

STABILITY OF TWO DIMENSIONAL (2D) STRUCTURES BASED ON GaAs

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IN
PHYSICS

By
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ON GaAs

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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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M.S. in Physics

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Graphene is a two dimensional material isolated for the first time in 2004. After this, two dimensional materials has become an appealing research area for the scientists because of their exotic properties.

In search for two dimensional materials, both experimental and theoretical investigations have been carried out. First-principles approaches have been used to predict silicene and germane theoretically. A technologically important semiconductor material is GaAs, however there is no report of two dimensional materials which is based on GaAs.

We attempted to find a new stable 2D structure which is formed from either Ga and As atoms based on GaAs or its functionalized form with O atoms. In search for such a system, we performed density functional theory based calculations by using a plane-wave pseudopotential method. We used local density approximation for the exchange correlation potential. First, we performed geometrical optimization calculation in order to identify possible stable structures. We obtained electron band diagrams and phonon dispersion relations to check electronic properties and stability of these materials. We found three structures which are based on GaAs (100), (110) and (110) surfaces. We found that these two dimensional materials are geometrically stable but after performing phonon calculations we observe that there are some negative energy modes. In addition we identified one system which is based on Ga, As, and O atoms. Even though this structure is stable after geometry optimization, it has negative phonon modes in its phonon band diagrams.

Keywords: Graphene, Two dimensional material, GaAs, DFT, Phonons, First-principles, Electronic structure.

ÖZET

GAAS TABANLI İKİ BOYUTLU (2B) YAPILARIN KARARLILIKLARI

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Keşfedilen ilk iki boyutlu malzeme olan grafenin bulunmasından sonra, iki boyutlu materyaller sıradışı özelliklerinden dolayı bilim insanları için oldukça ilgi çekiçi bir araştırma alanı haline gelmiştir.

İki boyutlu materyal araştırmalarında hem deneysel hem de teorik yaklaşımlar kullanılmaktadır. Örneğin bu yaklaşımların en önemlilerinden biri olan yoğunluk fonsiyoneli teorisi, silisen ve germanenin teorik olarak tahmininde kullanılmıştır. Teknolojik uygulamalarda en yaygın kullanılan yarıiletken materyallerden biri GaAs olmasına rağmen henüz GaAs temelli iki boyutlu bir yapı bulunamamıştır.

Bu tez çalışmasında ya GaAs temelli, Ga ve As atomlarından oluşan, ya da GaAs'ın O atomu ile işlevselleştirilmiş formunu baz alan yeni kararlı bir iki boyutlu bir yapı bulmaya çalıştık. Bu araştırmamızda yoğunluk fonksiyoneli teorisine dayanan düzlem-dalga yapay potansiyel metodu kullanarak hesaplamalar gerçekleştirdik. Değiş-tokuş korelasyon potansiyeli için yerel yoğunluk yaklaşımı kullandık. Önce, muhtemel kararlı yapıları tanımlamak için geometrik optimizasyon hesaplamaları yaptık. Bu materyallerin elektronik özelliklerini ve kararlılığını kontrol etmek için elektron bant diagramlarını ve fonon dağılım bağıntılarını elde ettik. GaAs (100), (110) ve (110) yüzeylerine dayanan üç yapı elde ettik. Bu iki boyutlu materyallerin geometrik olarak kararlı olduğu bulduk. Ancan fonon hesaplamaları uyguladığımızda negatif enerji kiplerinin olduğunu gözlemledik. Ayrıca Ga, As ve O atomlarına dayanan bir sistem bulduk. Ancak yapının geometrik olarak kararlı olmasına karşın fonon bant yapısında negatif enerji kipleri olduğu görülmüştür.

Anahtar sözcükler: Grafen, İki boyutlu materyaller, GaAs, Yoğunluk fonksiyoneli

teorisi, Fonon, Elektronik yapı.

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Chapter 1

2D Materials

1.1 Introduction

2D materials exhibit completely different properties compared to their 3D counterparts. 2D materials discovered up to now consist of one kind of atom or two different kind of atoms in their basis. These atoms are arranged in a two dimensional single layer which make chemical bonds with each other. Starting with the discovery of graphene, 2D materials have attracted great interest. The reason behind this is the exotic properties of graphene.

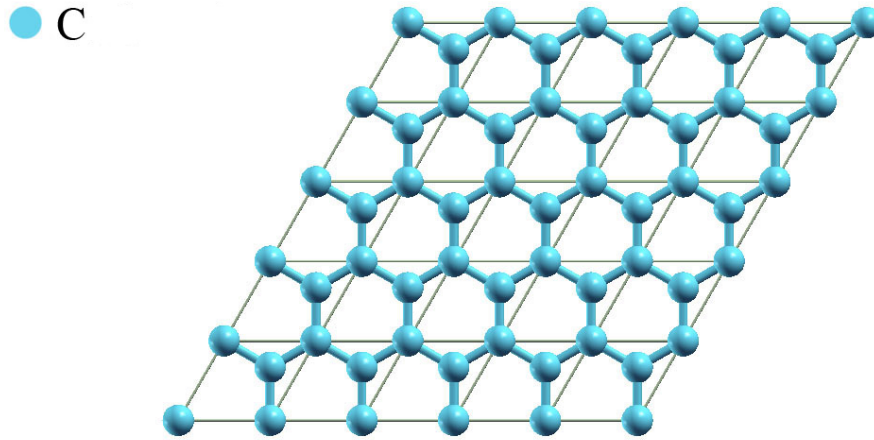


Figure 1.1: 2D structure for graphene

Figure 1.1 shows hexagonal lattice structure of single layer 2D graphene. Graphene's tensile strength is 130 GPa [1] and Young modulus is 1 TPa [1]. These results show that graphene is the strongest known material. Also, graphene has very interesting conducting properties. Its carrier density is 10^{12} cm^{-2} [2]. Thermal conductivity of freely suspended graphene at room temperature is approximately between $2000\text{-}4000 \text{ Wm}^{-1}\text{K}^{-1}$ [2], which makes one of the materials with highest thermal conductivities. Optical properties of graphene are very interesting as well. The incident visible light absorption (white light absorption) of graphene is 2.3% [3] and visible light transmission is 97.7 % [3]. This makes graphene almost completely transparent. Pristine graphene has no band gap [4].

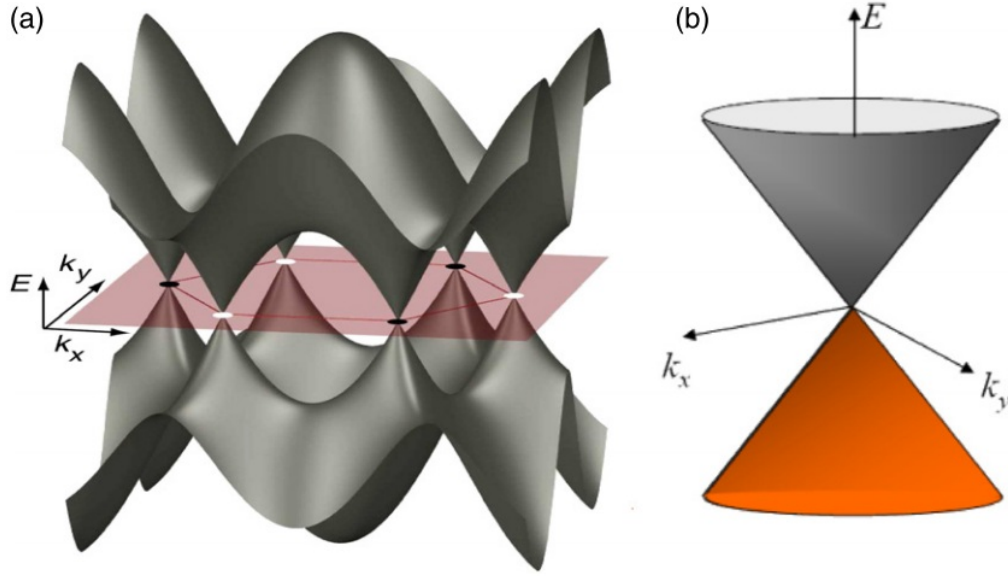


Figure 1.2: (a) Band structure of graphene. (Reproduced from Beenakker CWJ 2008 Andreev reflection and Klein tunneling in graphene Rev. Mod. Phys. 80 1337) (b) Energy band diagram at one K point form a dirac cone (Reproduced form Eva Y Andrei et al 2012 Rep. Prog. Phys. 75 056501 doi:10.1088/0034-4885/75/5/056501)

The figure 1.2 shows the valance band and the conduction band of graphene meet at the so called "Dirac points" or "charge neutrality points". Graphene band structure shows zero band gap, which means that it is a semi-metal. The main source of exotic behavior of graphene is the linear behavior of the graphene band structure (1.2 (b)). Cyclotron mass of electron is one of them. The cyclotron mass of graphene is [5]

$$m^* = \frac{\sqrt{\pi}}{v_f} \sqrt{n} \quad (1.1)$$

where, m^* is cyclotron mass of graphene, n is the charge density and v_f is Fermi velocity at Dirac point approximately $v_f \approx 10^6 \text{ ms}^{-1}$. The effective mass is charge density dependent.

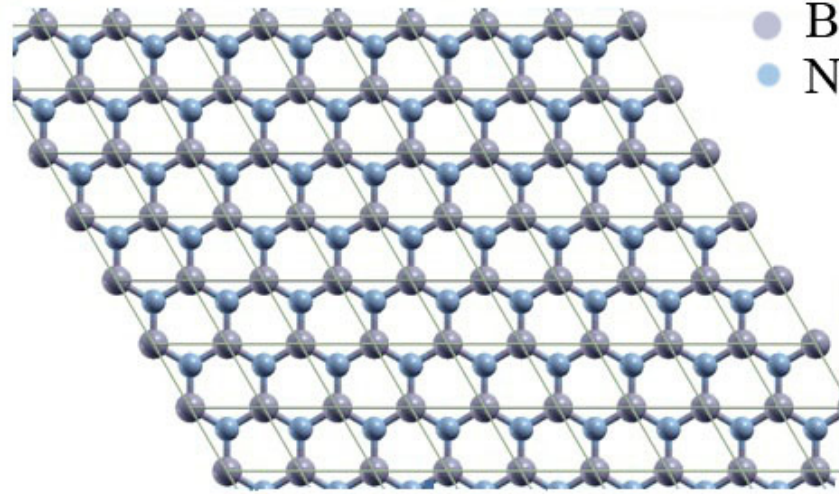


Figure 1.3: 2D structure of h-BN

Hexagonal boron nitride (h-BN) is another example for 2D materials. Similar to graphene, figure 1.3 shows (h-BN) composed of hexagonal lattice structure. It consists of equal number of sp^2 bonded boron and nitrogen atoms. There is no buckling between boron and nitrogen atoms.

2D (h-BN) layers are considered as insulator or wide band gap semiconductor which has a band gap of approximately 5.9 eV [6]. Because of this property it can be used as a barrier for leakage in electronics. Useful properties such as chemical stability and intrinsic insulation of (h-BN) attracts great interest.

