Electronic Structure and Optical Properties of Gaas$_{1-x}$p$_x$: A First-Principles Study

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Abstract

In this work, the effects of x-value on electrical and optical properties was studied for the two dimensional (2D)GaAs$_{1-x}$P$_x$structure by applying the density functional theory.We found that the gallium arsenide(GaAs) and gallium phosphide(GaP) monolayers are bound to each other, while the charge transfer between these two materialsleads to tuning the band gap value between 1.5 eV for GaAs to 2.24 eV for GaP. The density of state, band structure, and optical properties are investigated in this paper.

الخواص الكهربائيه والتركيبيه والبصريه للنظام GaAs$_{1-x}$P$_x$دراسه بأستخدام المبادئ الاولية

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الخلاصه

في هذا العمل تم دراسه تاثير قيمه x على الخواص الكهربائيهوالتركيبيهوالبصريهلانظمه$_{1}$GaAs P$_x$والثنائيه الابعاد باستخدام نظريه الدالهالوظيفيهللكثافه , حيث وجدنا ان النظامين GaAs وGaP الاحادي الطبقه يرتبطون بتجانس تام مع بعضهما البعض , وان انتقال الشحنه بين هاذين النظامين (GaP وGaAs) يقود الى ضبط فجوه الطاقه بين 1.5 eV الى 2.24 eV , وكذلك تم حساب بقيه الخواص الالكترونيهمثل كثافه الحاله و حزمه التركيب , والخواص البصريه لهذه الانظمه .

Introduction

Two-dimensional (2D) materials, such as graphene, transition metal dichalcogenide (TMD), and black phosphorene have intrigued tremendous studies over the past few years owing to their extraordinary electronic, mechanical and optical properties, promising for a wide range of applications [1-5]. Recently, the main research hotspot has transferred from mono-component systems to heterostructures which are made by stacking at least two types of 2D materials. By stacking of chemically different 2D materials, most of the novel phenomena such as high carrier mobility and visible light absorption can be achieved in such heterostructures [6-10]. GaP with a band-gap of 2.24 eV is one of the important wide band-gap semiconductors, being a potential material for optical and high-temperature electronic devices [11], GaP nanostructures attract scientist in the field of vision as a result of their sufficient satisfaction to the rapidly expanded commands for semiconductor devices.For the photo-voltaic cells by utilizing sustainable solar energy, GaP can be used both for

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photoelectrochemical water splitting as well as CO_2 reduction, along with its uses as a photocathode under reducing conditions [12-14]. In addition, GaAs is one of the important materials used in nano-electronic and optoelectronic devices. Due to its high carrier mobility, smalldielectric constance, high-temperature resistance, and directbandgap,GaAs is widely used in optoelectronic devices [15-17]. In the present work, we design a new 2D composed of GaP and GaAs monolayers and study its geometric, optical and electronic properties with first-principle calculations.

Computational method and details

    Electronic structure and optical calculations were performed using the firstprinciple calculations as implemented in the SIESTA(**S**panish **I**nitiative for **E**lectronic **S**imulations with **T**housands of **A**toms) Package [18]. The optimum geometries of the periodic system were obtained by relaxing the system until all forces on atoms were less than 0.04 eV/Å. Generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionalwas adopted to describe the exchange-correlation interaction developed for the calculations of surface systems. The SIESTA calculations employed a double-zeta plus polarization orbital basis set, norm-conserving pseudopotentials, and an energy cut-off of 200Rydergs.Optical calculations were carried out using 33x33x3 optical mesh and 0.2 eV optical broadening.

