ELECTRONIC STRUCTURE SIMULATION OF GALLIUM ARSENIDE CLUSTERS

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Specially dedicated to my beloved husband and parents for setting me on the path towards intellectual pursuit. My sisters and brother for their continuing support along the way

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ABSTRACT

Semiconductor clusters have occupied the centre of scientific interest because of their unique electronic nature. Among the group III-V compound clusters, the gallium arsenide clusters have been the focus of this research due to their importance in constructing fast microelectric devices. The electronic structures of gallium arsenide clusters were studied. The simulations were carried out by using VASP (*Vienna Ab-Initio Software Package*) which utilizes the method of density functional theory (DFT) and plane wave basis set. Gallium arsenide clusters with surface passivated by hydrogen, $\mathrm{Ga}_x\mathrm{As}_y\mathrm{H}_z$ were simulated to obtain the density of states (DOS) as well as bandstructure for each cluster. From the DOS graphs, discrete spectrum was observed instead of bulk-like continuous DOS which is the evolvement from bulk to nano-size. Bandstructure graphs also showed the discrete energy level in consistence with the discrete energy spectrum from DOS. It was found that the bandgaps for hydrogenated gallium arsenide clusters decreases with the increase in cluster size. Bare unhydrogenated gallium arsenide clusters, $\mathrm{Ga}_x\mathrm{As}_y$, with the number of atoms ($x + y \leq 15$) were also simulated. Optimization was performed to obtain the ground state structure. The bandgaps for the ground state gallium arsenide clusters do not show a decreasing trend with the increament of cluster size as that of hydrogenated gallium arsenide cluster. The electronic structures of optimized clusters are affected by the surface orientation of the clusters. Comparison of the bandgap values for $\mathrm{Ga}_x\mathrm{As}_y\mathrm{H}_z$ and $\mathrm{Ga}_x\mathrm{As}_y$ were also made.

ABSTRAK

Semikonduktor kluster menjadi matlamat kajian dalam bidang sains disebabkan oleh sifat elektronik semulajadinya. Antara gabungan kluster kumpulan III-V, kluster gallium arsenida menjadi tumpuan dalam kajian ini kerana kepentingannya dalam pembuatan peranti mikroelektrik yang lebih pantas. Struktur elektronik kluster gallium arsenida telah dikaji. Simulasi kajian telah dijalankan dengan menggunakan perisian VASP (*Vienna Ab-Initio Software Package*) yang menggunakan teori fungsian ketumpatan dan set basis gelombang satah. Simulasi ke atas kluster gallium arsenida yang permukaannya dipasifkan dengan hidrogen, $Ga_xAs_yH_z$ telah dilakukan untuk mendapatkan ketumpatan keadaan dan juga struktur jalur untuk setiap kluster. Daripada graf ketumpatan keadaan, spektrum diskrit telah diperolehi. Perubahan ketumpatan keadaan daripada selanjar bagi struktur pukal ke spektrum diskrit bagi struktur nano merupakan evolusi nano. Struktur jalur juga menunjukkan aras tenaga diskrit yang selaras dengan spektrum diskrit daripada ketumpatan keadaan. Jurang jalur untuk gallium arsenida terhidrogenasi semakin berkurang apabila saiz kluster meningkat. Simulasi ke atas kluster gallium arsenida tulen (tak terhidrogenasi), Ga_xAs_y yang mempunyai bilangan atom ($x + y \leq 15$) juga dilakukan. Optimasi dilaksanakan untuk mendapatkan struktur keadaan dasar. Jurang jalur bagi struktur keadaan dasar kluster-kluster itu tidak menunjukkan aliran yang menurun dengan peningkatan saiz kluster seperti yang berlaku pada kluster gallium arsenida terhidrogenasi. Struktur elektronik kluster-kluster optimum dipengaruhi oleh orientasi permukaan kluster. Perbandingan nilai jurang jalur bagi $Ga_xAs_yH_z$ dan Ga_xAs_y telah dilakukan.