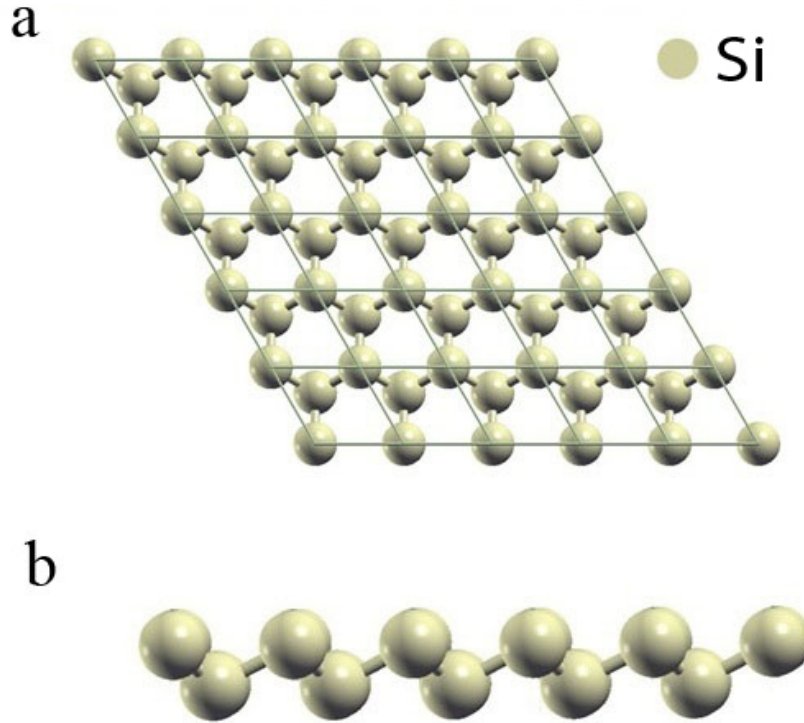


Figure 1.4: (a) Top view 2D structure of Silicene (b) Side view 2D structure of Silicene

There are group-IV elements which can take form of graphene-like 2D materials namely germanene and silicene. These materials were initially predicted by theoreticians [7] then confirmed by experimentalists [8]. Ge and Si are two appealing materials because of their chemical properties and their application areas in technology. Researchers thought that these 2D structures may bring new physical properties and can take their places in technology. Both Ge and Si, form a 2D planar hexagonal lattice structure like graphene. Figure 1.4 shows the structure of silicene. With using first-principles local density approach, it is shown that 2D germanene and silicene has small buckling in contrast to graphene. It is also shown that planar and the highly buckled silicene and germanene are not stable. But they are stable in the low buckled (LB) honeycomb structure,

with buckling $\Delta=0.44$ nm [9]. Figure 1.3 shows the 2D structure of silicene. Fermi velocity of silicene and germanene are 5.1×10^{15} m/s and 3.8×10^5 m/s respectively [10]. Properties of nanoribbons of these materials depend on size and topological structure. Because of its electronic properties silicene appeals electronic industries attention as a possible new application material.

After these discoveries scientists focused on other 2D materials. Several 2D materials are reported which have many application areas from optoelectronics to solar cells. Transition metal dichalcogenides (TMD) which include hexagonal layers with elements from the oxygen family (chemical elements in group 16 of the periodic table) and the transition metals can appear in more than 40 different categories [11]. One of the most significant one is Molybdenum disulfide (MoS_2) which has a direct band gap around 1.90 eV [12]. At room temperature, it shows an n-type conductivity which has mobility a between $(0.5-3)$ $cm^2/(Vs)$ [13], [14]. If we compare this value with the bulk MoS_2 which has a mobility at the room temperature between $(200-500)$ $cm^2/(Vs)$, mobility of the 2D single-layer MoS_2 is lower. Also using strain modifying the optical and electronic properties of MoS_2 can be manipulated [15]- [16].

There are some other examples of 2D structures, graphyne, borophene, stanene, phosphorene and fluorographene are some of them. These 2D materials can be combined with each other to obtain new materials on demand to meet the special needs in different applications. These new materials can be used in space technology, optoelectronics, automotive, electronics, solar cells, energy storage, paints, communications, sensors and in many other applications.

GaAs has many important properties. Its intrinsic carrier concentration at room temperature is 2.1×10^6 cm^{-3} [17]. It has a very wide using area. For a single-junction GaAs solar cell the efficiency is 28% [18]. It is the highest efficiency detected for this kind of solar cell. It can be used in solar cells. Also for X-Ray detection GaAs diodes can be used. Possible 2D materials based on GaAs can gain great importance.

In this thesis possible 2D structures based on GaAs were investigated by using

the pseudopotential plane wave calculations based on density functional theory.

1.1.1 Organization of the Thesis

The second chapter includes theoretical information about the first principle approach and computational details. In the third chapter, to investigate novel 2D materials based on GaAs, first principle study of ground state energy calculations are presented. In the fourth chapter conclusion of this thesis is given.

Chapter 2

Computational Methods

2.1 Introduction

In order to describe the physical properties of an atomic system, we have to solve Schrödinger equation. We can write Schrödinger equation as

$$\hat{H}\Psi(\vec{R}, \vec{r}) = E\Psi(\vec{R}, \vec{r}) \quad (2.1)$$

where $\vec{R}$ and $\vec{r}$ represent atomic and electronic coordinates. If we can solve the Schrödinger equation for a desired system, we can obtain all the information about that system. Unfortunately, it is impossible to get an exact solution for a many-body system. In general, the Schrödinger equation consist, $3N$ degrees of freedom for the electron and $3P$ degree of freedom for the ions, where N is number of electrons and P is number of ions. The Hamiltonian can be written as

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{I=1}^P \nabla_I^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \\ & + \frac{1}{2} \sum_{I=1}^P \sum_{J=1}^P \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{i=1}^N \sum_{I=1}^P \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \end{aligned} \quad (2.2)$$

where the atomic units $e = \hbar = m_e = \frac{1}{4\pi\epsilon_0} = 1$ have been employed. On the right hand side of this equation; the first term is the kinetic energy of the electrons, the second term is the kinetic energy of the ions, the third term is the electron-electron interaction, the fourth term is the electron-ion interaction and the last term is the ion-ion interaction. There is a factor of $\frac{1}{2}$ in the electron-electron and ion-ion interaction terms in order to avoid the double counting.

Hamiltonian can be written as

$$\hat{H} = T_e(\vec{r}) + T_N(\vec{R}) + V_{ee}(\vec{R}) + V_{eN}(\vec{R}, \vec{r}) + V_{NN}(\vec{R}) \quad (2.3)$$

where T_e is kinetic energy of electrons, $T_N(\vec{R})$ is kinetic energy of ions, $V_{ee}(\vec{R})$ is electron-electron interaction, $V_{eN}(\vec{R}, \vec{r})$ is electron-ion interaction and $V_{NN}(\vec{R})$ is ion-ion interaction. Then the Schrödinger equation can be written as:

$$[T_e(\vec{r}) + T_N(\vec{R}) + V_{ee}(\vec{R}) + V_{eN}(\vec{R}, \vec{r}) + V_{NN}(\vec{R})]\Psi(\vec{R}, \vec{r}) = E\Psi(\vec{R}, \vec{r}) \quad (2.4)$$

where $\vec{r}$ and $\vec{R}$ represent coordinate of N atoms. Because of many degrees of freedom we can not solve this equation analytically for many-body problems. In order to simplify this equation, first we can apply so called Born-Oppenheimer approximation.

2.1.1 The Born-Oppenheimer approximation

When we compare the mass of an ion and the mass of an electron we see that ions are much heavier than electrons. In the atomic units, mass of a proton is 1.007276466812 u, mass of a neutron is 1.00866491600 u and mass of an electron is $5.4857990943 \times 10^{-4}$ u. Because of this huge mass difference between the electron and the ion, the time scale of their dynamics be different and therefore it can be ions are moving much slower than the electrons. Therefore we can treat ions as

frozen. In the Born-Oppenheimer approximation using this fact we can separate the total wave function into two parts.

$$\Psi(\vec{R}, \vec{r}) = \theta(\vec{R})\Phi(\vec{R}, \vec{r}) \quad (2.5)$$

where the $\theta(\vec{R})$ is ionic part and the $\Phi(\vec{R}, \vec{r})$ is the electronic part of the wave function. Therefore, we can examine the electronic motion at different snapshots of the ionic motion by frozen ion approximation. Using this fact, the electronic Hamiltonian can be written as

$$\hat{H}_e = T_e(\vec{r}) + V_{ee}(\vec{R}) + V_{eN}(\vec{R}, \vec{r}) \quad (2.6)$$

This approximation is called Born-Oppenheimer approximation [19]. According to this, Schrödinger equation can be rewritten in terms of separated wave function. Then, electronic part of the Schrödinger equation can be written as

$$\left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{I=1}^P \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \Phi_R(\vec{r}) = E_{el}(\vec{R}) \Phi_R(\vec{r}) \quad (2.7)$$

Electrons are considered, moving in an effective potential due to the frozen ions. In the electronic Hamiltonian, the nuclear position can be taken as a parameter.

2.1.2 Hartree-Fock Method

In the previous chapter the Schrödinger equation was simplified with the Born-Oppenheimer approximation. However, the electron-electron interaction is still very complicated. There are many electrons which are interacting with each other and the ions. To make a model for these interactions in the Hartree approximation, it has been considered that electrons move in an effective potential produced

by the other electrons and the ions. In Hartree-Approximation (HA) we write the wave function of the system a product of the each particles wave function. Under this assumption, we can write the wave function of the electrons as single particle wave function. The simplest wave function for a many body system can be written in product form:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_N(\vec{r}_N) = \prod_{i=1}^N \phi_i(\vec{r}_i) \quad (2.8)$$

Simply this wave function is the product of each single electron wave function. Because of antisymmetry condition of quantum mechanics it is not possible to write the wave function of a fermionic system as a simple product of wave functions. In the Hartree approximation the behavior of the fermionic particles is not described properly. This problem is tackled by Hartree-Fock method by writing electronic wave function as a Slater determinant:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \dots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \dots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \dots & \psi_N(\vec{r}_N) \end{vmatrix}$$

Here $\frac{1}{\sqrt{N!}}$ is the normalization constant. Now in order to solve the Schrödinger equation we can use this wave function and employ the variational principle. Simply our electronic Hamiltonian has three parts.

$$\hat{H}_e = T_e(\vec{r}) + V_{ee}(\vec{R}) + V_{eN}(\vec{R}, \vec{r}) \quad (2.9)$$

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{I=1}^P \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (2.10)$$

In this equation, the first and the second terms are single particle operators

and the third term is a two particle operator. Then, we can write the electronic Hamiltonian as

$$\hat{H}_e = \sum_i^N \hat{h}(\vec{x}_i) + \frac{1}{2} \sum_{i \neq j}^N \hat{g}(\vec{x}_i, \vec{x}_j) \quad (2.11)$$

where $\hat{h}$ is a single particle operator and $\hat{g}$ is two particle operator.

Next we apply the variational principle to the wave functions and obtain

$$\begin{aligned} \hat{h}\phi_k(\vec{x}_1) + \sum_i \left\{ \int \phi_i^*(\vec{x}_2) \hat{g}[\phi_i(\vec{x}_2) \phi_k(\vec{x}_1)] d\vec{x}_2 - \int \phi_i^*(\vec{x}_2) \hat{g}[(\phi_i(\hat{x}_1) \phi_k(\hat{x}_2))] d\vec{x}_2 \right\} \\ = \sum_i \lambda_{ki} \phi_i(\vec{x}_1) \end{aligned} \quad (2.12)$$

We have the freedom to concentrate upon those Lagrange multiplier λ_{ki} which satisfies

$$\lambda_{ki} = \delta_{ki} \epsilon_k \quad (2.13)$$

Then equation 2.12 can be written as :

$$\hat{F}\phi_k = \epsilon_k \phi_k \quad (2.14)$$

where $\hat{F}$ is the Fock operator. In order to solve the system of equations in 2.14 we first guess an initial set of orbital. Then, we build the Fock operator. As a third step, using the Fock operators, we solve the HF equations to get a new set of orbitals with respect to the lowest energy orbitals. Then, we repeat the procedure from the the second step till the orbitals show little change.

Here, the Hartree-Fock potential does not take into account the real electron-electron interaction [20]- [21], because in the Hartree-Fock approximation we use a single Slater determinant. The electron-electron interaction is neglected in the wave function. In this system, we are representing many-body wave function with single particle wave functions via Slater determinant. The main problem in Hartree-Fock Approximation is the correlation between the electrons.