Results and discussion

1-*Structural Optimization*

    Figure-1 shows the structural optimization of $GaAs_{1-x}P_x$ system with varied X mol from 0 to 1.The system has 32 atoms in total,which is changing depending on X ratio, lattice constant, and bond length,as illustrated in Table-1.The lengths of the bonds of $GaAs_{1-x}P_x$ compounds are almost constant except for X=1 where it is shorter by 1.5 Å than X=0. The lattice constant *b* is decreased when P increases in the system from 28.16 to 26.68 Å, when comparedwith the small change for the lattice constant *c*.The reason is that we selected only two-units cell in the *z-direction* and four-units cell in *y-direction* and , therefore, the change appeared more clearly in the *y-direction.*
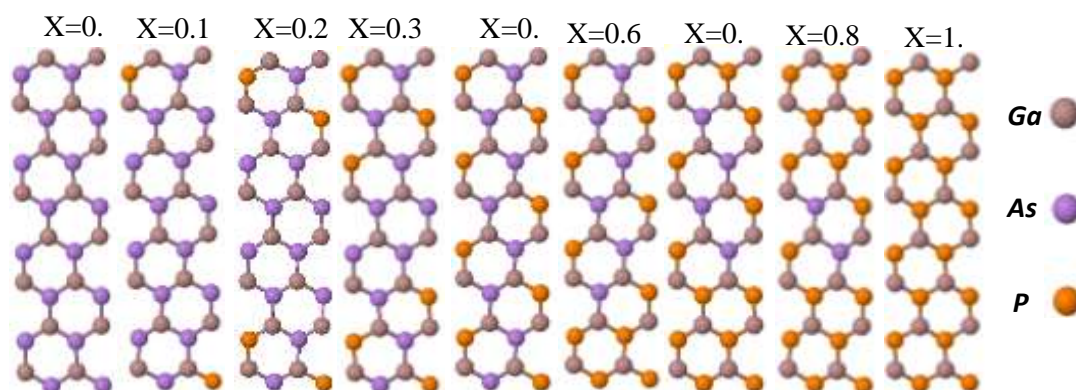

Figure 1-Optimized structures of periodic GaAs1-xPx system for X=0 to 1.

Table 1-The structural parameters of $GaAs_{1-x}P_x$system for the x mol.

	Unit cell (Å)		Ga-As bond (Å)	Ga-P bond (Å)	P-P bond (Å)	As-As bond (Å)	Band gap (eV)
	b	c					
X=0.0	28.16	8.12	2.42	--	--	4.06	1.56
X=0.125	28.14	8.04	2.41	2.33	--	4.03	1.60
X=0.25	28.00	8.07	2.42	2.32	--	4.01	1.61
X=0.375	27.87	8.06	2.42	2.32	--	4.01	1.65
X=0.5	27.77	8.08	2.42	2.32	--	4.01	1.62
X=0.625	27.67	8.04	2.42	2.31	3.97	4.01	1.63
X=0.75	27.60	8.00	2.42	2.32	3.95	4.01	1.68
X=0.875	27.41	7.92	2.42	2.32	3.94	4.01	1.94
X=1.0	26.68	7.70	--	2.28	3.85	--	2.24