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LIST OF ABBREVIATIONS

ATLAS	-	Automatically Tuned Linear Algebra Software
BLAS	-	Basic Linear Algebra Subprograms
BO	-	Born Oppenheimer
BP	-	Becke-Perdew
BSSE	-	Basis set superposition error
CC	-	Coupled cluster theory
CG	-	Conjugate gradient
CI	-	Configuration Interaction
CMS	-	Computational materials science
DFT	-	Density functional theory
DOS	-	Density of states
ETB	-	Empirical tight binding
EPM	-	Empirical pseudopotential method
EMA	-	Effective mass approximation
FFT	-	Fast-fourier transform
GEA	-	Gradient expansion approximation
GGA	-	Generalized gradient approximation
GTO	-	Gaussian-type orbital
GVB	-	Generalized valence bond
HF	-	Hartree Fock theorem

HK	-	Hohenberg-Kohn
HOMO	-	Highest Occupied Molecular Orbital
HPC	-	High-performance cluster
IFC	-	Intel Fortran Compiler
Intel® MKL	-	Intel Math Kernel Library
KS	-	Kohn-Sham theorem
LCAO	-	Linear combination of atomic orbitals
LDA	-	Local density approximation
LAPACK	-	Linear Algebra PACKage
LM	-	Langreth-Mehl
LSDA	-	Local spin density approximation
LUMO	-	Lowest Unoccupied Molecular Orbital
LYP	-	Lee-Yang-Parr
MCSCF	-	Multi-Configurations Self Consistent Field
MD	-	Molecular dynamics
MGGA	-	Meta-Generalized Gradient Approximation
MPI	-	Message Passing Interface
NC-PP	-	Norm-conserving pseudopotential
NFS	-	Network file system
PAW	-	Projected Augmented Wave
PBE	-	Perdew-Burke-Ernzernhof
PES	-	Potential energy surfaces
PP	-	Pseudopotential
PW	-	Plane Wave
PW91	-	Perdew-Wang 1991
RMM	-	Residual minimization scheme
rPBE	-	Revised-Perdew-Burke-Ernzernhof
RPA	-	Random phase approximation
SA	-	Simulated annealing
SCF	-	Self-consistent functional

SSH	-	Secure Shell
SET	-	Single-electron transistor
STO	-	Slater-type orbitals
US-PP	-	Ultrasoft Vanderbilt pseudopotential
VASP	-	Vienna Ab-Initio Software Package
VWN	-	Vosko-Wilk-Nusair
QMC	-	Quantum Monte Carlo
WF	-	Wavefunction

LIST OF SYMBOLS

E - Energy

E_F - Fermi Energy

E_g - Energy gap / bandgap

E_{XC} - Exchange-correlation energy

$f(E)$ - Fermi energy

F - Force

$g(E)$ - Density of states

g - Spin-scaling factor

G - Reciprocal lattice vector

$\hbar$ - Planck’s constant

h - Dirac constant

H - Hamiltonian

$J[n]$ - Coulomb interaction

k - Wavenumber

k_B - Boltzmann’s constant

L - Edge length

$\hat{L}$ - Angular momentum operator

m - Mass

n - Quantum number of state (integer)

N - Number of electron

$n(\vec{r})$ - Electron density

p - Momentum

$\hat{p}_r$ - Linear momentum operator

$\tilde{p}_{lm\varepsilon}$ - Projector function

r, $\vec{r}$ - Position vector

r_i - Electron spatial coordinates

r_s - Wigner-Seitz radius

$R_{nl}(r)$ - Radial wavefunction

R - Radius

R_A - Nuclei spatial coordinates

s, t - Dimensionless density gradient

t - time

T_o - Kinetic energy

T - Temperature

u_k - Bloch function

U - Potential Energy

V - Volume

$Y_l^m(\theta,\varphi)$ - Spherical harmonic

Z_A - Nuclei charge

λ - Wavelength

$^2\Delta$ - Second-order difference energy

Ψ - Wavefunction

υ - Velocity

ω - Angular frequency

ν - Frequency

$\phi(r)$ - Envelope function

Θ - Unit step function

ε - Energy

ε_i - Single-particle energy level

μ - Chemical potential

∇ - Laplacian operator

ξ - Spin-polarization

$\tau(\vec{r})$ - Kinetic energy density

Ω - Volume of unit cell

η - Voltage division factor

ρ - Density matrix

Ga - Gallium

As - Arsenide

Ga_xAs_y - Gallium arsenide cluster with x,y atom

$Ga_xAs_yH_z$ - Hydrogenated gallium arsenide cluster with x,y atom and z hydrogen atom

S_N - Speedup

E_N - Efficiency

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

In recent years, the structure and properties of microclusters of pure and compound semiconductors have received much attention and have been the subject of great interest both for experimental and theoretical studies. The structure and electronic properties of clusters can be dramatically different from those of the bulk due to the high surface area to volume ratio. The addition of a few atoms to a cluster can also result in major structural rearrangement [1].