2.2 Density Functional Theory

Density Functional Theory (DFT) is a framework for investigating electronic properties of materials. This technique uses the fact that energy of a system can be written as functional of electron density.

2.2.1 Hohenberg-Kohn Theorem

Hohenberg and Kohn introduced two fundamental theorems in 1964 which form the basis of the DFT [22]. The first theorem states that density exists and is uniquely determined for any system of interacting particles in an external potential. Second theorem states that a universal functional for the energy can be defined in terms of the density. The exact ground state energy is the global minimum value of this functional. These two theorems construct the foundation of DFT. The energy is given by

$$E[n] = T[n] + E_{int}[n] + \int V_{ext}(\vec{r})n(\vec{r})dr^3 = F[n] + \int V_{ext}(\vec{r})n(\vec{r})dr^3 \quad (2.15)$$

where the $T[n]$ is the kinetic energy of the system, the $V_{ext}(\vec{r})$ is the external potential and $n(\vec{r})$ is the density of the system

2.2.2 Kohn-Sham (KS) Approach

The density operator defined as

$$\hat{n} = \sum_{i,N} \delta(\vec{r} - \vec{r}_i) \quad (2.16)$$

There, we can obtain the density with expectation value of the $\hat{n}(\vec{r})$.

$$n(\vec{r}) = \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = N \int |\Psi(\vec{r}, \vec{r}_2 \dots \vec{r}_N)|^2 d\vec{r}_2 \dots d\vec{r}_N \quad (2.17)$$

Expectation value of ion-electron interaction can be written as

$$\langle \Psi(\vec{r}_1, \dots, \vec{r}_N) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_N) \rangle = - \sum_i^{N_e} \sum_I^{N_n} \int \Psi^*(\vec{r}_1, \dots, \vec{r}_N) \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} d\vec{r}_1 \dots d\vec{r}_N \quad (2.18)$$

$$E_{ne} = \int n(\vec{r}) \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} d\vec{r} = \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r} \quad (2.19)$$

Also, the expectation value of interaction will be

$$E_{ee} = \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n^{(2)}(\vec{r}, \vec{r}')}{|\vec{r}_i - \vec{r}'|} \quad (2.20)$$

We can assume that

$$n^{(2)}(\vec{r}, \vec{r}') = n(\vec{r})n(\vec{r}') + \Delta n^{(2)}(\vec{r}, \vec{r}') \quad (2.21)$$

Hence we can write

$$E_{ee} = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}_i - \vec{r}|} + \Delta E_{ee} \quad (2.22)$$

So we obtain the expectation value of electron-electron interaction. But, it is impossible to write expectation value of kinetic energy (T) as a functional of density because of Δ operator.

$$T = -\frac{1}{2} \int d\vec{r} \Psi^*(\vec{r}_1, \dots, \vec{r}_N) \nabla^2 \Psi(\vec{r}_1, \dots, \vec{r}_N) \quad (2.23)$$

For the unknown kinetic energy part, Kohn and Sham introduces a non interacting systems kinetic energy with a correction [23]. This artificial systems density can be written as

$$n(\vec{r}) = \sum_n^{N_e} |\phi_n(\vec{r})|^2 \quad (2.24)$$

Therefore, the expectation value of the energy can be written as

$$E = \frac{-1}{2} \sum_{i=1}^N \int d^3\vec{r} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) + \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r} + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \Delta T + \Delta E_{ee} \quad (2.25)$$

where $E_{xc} = \Delta T + \Delta E_{ee}$ is Exchange-Correlation energy.

Finally Kohn-Sham equation can be written as in a simplest form

$$(\hat{T}_s + \hat{V}_H + \hat{V}_{XC} + \hat{V}_{ext})\phi_i(\hat{r}_i) = \epsilon_i \phi_i(\hat{r}_i) \quad (2.26)$$

where $\hat{T}_s$ is noninteracting system's kinetic energy and $\hat{V}_H, \hat{V}_{XC}, \hat{V}_{ext}$ are effective potential. The ϕ_i functions are Kohn-Sham (KS) orbitals.

Here we can write the effective potential as

$$\hat{V}_{eff} = V(\vec{r}) + \frac{1}{2} \int d\vec{r}'^3 \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{XC}}{\delta n(\vec{r})} \quad (2.27)$$

where, on the right hand side of equation, the first term is external potential, the second term is Hartree potential and the third term is exchange-correlation potential.

Up to this point Kohn-Sham theorem is exact. If we know the exchange-correlation function this representation would be exact.

2.2.3 Local Density Approximation(LDA) and General Gradient Approximation (GGA)

In the KS equation

$$\hat{V}_{XC} = \frac{\delta E_{xc}}{\delta n(\vec{r})} \quad (2.28)$$

is not known. Hohenberg and Kohn proposed LDA [24]. According to this approximation, we can replace E_{xc} with a linear functional of the density

$$E_{xc}^{LDA}[n(\vec{r})] = \int d\vec{r} \epsilon_{xc}^{hom} n(\vec{r}) \quad (2.29)$$

where ϵ_{xc}^{hom} is the exchange-correlation energy density of an interacting homogeneous electron gas at the density $n(\vec{r})$.

Real systems are inhomogeneous, so we need corrections to LDA, one way is including higher order terms in the expansion of density in exchange-correlation energy. The more general form of correction is:

$$E_{xc}^{GGA}[n(\vec{r})] = \int d\vec{r} f(n(\vec{r}), \nabla n(\vec{r})) \quad (2.30)$$

2.2.4 Lattice Structure and Periodicity Conditions

Crystal structures are modeled by lattices in terms of primitive vectors and lattice vectors. A translation vector is that preserved lattice symmetry is

$$\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3 \quad (2.31)$$

The vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are primitive lattice vectors and u_1, u_2, u_3 are integers. We defined our translation vector $\vec{T}$ in terms of these primitive lattice vectors. Physical properties such as electron density and magnetic moment are invariant under this translation vector. Most importantly the electron number density $n(\vec{r})$ is a periodic function of $\vec{r}$ and invariant under translation vector $\vec{T}$:

$$n(\vec{r} + \vec{T}) = n(\vec{r}) \quad (2.32)$$

To proceed further to define our crystal structure, we first define our reciprocal lattice(inverse space) [25] vector $\vec{G}$:

$$\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3 \quad (2.33)$$

where the vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are reciprocal lattice vectors and v_1, v_2, v_3 are integers. Now, we can write the Fourier series representation of the electron density under any crystal translation:

$$n(\vec{r} + \vec{T}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}} \quad (2.34)$$

where $\exp(i\vec{G} \cdot \vec{T}) = 1$

Then we have the desired invariance:

$$n(\vec{r} + \vec{T}) = n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \quad (2.35)$$

2.2.5 Bloch Theorem

In 1928 Felix Bloch proposed that for a periodic potential solution of the Schrödinger Equation can be written as as [26] [27] [28] :

$$\psi_k(\vec{r}) = u_k(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) \quad (2.36)$$

where $u_k(\vec{r})$ has the period of the crystal lattice with $u_k(\vec{r}) = u_k(\vec{r} + \vec{T})$. Here $\vec{T}$ is translational vector of the lattice. This equation expresses the Bloch's Theorem.

The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $\exp(i\vec{k} \cdot \vec{r})$ times a function $u_k(\vec{r})$ with the periodicity of the crystal lattice.

where

$$u_k(\vec{r}) = u_k(\vec{r} + \vec{T}) \quad (2.37)$$

$$u_k(\vec{r}) = \sum_G a_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}} \quad (2.38)$$

2.2.6 Plane Waves

Plane waves are useful and simple for describing the electronic wave function in a periodic system. Because of this reason, to solve the Kohn-Sham equations, we expand the wave function at each k point in terms of plane wave basis. While doing this as a computational technique to simplify the calculation, we can use Fast Fourier Transformation (FFT). But it is impossible to make an expansion with infinite number of plane wave basis set. For this reason, we have to truncate our plane wave expansion. We can define an upper bound for the kinetic energy. Hence, we will only use plane waves which have less kinetic energy than our

defined kinetic energy. In order to reduce errors we can increase the cut-off energy [28].

2.2.7 Pseudopotential

The coulomb interaction is inversely proportional to the radial distance $\vec{r}$. Because of this in the core region of the atom, potential becomes too large when electron is too close to core. The wave functions of valance and core electrons have to be orthogonal. So that plane waves of these valance electrons are oscillating too much. To avoid this we can define a pseudo potential.

Instead of considering the potential of all core electrons, we can define a single pseudopotential which can describe the system with a good approximation. Figure 2.1 shows this behavior.

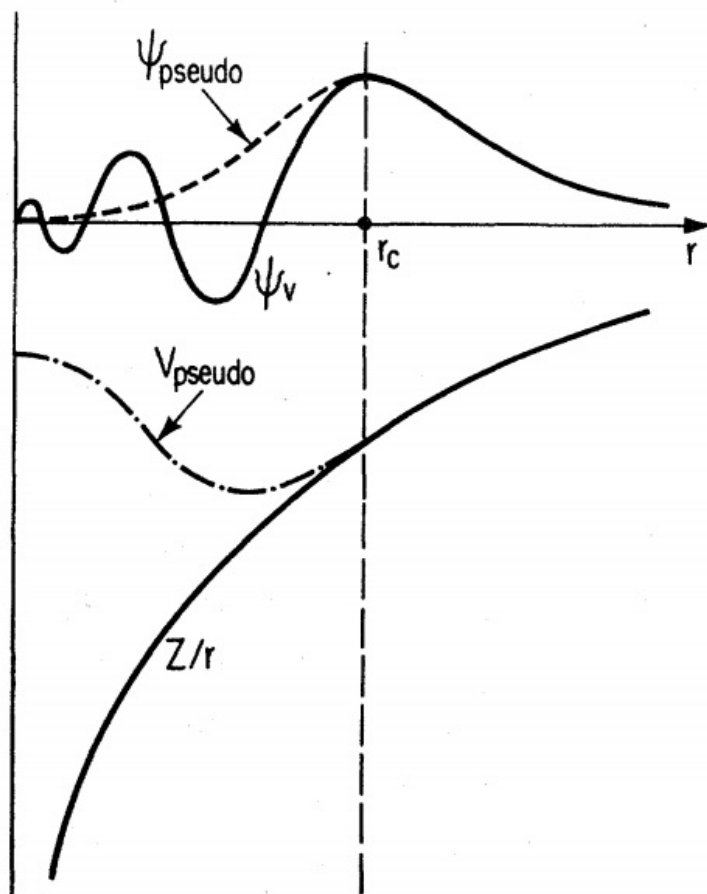


Figure 2.1: Illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all electron and pseudo electron values match is designated r_c (Reproduced from [28])

Chapter 3

First Principle Study

3.1 2D Structures Based On GaAs

GaAs has a very wide application area which is already known. In this study, we searched for possible 2D structures which can be obtained from GaAs. For this purpose, we used GaAs (100), (110) and (111) lowest surface energy structures to obtain 2D materials. After this to avoid polar effect of (100) surface of GaAs we used Oxygen. We calculated the energy band diagrams of these structures. Then for stability we checked phonon dispersion relations of these possible structures.

3.2 Methodology

In this study, all calculations are carried out using on Density Functional Theory plane wave basis sets and pseudo potential method. For the exchange-correlation term we have chosen local density approximation and performed all calculations in Quantum Espresso package [29]. As pseudopotential we have used nonlinear core correction Perdew-Zunger exchange-correlation functional type. At first for bulk GaAs we have performed cut-off energy, k point and lattice parameter

optimizations.

