Analyzing the energy-loss function, indicated the energy region of appearing energy loss can be changed by doping As and Ga atoms or changing their doping concentration.

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Figure 10. The energy-loss function of the intrinsic and doped Ca$_2$Ge.
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