Studies of clusters become important also because bulk and surface effects can be modeled using only a few atoms or a supercell of a typical cluster size. Moreover, with the rapid advancement in science and technology, electronic devices have been reduced in size and the behavior of semiconductor surface properties has thus gained more attention. The relation between the geometry and the electronic structure plays a critical role in dictating the properties of a material.

In the case of semiconductors, this evolution is remarkable. Semiconductor clusters have been shown to exhibit exotic properties quite different from those in molecules and solids. Compared to homogeneous clusters such as carbon and silicon, heterogeneous semiconductor clusters like gallium arsenide are more attractive because their properties can be controlled by changing the composition, in addition to the size. For these reasons, theoretical studies on clusters are critical to the design and synthesis of advanced materials with desired optical, electronic, and chemical properties.

However, theoretical studies of heterogeneous semiconductor clusters have been limited due to computational difficulties arising from the large number of structural and permutational isomers formed due to multiple elements. On one hand, sophisticated computational method such as self-consistent quantum mechanical calculation is required to make reliable prediction on the properties of these clusters, in the absence of comprehensive experimental results. On the other hand, the amount of computational work is enormous in order to find all the stable isomers for a given cluster size and composition. A number of theoretical and experimental attempts [2-14] have been made to determine the structure and properties of small Ga_xAs_y clusters. Most of the theoretical studies have been focused on clusters of a few atoms due to the above mentioned difficulties.

1.2 Atomic and Molecular Clusters

Study of physical and chemical properties of clusters is one of the most active and emerging frontiers in physics, chemistry and material science. In the last decade or so, there has been a substantial progress in generation, characterization and understanding of clusters. Clusters of varying sizes, ranging from a few angstroms to nanometers, can be generated using a variety of techniques such as sputtering, chemical vapor deposition, laser vaporization, supersonic molecular beam etc. Their electronic, magnetic, optical and chemical properties are found to be very different from their bulk form and depend sensitively on their size, shape and composition.

Thus, clusters form a class of materials different from the bulk and isolated atoms/molecules. Looking at the mass distribution of clusters, some are found to be much more abundant than others. These clusters are therefore more stable and are called magic clusters. They act like superatoms and can be used as building blocks or basis to form a cluster assembled solid. It is these kinds of developments that add new frontiers to material science and offer possibilities of designing new materials with desirable properties by assembling suitably chosen clusters. The Table 1 show the schematic classification of clusters according to the number N of atoms.

Table 1.1: Schematic classification of clusters according to the number N of atoms.

Observable	**Very small clusters**	**Small clusters**	**Large clusters**
Number of atoms N	$2 \leq N \leq 20$	$20 \leq N \leq 500$	$500 \leq N \leq 10^7$
Diameter d	$d \leq 1$ nm	1 nm $\leq d \leq$ 3 nm	3 nm $\leq d \leq$ 100 nm
Surface fraction f	undefined	$0.5 < f < 0.9$	$f \leq 0.5$

It should be recognized that if we are to harness full technological potential of clusters, we have to gain a fundamental scientific understanding of them. This involves, for example, understanding why clusters are different from atoms and bulk, what is their geometry and structure and how it evolves with size, the evolution of their electronic, optical, magnetic and chemical properties with size and the high stability of some clusters.

Such an understanding will teach us how we can modify the cluster structure to get a desired property. These are difficult research problems because clusters are species in their own right and do not fall into the field of atoms or solid state. Thus many techniques of atomic or solid state physics are just not applicable to clusters. New techniques of applying quantum mechanics have to be developed to handle clusters. Similarly, thermodynamics of clusters is of great importance. Many thermodynamical relationships which are derived for the bulk form are not applicable to clusters. Thus one requires new approaches to concepts of melting, freezing and phase changes in dealing with finite clusters and their dependence on size. An understanding of these concepts is important for developing technologies based on clusters.