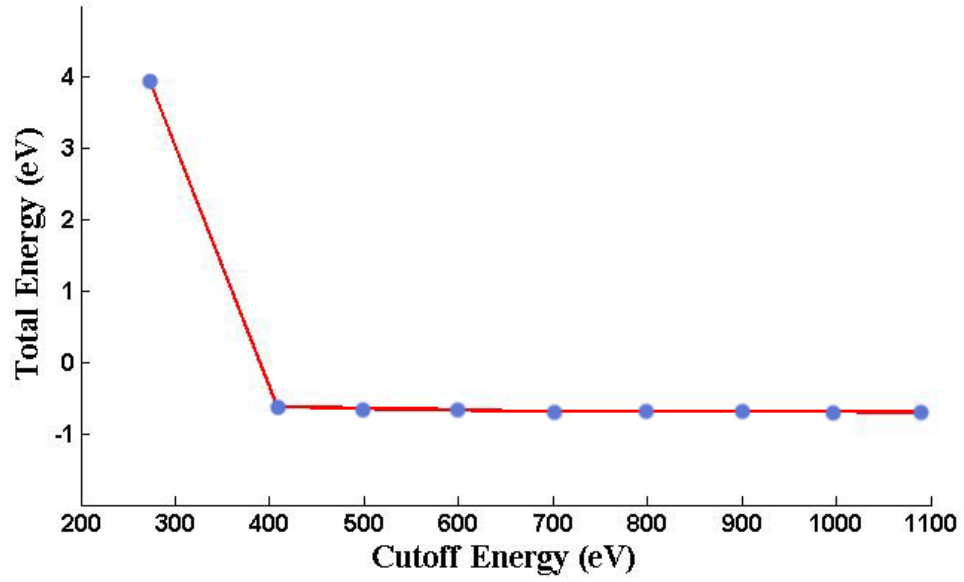


Figure 3.1: Minimum energy convergence for the total energy. y axis rescaled as $y+6016$ eV

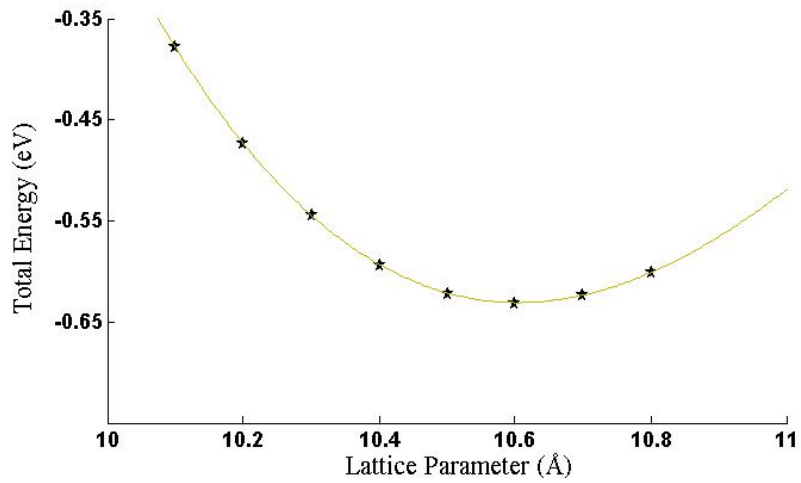


Figure 3.2: Minimum energy convergence for the lattice parameter of (100) surface of GaAs. y axis rescaled as $y+6016$ eV

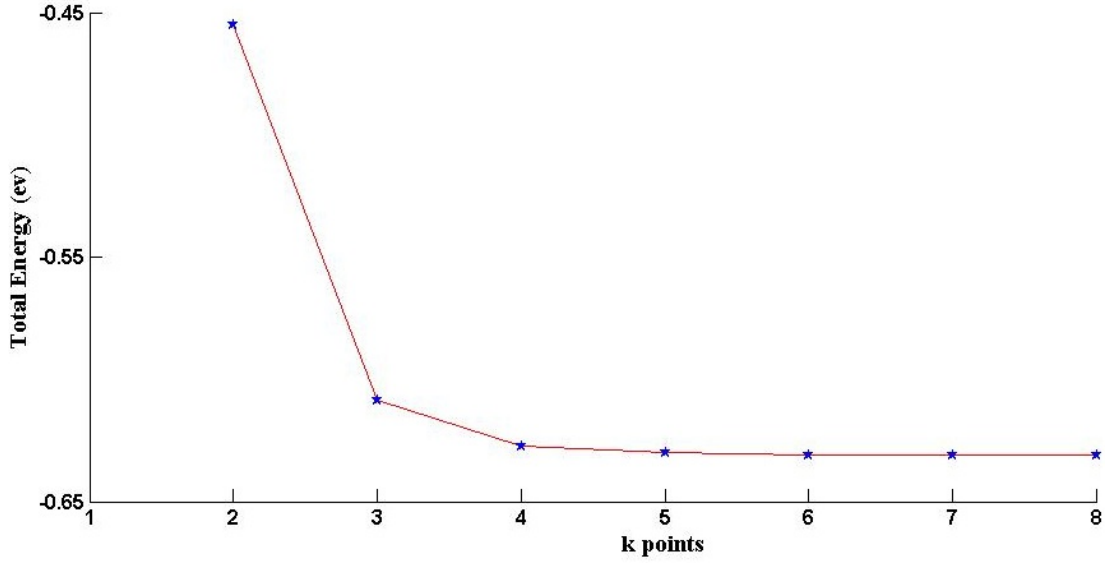


Figure 3.3: Minimum energy convergence for the k points of GaAs (100) surface. y axis rescaled as $y+6016$ eV

As seen from 3.1 it shows that at 680 eV is a sufficient cutoff energy for bulk GaAs. Also, as seen from 3.2, lattice parameter is 5.6 Å. Also in 3.3 we examined the k point convergence for bulk GaAs. With obtained all the rest of the parameters from these convergence results we performed our remaining calculations.

As a summary, we have used plane wave basis set in the Kohn Sham equations and we have taken cutoff energy as 680 eV for reducing the computational cost. Accurate lattice constant is obtained as 5.60 Å. We have used a Monkhorst-Pack mesh [30] of 4x4x4 for the bulk GaAs. Because of the symmetry in 2D systems we have taken Monkhorst-Pack mesh of 4x4x1.

As possible structures, first we considered (111), (110) and (100) surfaces of GaAs. We cut these surfaces from the bulk GaAs, then to get 2D systems we construct at least 10 Å vacuum region between two GaAs surfaces. Then, we performed our ground state energy calculations for geometry optimization of these systems and look for which has the minimum ground state energy after relaxation. When we found the state which has minimum energy we examined the possible 2D

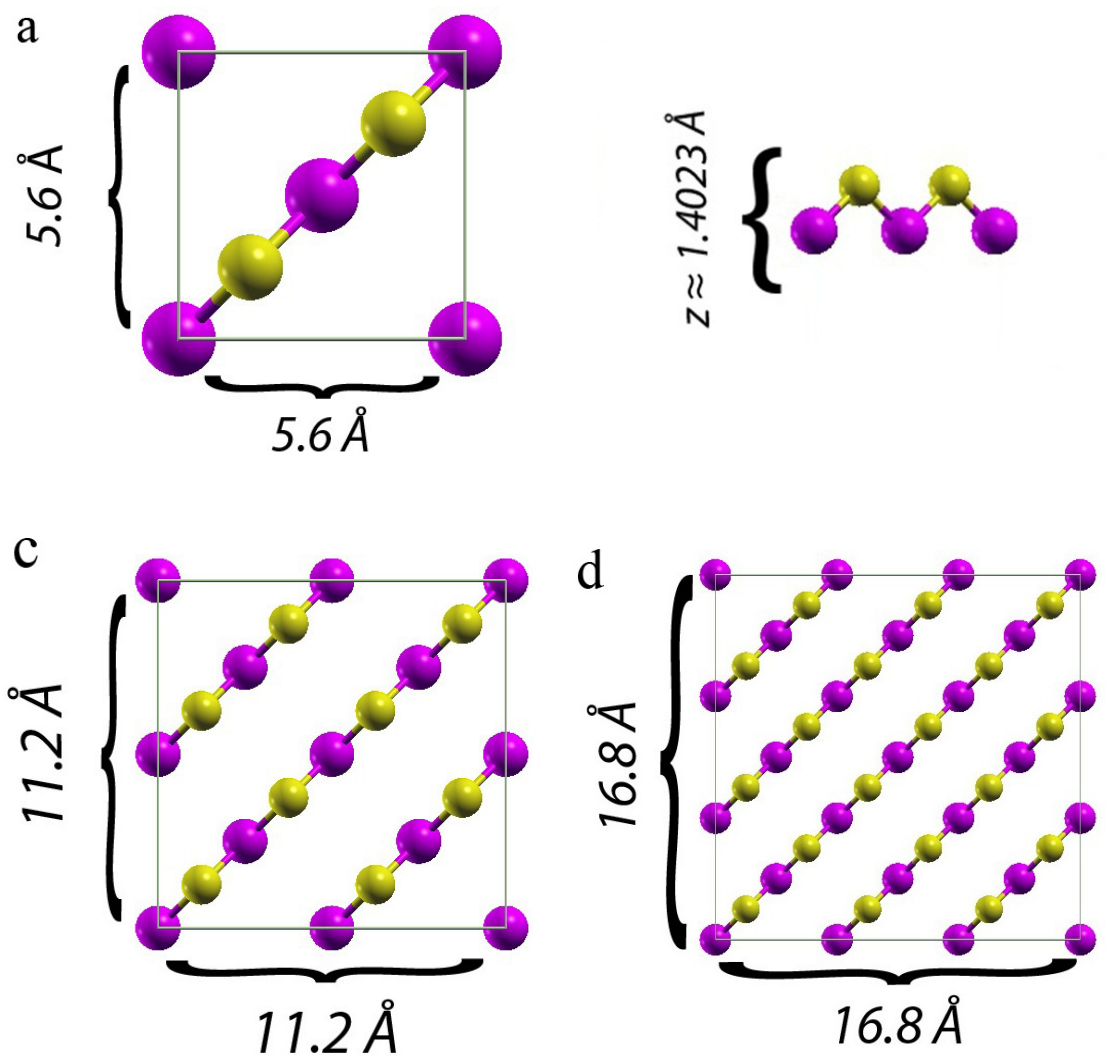


Figure 3.4: (a) Top view of (100) surface in 1x1 cell. (b) Side view of (100) surface in 1x1 cell. (c) Top view of (100) surface in 2x2 cell. (d) Top view of (100) surface in 3x3 cell.

structures. While doing our calculations, we started from 1x1 cell and with using supercell method we performed relaxation calculations for 2x2 and 3x3 supercells as well in order to address to constraint because of the unitcell size and periodic boundary condition.

Figure 3.4 illustrates our 2D surfaces. After seeing that these structures which are only based on GaAs surfaces, has negative phonon modes, we suggested that the reason behind this negative modes, might be caused by the polar surfaces of GaAs. To avoid this polar behavior we added oxygen to our system.

Then after performing geometry optimization we checked the system's electronic behavior and phonon band structures of each system. Phonon calculation performed with using the Density Functional Perturbation Theory (DFPT) [31]. Figure 3.4 shows that our initial parameters for the 2D structure which is based on (100) surface of GaAs. We performed the same method for (110) and (111) surfaces of GaAs.