2- *Electronic Band Structure*

The calculated band structure and partial density of state (PDOS) of theoptimized monolayer $GaAs_{1-x}P_x$ are shown in Figures-(2 and 3). The overall profile of the indirect bandgap (E_c-E_v) is in a good agreement with previous theoretical and experimental work [5], [19-21]. The electric energy gap increased with the increase of phosphorene *P* in the system which was1.56 eV for GaAs and 2.24 eV for GaP.The bandgapis strongly related to the bond length and lattice constant. In other words,the variation in the lattice parameters is related to the radius of the atoms, meaning that the bandgap is decreased with the increase in the lattice constant, which is clear in Table-1.The lattice constant *b* varied from 28.16 Å for GaAs to 26.68 Å for GaP. IThe partial density of the state is shown in Figures-(2 and 3). To gain further insight into electric properties,we analyzed the contribution of each atom state by decomposing the PDOS.The results of the partial density of states showed that the higher peak of states is observed to minimum conduction band and maximum valence band for Ga and As atoms, with small contribution of P for low x- value, while this ratio is then reversedwith the increase in x-value.
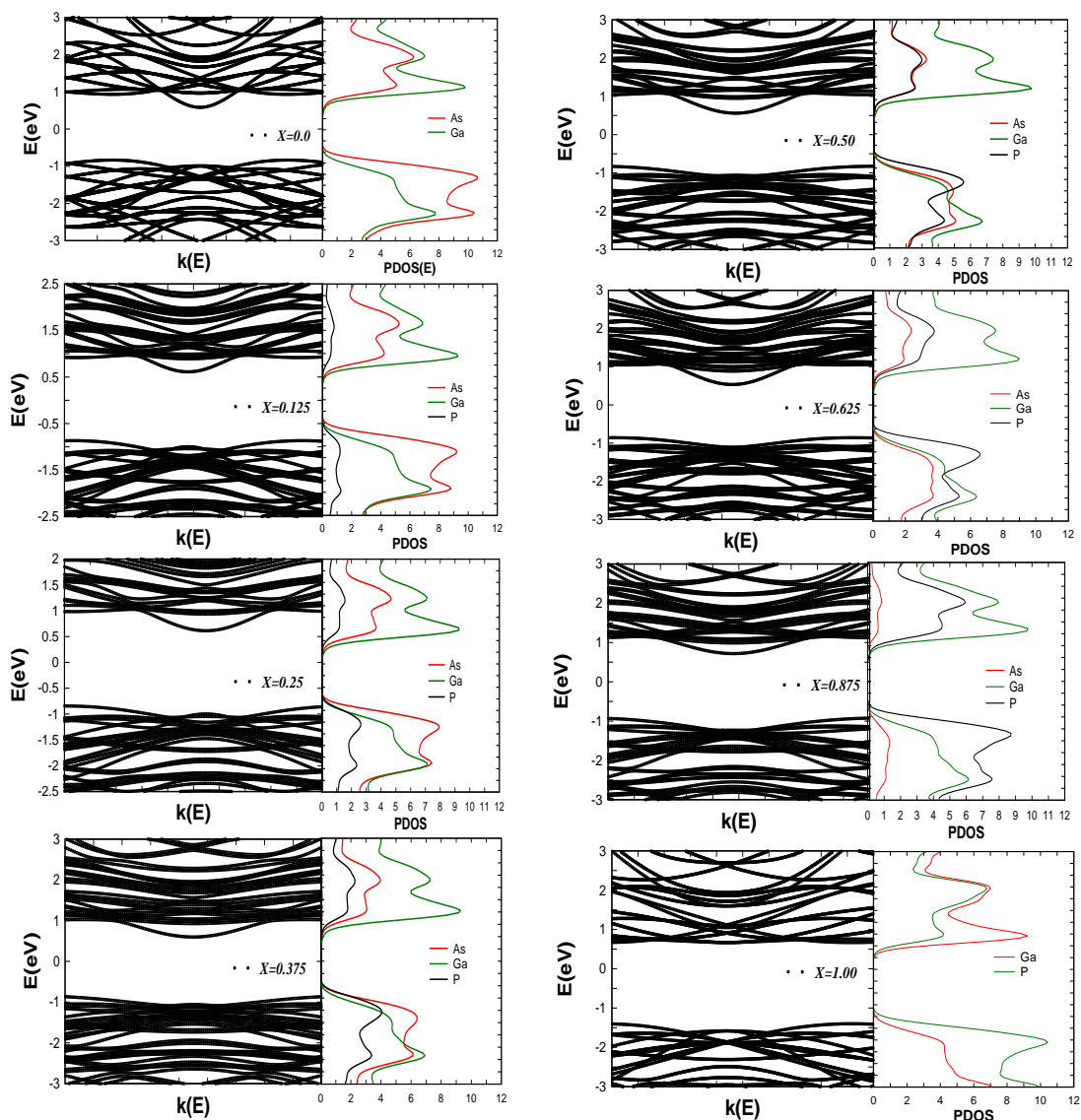
Figure 2-Band structure and partial density of state as a function of energy for all x values of $GaAs_{1-x}P_x$.