Since many cluster properties such as geometry and structure of a cluster are not directly measurable from experiments, theoretical models and computation play an important role in the study of clusters. In this respect, the Density Functional Theory (DFT) which is designed to handle a large number of electrons quantum mechanically, has been found to be extremely useful. Using this theory one can calculate very accurately the total energy and other properties of a many electron system in its ground state (ground state energy is the lowest energy of a system; lately, the DFT has also been developed to calculate excited states).

1.3 Applications of Clusters

Clusters are an important state of matter, consisting of aggregates of atoms and molecules that are small enough not to have the same properties as the bulk liquid or solid. Quantum states in clusters are size-dependent, leading to new electronic, optical, and magnetic properties. Clusters offer attractive possibilities for innovative technological applications in ever smaller devices, and the ability to "tune" properties, especially in semiconductors, may produce novel electronic and magnetic capabilities.

Semiconductors are one of the most active areas of cluster research. Many of their properties are very dependent on size; for example, optical transitions can be tuned simply by changing the size of the clusters. Alivisatos [15] describes current research on semiconductor clusters consisting of hundreds to thousands of atoms--"quantum dots." These dots can be joined together in complex assemblies. Because of the highly specific interactions that take place between them, a "periodic table" of quantum dots is envisioned. Such coupled quantum dots have potential applications in electronic devices.

The magnetic properties of clusters are of fundamental interest and also offer promise for magnetic information storage. Shi *et al*. [16] describe recent developments in the study of magnetic clusters, both isolated and embedded in a host material. Such clusters can behave like paramagnets with a very large net moment--superparamagnets. Superparamagnetic particles can be embedded in a metal and show dramatic field changes in electrical conduction. Ion implantation has generated ferromagnetic clusters embedded in a semiconductor host, which can be switched individually.

The constituents of clusters can be arranged in many different ways: Their multidimensional potential energy surfaces have many minima. Finding the global minimum can be a daunting task, to say nothing of characterizing the transition states that connect these minima. Wales [17] describes the fundamental role of the potential energy surface in the understanding of the structure, thermodynamics, and dynamics of clusters. In a Report accompanying the special section, Ball *et al*. [18] analyze Ar_{19} and $(KCl)_{32}$ clusters and illustrate how potential energy surface topography (the sequences of minima and saddles) governs the tendency of a system to form either amorphous or regular structures.

Water is essential to life and to a great number of chemical processes. Hydrogen bonding, the source of many of water's most interesting properties, requires at least two water molecules. Far-infrared laser vibration-rotation tunneling experiments on supersonically cooled small clusters allow characterization of geometric structures and low-energy tunneling pathways for rearrangement of the hydrogen bond networks. Liu *et al.* [19] describe how these and other recent experiments on water clusters give insight into fundamental properties of water.

Simple aggregates of carbon atoms, especially C_{60}, are remarkably stable. Determination of their actual physical and electronic structures is a formidable task because of the large number of electrons and the many possible isomeric arrangements involved. Scuseria [20] reviews the status of the field, including recent advances and current challenges in ab initio algorithms.

1.4 Introduction to Modeling and Simulation

Modeling is the technique of representing a real-word system or phenomenon with a set of mathematical equations or physical model. A computer simulation then attempts to use the models on a computer so that it can be studied to see how the system works. Prediction may be made about the behavior and performance of the system by changing its variables. In this research, nanostructures are the system targets of the modeling and simulation.

Simulation is a useful and important part of modeling nanostructures to gain insight into the attributes of a structure or a whole system with several structures connected. It is a method to predict the behavior transformation for a variable changing before performing a practical experiment. The simulation can then be proven by the results of experiment. This is also a beneficial approach to test the most optimal and the best performance of a device which is built by those nanostructures before the real fabrication.

Besides, simulation can give detailed theoretical explanation to the phenomenon that could not be solely explained by experiment . Among the examples are the reconstruction of the small cluster structures and the occupation of the electrons. With the 3D graphical viewer and animation, we can view the atomic structure models and the process of the structure transformation. With computer simulation done prior to experiment, the mastering of the small cluster structures principles is improved and ‘trial and error’ could be reduced during experiment.