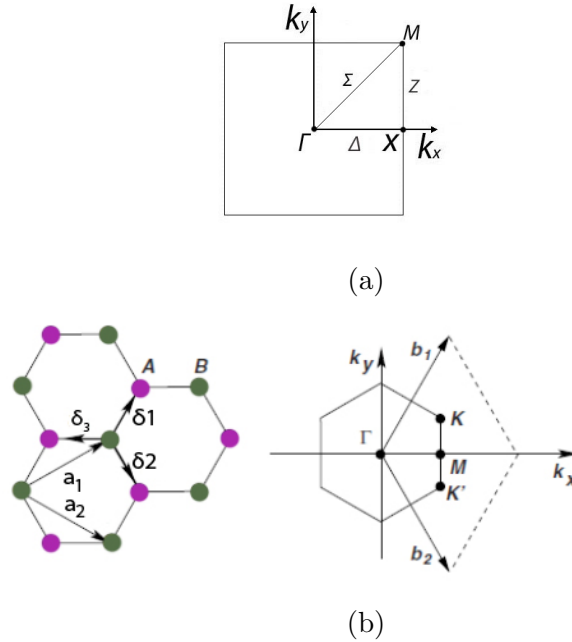


Figure 3.5: (a) Brillouin zone for square 2D GaAs surface. (b) Brillouin zone for hexagonal lattice.

For the square Brillouin zone in figure 3.5 (a) high symmetry points are defined as $\Gamma = (0, 0)$, $X = (\frac{\pi}{a}, 0)$, $M = (\frac{\pi}{a}, \frac{\pi}{a})$.

The three nearest neighbors are located in the real space of figure 3.5 (b) $\delta_1 = \frac{a}{2}(1, \sqrt{3})$, $\delta_2 = \frac{a}{2}(1, -\sqrt{3})$, $\delta_3 = a(-1, 0)$,

High symmetry points in the momentum space of figure 3.5 (b) are $K = (\frac{2\pi}{3a}, \pm \frac{2\pi}{3\sqrt{3}a})$, $\Gamma = (0, 0)$, $M = (\frac{2\pi}{3a}, 0)$

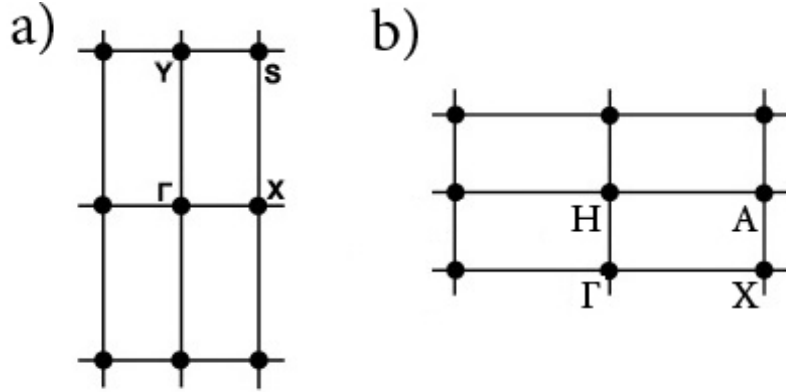


Figure 3.6: Brillouin zone of rectangular cells

In figure 3.6 (a) high symmetry points are $\Gamma = (0, 0)$, $X = (\frac{2\pi}{a}, 0)$, $A = (\frac{2\pi}{a}, \frac{5\pi}{4a})$ and $H = (0, \frac{5\pi}{4a})$. In figure 3.6 (b) high symmetry points are $\Gamma = (0, 0)$, $X = (\frac{2\pi}{a}, 0)$, $S = (\frac{2\pi}{a}, \frac{3\pi}{2a})$ and $H = (0, \frac{3\pi}{2a})$.

To calculate energy band diagram and phonon dispersion relations we used high symmetry point of these Brillouin zones.

3.3 2D Structures Based on GaAs

3.3.1 Investigation of the (100) surface

At first, we investigated the (100) surface of GaAs. This surface is the polar surface of GaAs. We have taken the upper two layers of GaAs in the (100) direction and removed the other parts. Hence we obtained one layer of As atoms on top of the one layer of Ga atoms. Also, we wanted to avoid interaction between periodic images in the z direction. For this we set at least 10 Å of free space between the one set and second set of GaAs layer in the z direction. Figure 3.7 illustrates our initial values. We carried out our geometry relaxation calculations with using these 1x1, 2x2 and 3x3 cells.

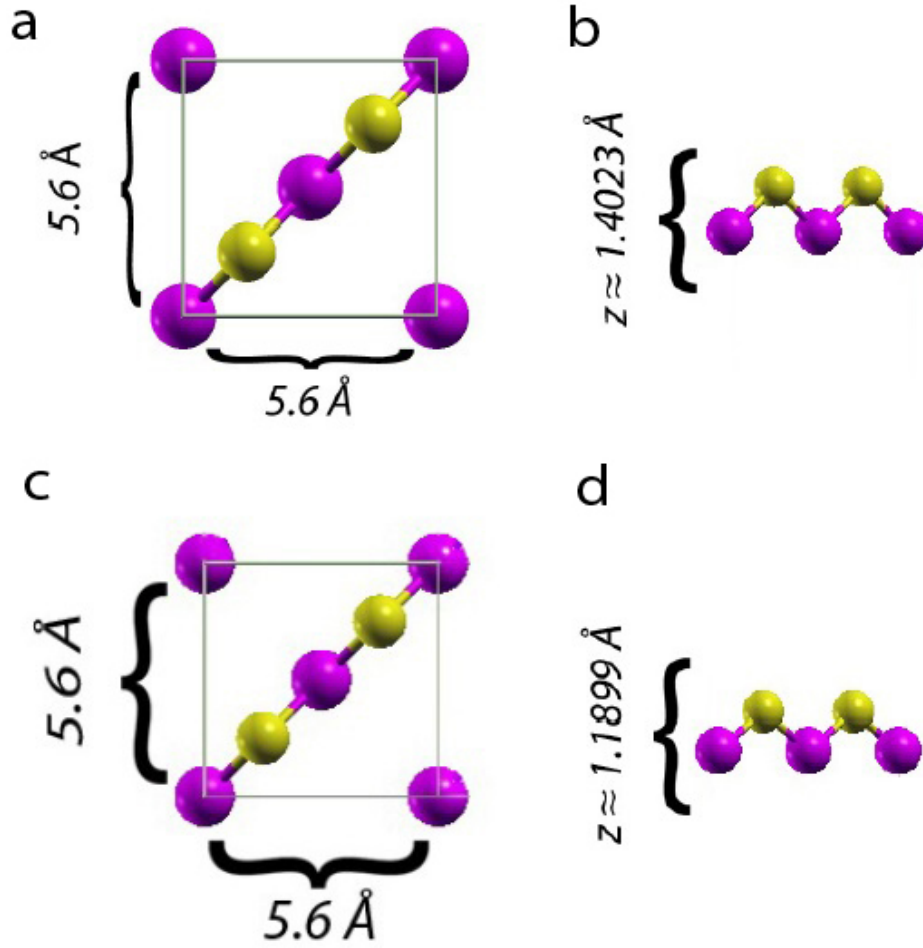


Figure 3.7: (a) Initial structure's top view of 2D material based on (100) surface. (b) Initial structure's side view of 2D material based on (100) surface. (c) Final structure's top view of 2D material based on (100) surface. (d) Final structure's side view of 2D material based on (100) surface.

Figure 3.7 (a) and (b) displays initial structures before geometric optimization. Figure 3.7 (c) and (d) show the final structure after geometry optimization. The lattice is not a honeycomb like graphene but after relaxation calculation system showed tendency to reduce the buckling. As it can be seen that after relaxation buckling is reduced from $\Delta = 1.40 \text{ nm}$ to $\Delta = 1.19 \text{ nm}$. For further investigation of stability we calculated phonon dispersion relation.

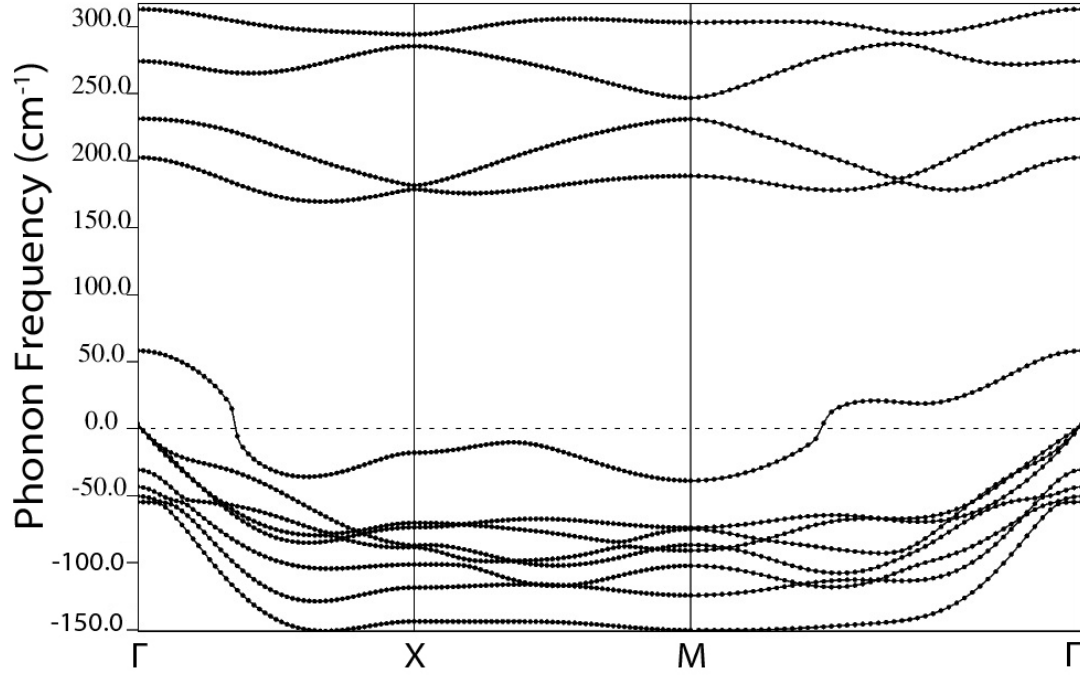


Figure 3.8: Phonon band diagram of 2D structure which is based on (100) surface of GaAs

Figure 3.8 shows that system has negative phonon modes. This means that this 2D structure is not stable. These negative phonon modes are the result of $w^2 < 0$ equation. Here w is the frequency. This equation gives us imaginary modes. Negative frequencies (i.e., negative squared frequencies) actually mean imaginary.