3- *Optical Properties*

In this section, we introduce the optical properties of 2D $GaAs_{1-x}P_x$structure.These properties are related to a complex dielectric constant ε_2 which is important to understand the reaction between the
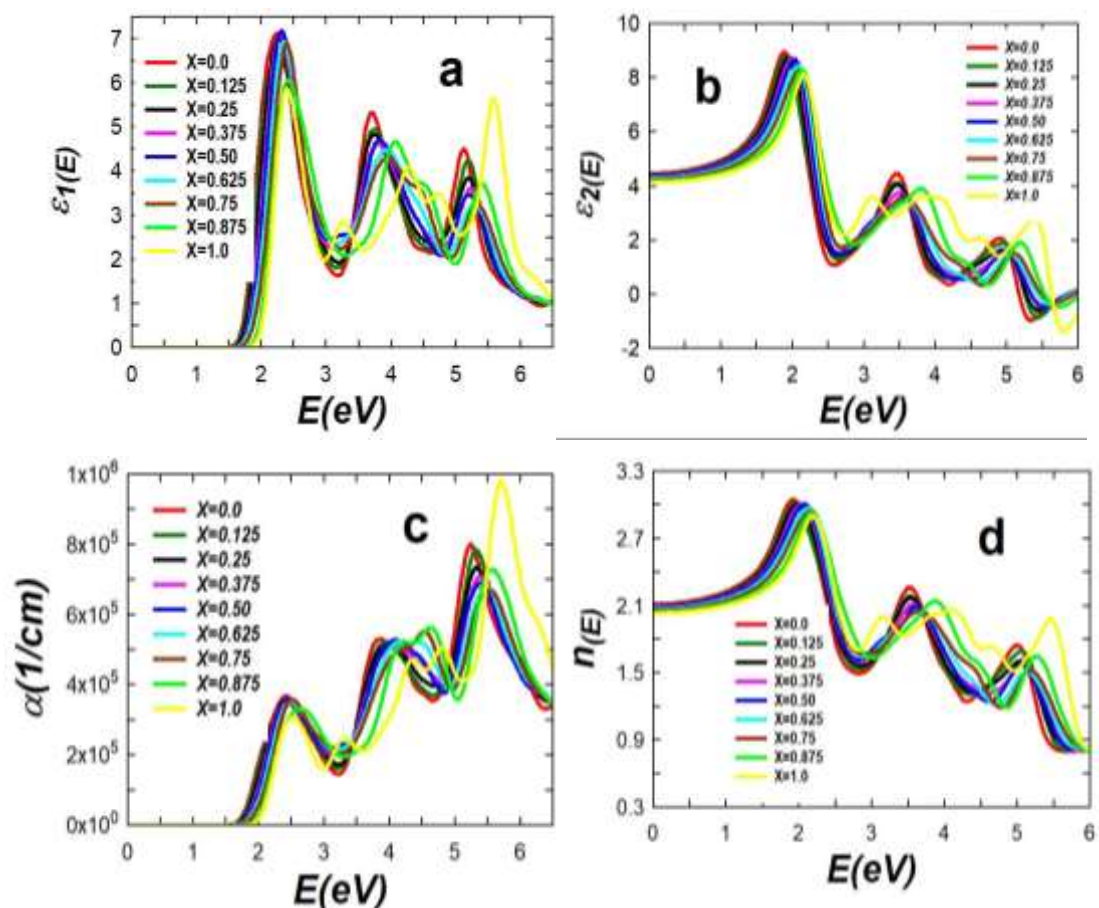
crystal system and the electromagnetic waves. It is too difficult to experimentally make a sample of a single-crystal structure.Therefore,the first principle is a good approximation to analyze optical properties, including dielectric constant, reflectivity, and absorption coefficient. The dielectric constant is the ability of the system to contain and store electrons. The imaginary part of the dielectric constant ε_2 can be obtained from equation 1, which led to the calculation of the real part of the dielectric constant ε_1, as shown in equation 2.The absorption coefficient α can be calculated by combining ε_1 and ε_2, as described in equation 3. Equation 4 shows the refractive index n[22].

$$\varepsilon_2 = \frac{e^2 h}{\pi m^2 \omega} \sum \sum \int |eP_{if}|^2 \delta(E_f^k - E_i^k - \hbar\omega) d^3 k \quad (1)$$

$$\varepsilon_1 = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\acute{\omega}\, \varepsilon_2}{\acute{\omega}^2 - \omega^2}\, d\omega \quad (2)$$

$$\alpha = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1 \right]^{\frac{1}{2}} \quad (3)$$

$$n = \sqrt{\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1}{2}} \quad (4)$$

Figure 3-The optical properties of GaAs$_{1-x}$P$_x$ structure as a function of energy, in which a and b are real and imaginary parts of dielectric constant, c is the absorption coefficient, and d is the refractive index.

The values of the real and imaginary parts of the dielectric constant of 2D GaAs$_{1-x}$P$_x$ structure are shown in Figures-(3a and b).The main peaks of ε_1 and ε_2 were in the visible region for all values of x, with a small shift toward higher energies when x value increases, followed by a decrease with

increasing photon energy.The values of ε_1 and ε_2 varied between 7 and 8 at this region.This peakcorresponds to the optical transitions between valence and conduction band. The absorption coefficient is defined as the transitions between valance and conduction states caused by means of excitations. It wasfound that the absorption edges are in the range of 1.6 to 2.1 eVfor all x values, as shown in Figure-3*c*, which gives the threshold for direct optical transitions between the top of the occupied orbital and the bottom of the unoccupied orbital. This indicates that, in the visible region with a wavelength of 775–590 nm, all systems can absorb a large amount of light.

The refractive index of the material is a more important property of an optical system. Figure-3*d*demonstrates the refractive index of GaAs$_{1-x}$P$_x$ system with a higher value at the visible region.The refractive index decreases gradually with the increase in photon energy.

Conclusions

In this study, we investigated the electrical, structural, and optical properties of GaAs$_{1-x}$P$_x$ system by means of DFT-GGA-SIESTA code. Our resultsshowed that the lattice constants are decreased from 28.16 to 26.28 Å with the increase in x-mol from 0 to 1, which leads to a change of the band gap from 1.56 to 2.24 eV at the same x-mol. Optical parameters, such as real and imaginary parts of dielectric constant, absorption coefficient, and refractive index,were calculated.

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