However, there isn’t a comprehensive simulator which can take into account every factor that would contribute to the system changes. Many of those only adopt the approximation which is the most optimal and closest to the real system for the representation. For nanostructures, first principle calculation is an appropriate simulation approach for studying the electronic structures and properties. The advantage of this calculation is that, it can be done without any experimental data. However, it could be a massive calculation that consumes a very long time to accomplish.

Computational science becomes an essential tool in modeling and simulation. It is the application of computational and numerical technique to solve large and complex problem, for example, complex mathematics that involved a large number of calculations. Therefore, modeling and simulation are commonly accomplished by the aid of computational science and therefore they are always referred to computer modeling and computer simulation. Computational science could be defined as an interdisciplinary approach that uses concepts and skills from the science, computer science and mathematic disciplines to solve complex problems which allow the study of various phenomena. It can be illustrated by Figure 1.1. To improve the performance and speed of large computation, one of the approaches is parallel computing. Parallel computing can reduce the computing time of computational costly calculations such as first principle calculations mentioned above, where it distributes the calculation to two or more processors or computers.

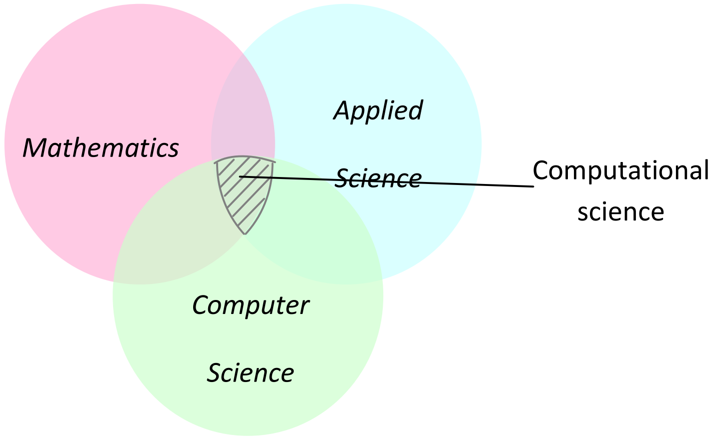

Figure 1.1: Computational science is defined as the intersection of the three disciplines, i.e. computer science, mathematics and applied science.

1.4.1 Modeling and Simulation Approach Used in This Research

In this research, Vienna Ab-initio Simulation Package (VASP) is used as the simulation tools for electronic structures of the gallium arsenide clusters. VASP is the leading density functional code to accurately compute structural, energetical, electronic and magnetic properties for a wide range of materials including solids and molecules. VASP is highly efficient for structural optimizations and ab-initio molecular dynamics (MD). It covers all elements of the periodic table of practical interest. With its projector-augmented-wave (PAW) potentials, VASP combines the accuracy of all electron methods with the elegance and computational efficiency of plane wave approaches.

1.5 Research Objectives

The main interest of this research is to study the electronic structures of gallium arsenide clusters. The objectives of this research can be summarized as the following:

a) to study the electronic structures of gallium arsenide clusters with variable size and structures.

b) to study the relation between the bandgap and the structures size of the gallium arsenide clusters.

1.6 Scopes of Study

The scopes of this research are as the following:

a) Clusters is simulated as isolated small range nanocluster.

b) Gallium arsenide is adopted as the material of the clusters.

c) Bandstructures and energy spectrum are studied for the electronic structures of gallium arsenide clusters.

d) Density functional theory is used to calculate and simulate the electronic structures of gallium arsenide clusters.

1.7 Outline of Dissertation

A general background of study and brief introduction to clusters are discussed in Chapter 1. This is followed by introduction of modeling and simulation, objective and scope of study. There are a lot of approaches to simulate the electronic structures of gallium arsenide clusters. Density functional theory (DFT) is a sufficient method in doing this. Its theory is discussed in the Chapter 2. The methodology of the simulation VASP which is utilized in this study is introduced in Chapter 3. Following this, Chapter 4 would be results and discussion. Figures and graphs of the electronic structures of gallium arsenide clusters are showed and the results are discussed and interpreted. Finally Chapter 5 which is the conclusion. Theories and results discussed in the previous chapters are summarized and concluded here. Furthermore, suggestion is given on how to make the simulation better and more complete.