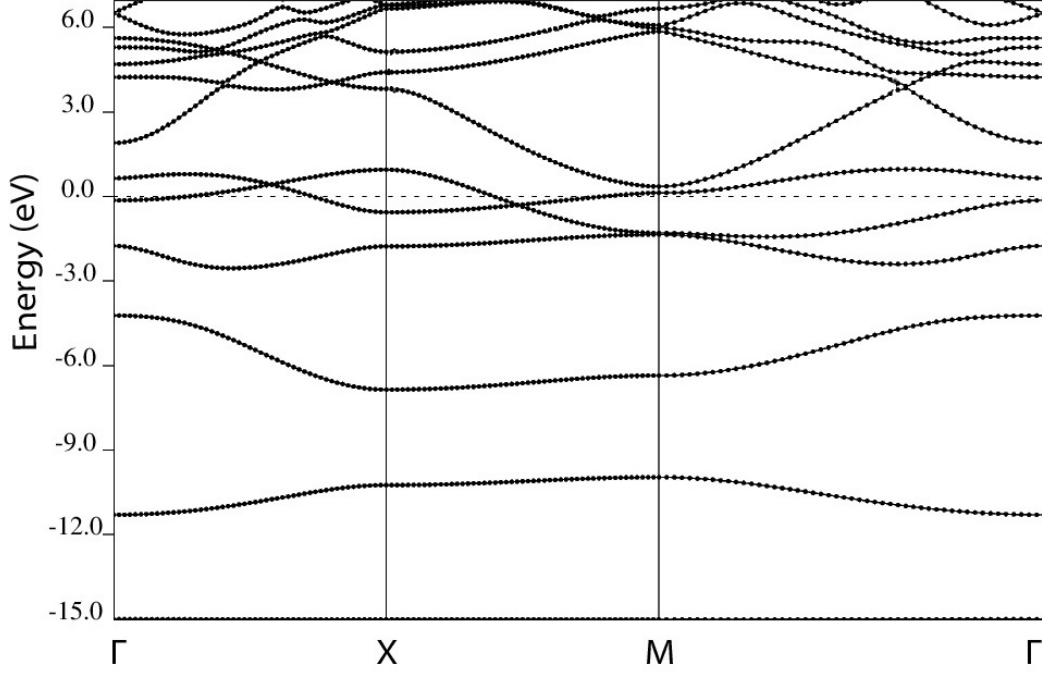


Figure 3.9: Energy band diagram of 2D structure which is based on (100) surface of GaAs

Then we examined the electronic properties of this system. The energy band diagram in figure 3.9 shows us this system in figure 3.7 has no band gap between the valance and conduction band. From this result we can say that this system shows metallic behavior in contrast to bulk GaAs

3.3.2 Investigation of the (110) surface

To obtain a 2D structure from the (110) surface we used the same method with the previous (100) surface. We carried out geometry relaxation calculations in 1x1, 2x2 and 3x3 cells. But in this calculation to reduce computational time we reduced our primitive cell to the most simplest one as in figure 3.10. In (110) surface Ga atoms and As atoms are in the same layer. After we performed geometry relaxation and find optimized structure, to examine the electronic properties of

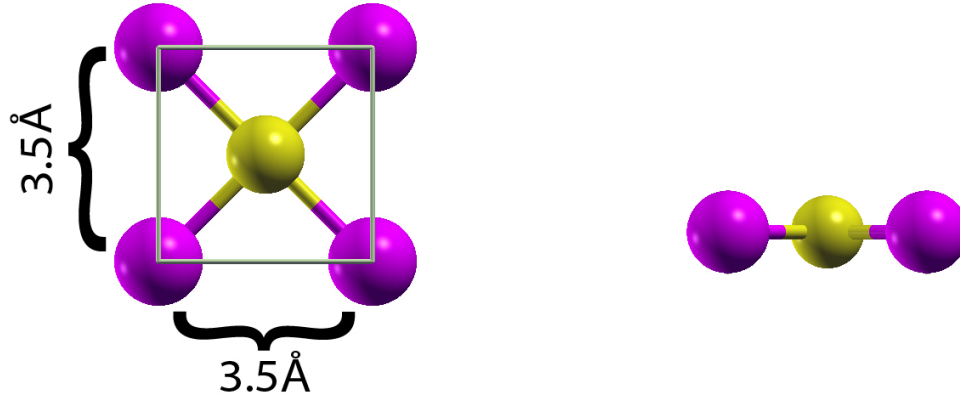


Figure 3.10: a) Top view of 2D final structure, based on (110) surface(1x1). b) Side view of 2D final structure, based on (110) surface(1x1).

this structure we carried out energy band diagram calculation. From this surface we obtained two possible structures which can form 2D materials. For both of them we performed geometry relaxation calculations. First cell is a square cell which has the length $a=3.5\text{\AA}$ for one side of the cell.

After the relaxation this system remained flat. After this we performed phonon and energy band structure calculations.

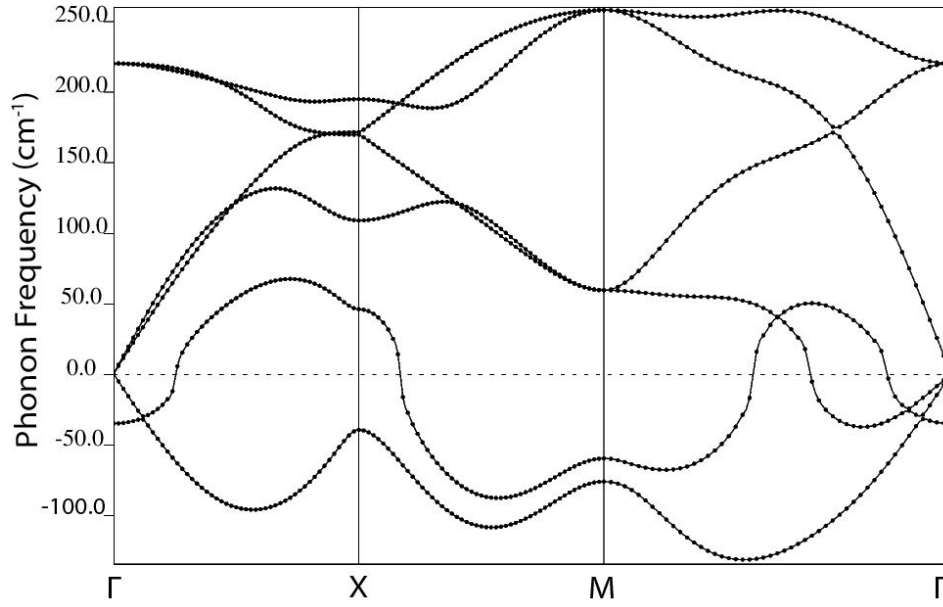


Figure 3.11: Phonon dispersion relation of 2D surface which has a square lattice based on (110) surface of GaAs

Figure 3.11 has negative phonon modes. This shows that 2D material which has a square lattice obtained from (110) surface of GaAs is not stable.

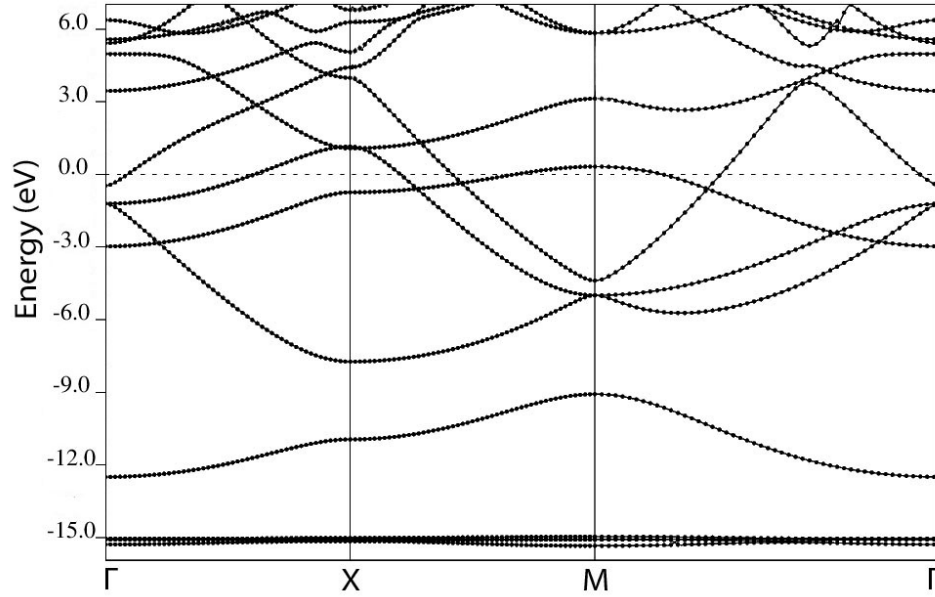


Figure 3.12: Energy band diagram of 2D structure which is based on (110) surface of GaAs

Then we performed energy band calculations. From figure 3.12 we see that there is no band gap. Because of this we can say that this system in figure 3.10 shows metallic behavior.

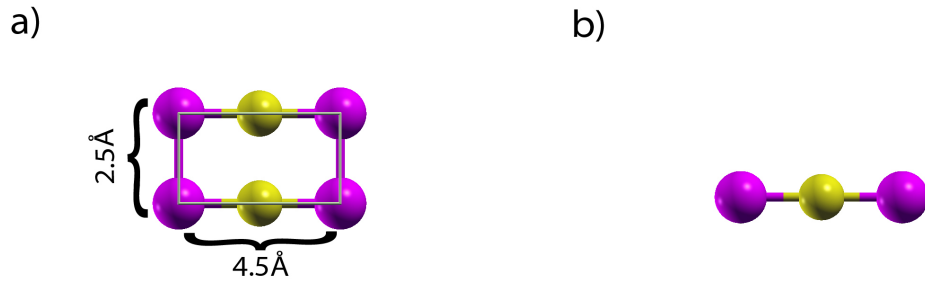


Figure 3.13: a) Top view of 2D final structure, based on (110) surface(1x1). b) Side view of 2D final structure, based on (110) surface(1x1).

The second possible 2D surface which we obtained from (110) surface of GaAs

is similar to (100) surface structure, but it has a rectangular unit cell as shown in the figure 3.13.

As before the previous structure after performing the geometry relaxation calculation this system saved its geometrical shape. To check stability we performed phonon band calculation.

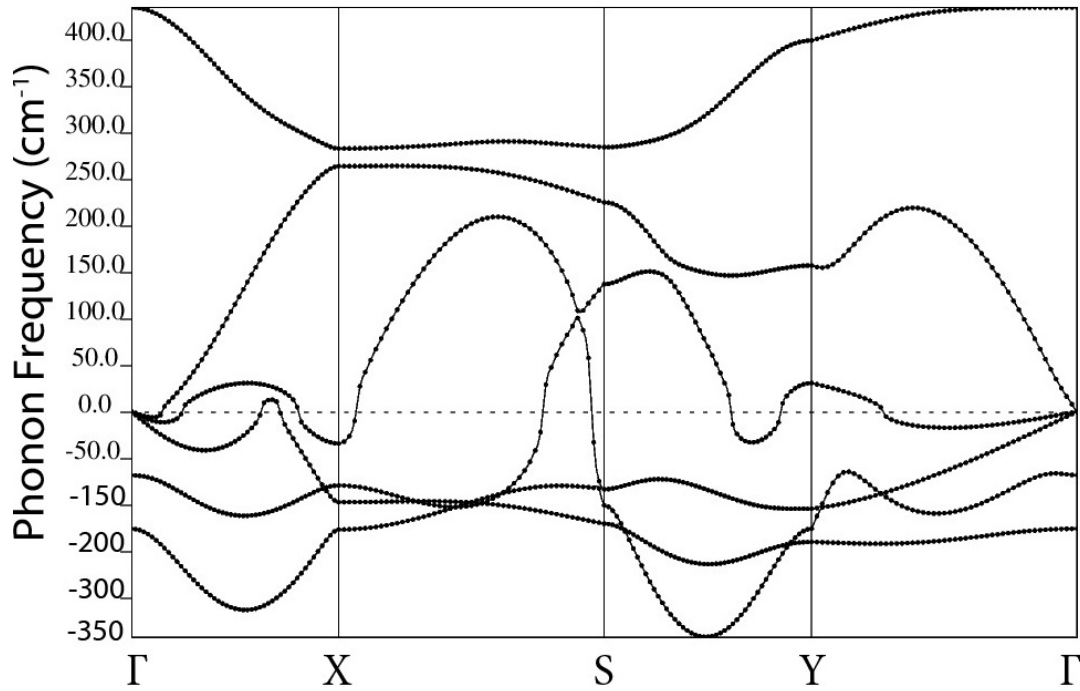


Figure 3.14: Phonon dispersion relation of 2D structure which is based on (110) surface of GaAs

This phonon diagram in figure 3.14 shows that again we have negative phonon modes. Hence we can say that system in figure 3.13 is unstable. After this we carried out energy band diagram calculation as it shown in the figure 3.15

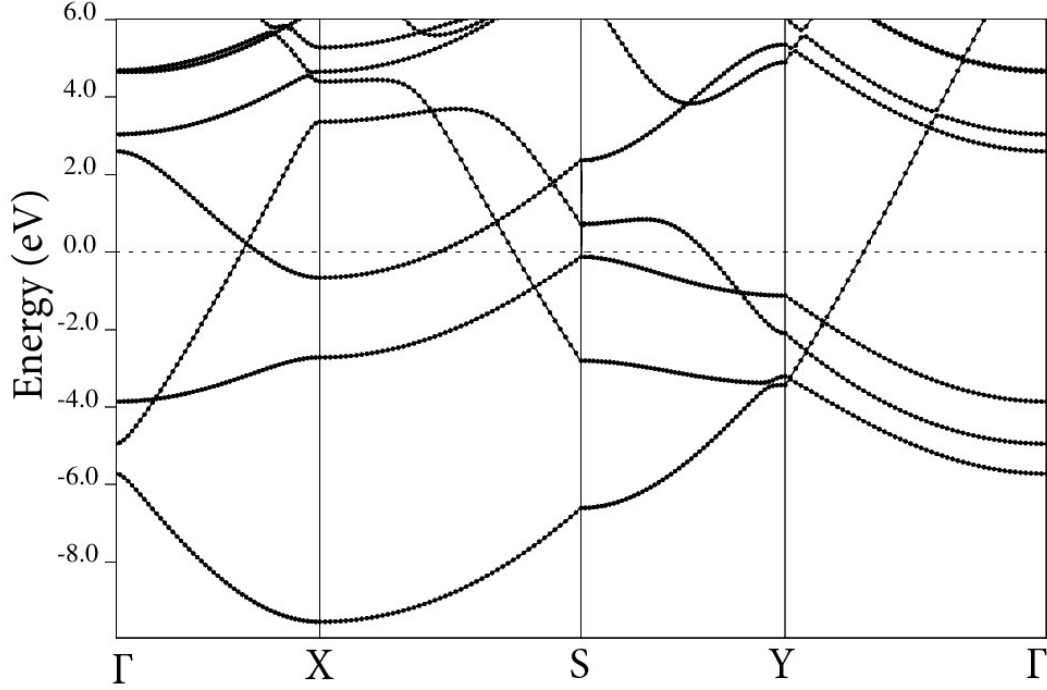


Figure 3.15: Energy band diagram of 2D structure which is based on (110) surface of GaAs

As in the previous structure, from figure 3.15 energy band diagram this system hasn't got an energy band gap between the valance band and conduction band. Hence we can say that the system in figure 3.13 shows metallic behavior.

3.3.3 Investigation of the (111) surface

As in the previous parts, we investigated 2D structures which are based on (111) surface of GaAs. This surface has differences from (100) and (110) surfaces. It has a triangular lattice similar the honeycomb structure of graphene. Instead of one kind of atom (C) as in the graphene we have two different kind of atoms, Ga and As, in our basis. To avoid computational costs we used the smallest possible primitive cell for phonon calculation. The Brillouin zone of this structure similar with the graphene. For this structure, we have performed geometry optimization for 1x1, 2x2 and 3x3 cells. In each calculation, we obtained an optimized structure

from geometry relaxation. Then we examined the electronic properties of this material.

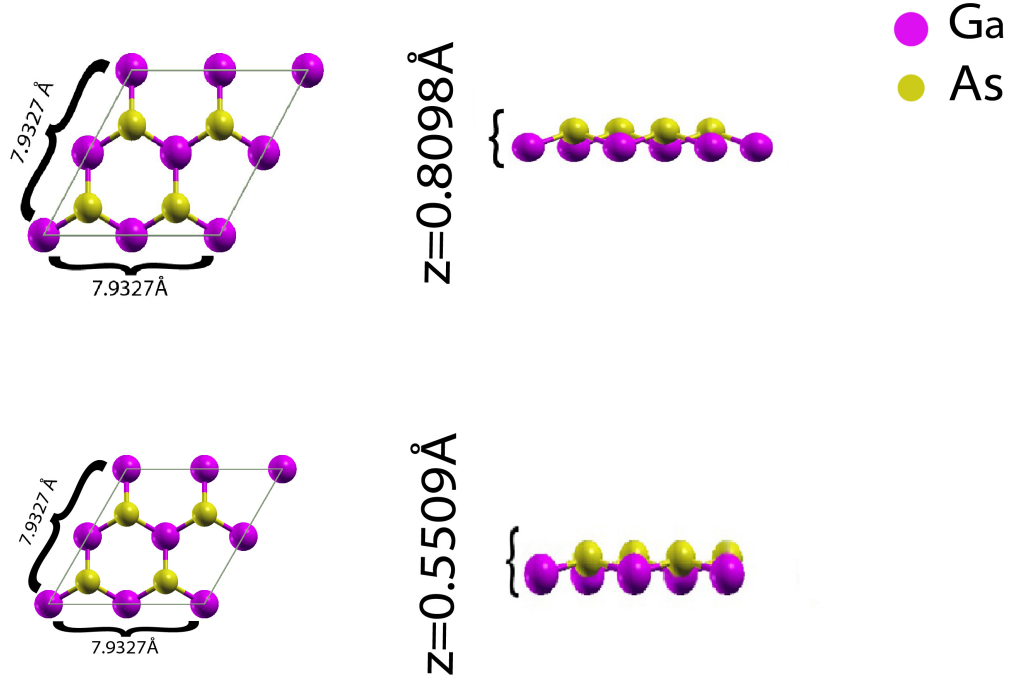


Figure 3.16: a) Top view of initial 2D structure of (111) surface(1x1), b) Side view of initial 2D structure of (111) surface(1x1), c) Top view of final 2D structure of (111) surface(1x1), d)Top view of final 2D structure of (111) surface(1x1)

As it can be seen from figure 3.16 after geometry relaxation this 2D structure shows tendency to reduce buckling from $\Delta = 0.81 \text{ \AA}$ to $\Delta = 0.55 \text{ \AA}$. Even we have an hexagonal lattice structure as in the graphene case this system has small buckling (LB). Then to check stability, we performed phonon dispersion relation for this system.

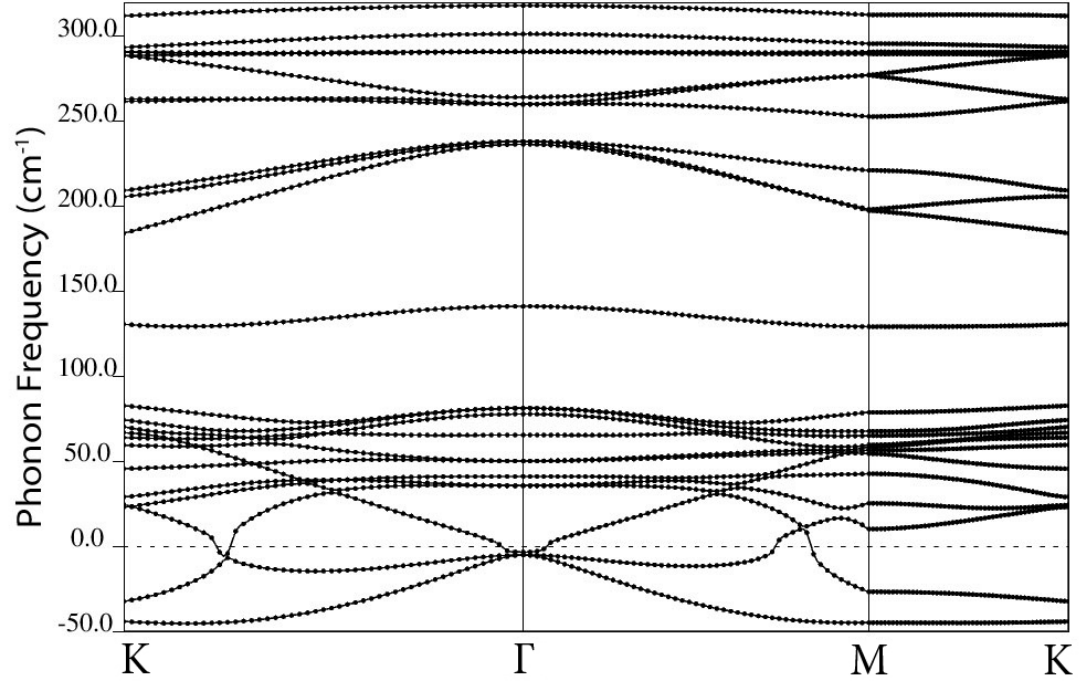


Figure 3.17: Phonon band diagram of 2D structure which is based on (111) surface of GaAs

As seen in figure 3.17 this 2D system has negative phonon modes. Because of this we can say that this system is not stable. After this we checked its electronic properties.

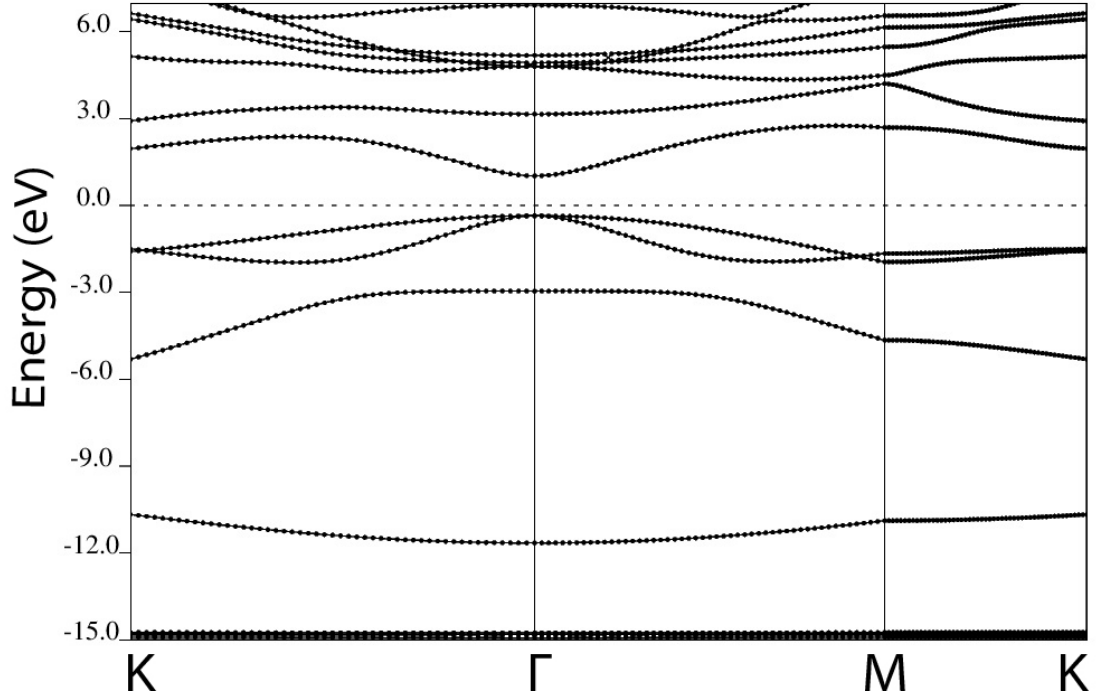


Figure 3.18: Energy band diagram of 2D structure which is based on (111) surface of GaAs

In figure 3.18 we see that energy band gap of this system in figure ?? is approximately 1.7 eV. Hence we can say that this material shows semiconductor behaviors.

3.3.4 Investigation of Oxygen used 2D material which is based on GaAs

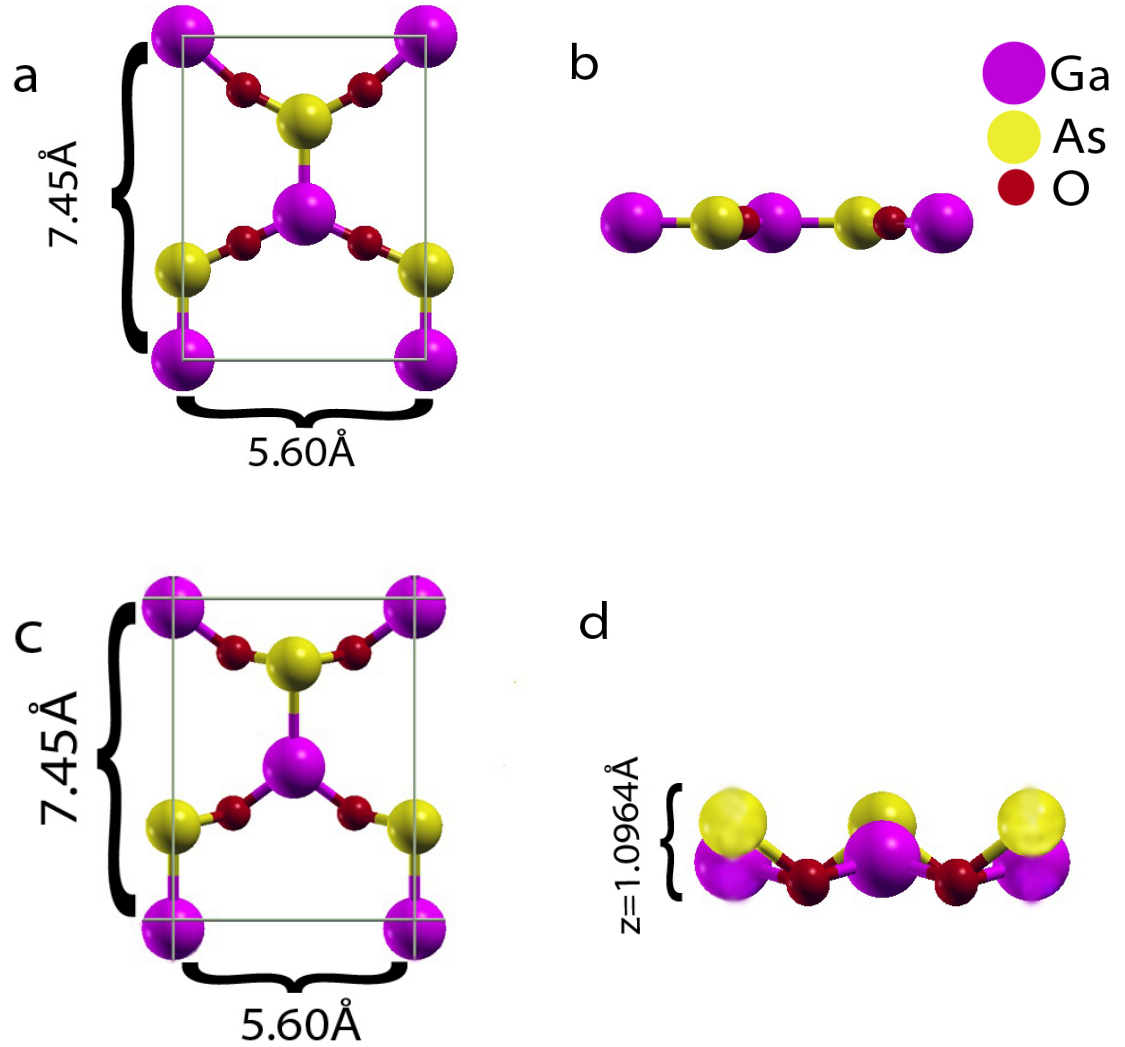


Figure 3.19: a) Top view of initial structure b) Side view of initial structure c) Top view of optimized structure d) Side view of optimized structure

To reduce the dipole moment of GaAs (100) surface we added oxygen to our system. After geometry optimization, we tried to find the most probable structure for this system. While examining these possibilities we tried to find optimized states among the many possibilities. In the end we defined a possible state as

in figure 3.19 and performed our calculations for this system. After geometry relaxation, we examined the electronic properties of this material and phonon dispersion relations. Hence, we identified the stability of this system.

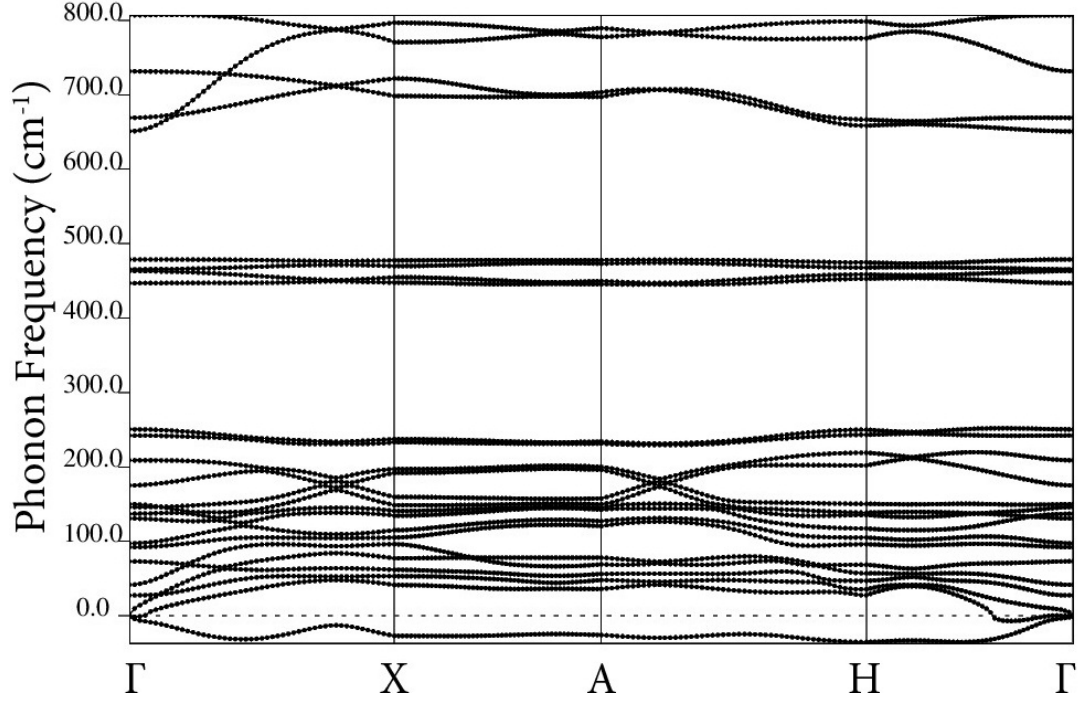


Figure 3.20: Phonon band diagram of 2D structure which is based on Oxygen and GaAs surfaces

In figure 3.20 phonon dispersion relation has a negative mode. If we compare the previous 2D materials which are obtained from GaAs surfaces, it is small but still this causes an instability.

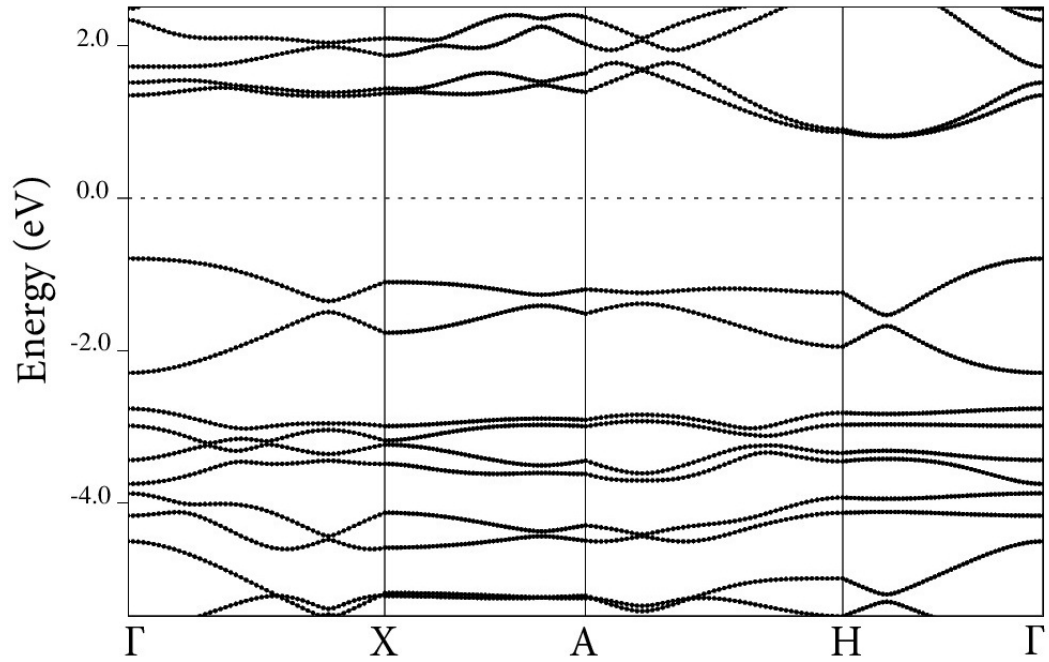


Figure 3.21: Energy band diagram of 2D structure which is based on oxygen and GaAs surfaces

Figure 3.21 shows a band gap between the valance and the conduction band has an energy band gap approximately band gap is approximately 2.7 eV. This tells us this material shows semiconductor behavior.

Chapter 4

Conclusion

In this study, we presented possible two dimensional structures based on GaAs (100), (110) and (111) surfaces with Ga, As and O atoms. There is no such kind of two dimensional material, which is reported, yet. To find possible structure types to get a two dimensional lattice, we performed geometry optimization and after that we identified, stable structures. But phonon dispersion relations showed that these systems have phonon modes with negative energy which indicates that systems instable. We showed that even we get such kind of instability still it may be possible to get stable systems which is based on GaAs surfaces with Ga, As and O atoms. The reason behind that there are many possibilities to get such kind of behavior with using these atoms and there isn't any defined lattice structure. The lattice structure may affect phonon dispersion relations and can cause instability. If optimization process may lead new structure for lattices it may possible to get stable two dimensional materials.

Another way to get a stable system from these structures we can change the number of atoms as well as cell structure. This may lead new relaxed surfaces with different number of atoms and with a different geometry. These two things may completely change the stability and other physical properties of these possible structures.

For these possible two dimensional systems, we found negative phonon modes. This tells us our two dimensional systems are not stable. But still this study gives us important knowledge about these possible systems. Further investigation, may lead us to predict theoretically such kind of two dimensional materials as in case of silicene and germanene.

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Appendix A

Quantum Espresso Input

Input file sample for geometry relaxation

```
&control
  calculation='relax'
  prefix='GaAs'
  tstress = .true.
  tprnfor = .true.
  pseudo_dir = '/truba_scratch/merol/espresso/',
  outdir = '/truba_scratch/merol/espresso/TMP3x3/'
  nstep=200

/
&system
  ibrav= 8, celldm(1) = 11.0, celldm(2) = 1.2808644198, celldm(3)=3, nat
  ecutwfc =50, occupations = 'smearing', degauss = 0.05
/
&electrons
  electron_maxstep=200
  mixing_beta = 0.7
  conv_thr = 1.0d-6
```

```

/
&ions
ion_dynamics='damp',
pot_extrapolation = 'second_order',
wfc_extrapolation = 'second_order'
/
ATOMIC_SPECIES
Ga 69.723 Ga.pz-dn-kjpaw_psl.0.2.UPF
As 74.921595 As.pz-n-kjpaw_psl.0.2.UPF
O 15.9994 O.pz-n-kjpaw_psl.0.1.UPF
ATOMIC_POSITIONS (alat)
Ga .
Ga .
As .
As .
O .
O .
O .
O .
KPOINTS automatic
6 6 1 1 1 1

```

Input file sample for phonon calculation

```

phonons of GaAs
&inputph
tr2_ph=1.0d-14,
ldisp=.true.,
nq1=4, nq2=4, nq3=1
amass(1)=69.72,
amass(2)=74.92,
prefix='GaAs',
outdir='/truba_scratch/merol/espresso/Phonon/Layer4/'

```

```
outdir='./tmplayer4/'  
fildyn='layer4.dyn',  
/
```