

ELECTRONIC STRUCTURE OF III - V TERNARY AND QUATERNARY ALLOYS

BY
V. B. GERA

SUBMITTED TO THE
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
NEW DELHI-110016
INDIA**

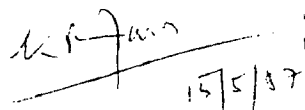
MAY, 1987

Dedicated
to
My Parents

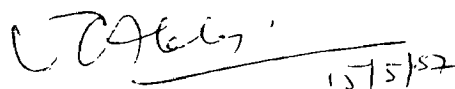
CERTIFICATE

This is to certify that the Thesis entitled "Electronic Structure of III-V Ternary and Quaternary Alloys" which is being submitted by Miss V.B. Gera for the award of Degree of Doctor of Philosophy to the Indian Institute of Technology, Delhi, is a bonafide record of research work carried out by her under our guidance and supervision.

The results have reached the standard, fulfilling the requirements of the regulations relating to the degree. The results submitted in this Thesis have not been submitted to any other university or institute for the award of any degree or diploma.


15/5/87

(PROF. K.P. JAIN)
Professor of Physics & Coordinator
Laser Technology Research Programme
Indian Institute of Technology, Delhi
New Delhi-110016


15/5/87

(PROF. S.C. ABBI)
Professor of Physics
Indian Institute of Technology, Delhi
New Delhi-110016

ACKNOWLEDGEMENT

I express my deep sense of gratitude to Professor K.P. Jain for his continuous supervision and kind encouragement at all stages of the present work. His keen interest and understanding is of far greater value to me than these formal thanks can indicate.

My sincere thanks are also due to Professor S.C. Abbi for his constant guidance and constructive suggestions throughout the tenure of this work.

It is indeed a pleasure to thank Dr. Rita Gupta whose stimulating day-to-day discussions and invaluable suggestions made it possible for me to do this work.

I am thankful to all my friends and colleagues for their encouragement and help during the course of this work.

I gratefully acknowledge the awards of fellowship provided by Electronics Commission, IIT Delhi and DST.

I extend my thanks to Mr. V.N. Sharma for neat and flawless typing of the manuscript.

I take this opportunity to express my heartfelt gratitude to my brother Ajay, to my mother and, above all, to my father, without whose inspiring guidance and moral support, it would have been impossible for me to reach this stage.

Vivian Gera

(V.B. GERA)

ABSTRACT

The electronic band structure of III-V substitutional alloys calculated within the framework of coherent-potential approximation (CPA) and tight-binding formalism are presented. The major advantage of semiconductor alloys over binary compounds is that the semiconductor alloys extend the opto-electronic properties in the spectral region intermediate to two constituent compounds. The III-V semiconductor alloys studied presently are the anion substituted ternary alloys $\text{GaAs}_{1-x}\text{P}_x$ and $\text{InAs}_{1-x}\text{P}_x$, the cation substituted ternary alloys $\text{Ga}_x\text{In}_{1-x}\text{P}$ and $\text{Ga}_x\text{In}_{1-x}\text{As}$, and the quaternary alloys $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ lattice-matched to InP and GaAs as well as the quaternary $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}_{0.5}\text{P}_{0.5}$.

The disorder in substitutional semiconductor alloys arises due to the random distribution of atoms at lattice sites, so that the translational symmetry does not exist in substitutional alloys. The disorder-induced effects have been computed within coherent-potential approximation which is treated as the best single-site approximation. The disorder in the diagonal atomic term values has been treated in CPA, while the off-diagonal disorder has been treated in virtual crystal approximation (VCA).

Band structure calculations have been performed using tight-binding method where the interactions upto and including second neighbor have been taken into account. The spin-orbit interactions have been taken into account explicitly. Tight-binding parameters of Porod et al. [J. Vac. Sci. Technol. 21,

965 (1982)] reproduce all the important gaps of involved binaries - GaP, GaAs, InP and InAs, which agree very well with the recent experimental data.

Partial s and p cation as well as anion density of states (DOS) have been computed using sampling procedure. Calculation of partial CPA self-energy Σ from partial VCA DOS is an iterative procedure starting from the value of $\Sigma = 1/4(\Delta - i\Delta)$, where Δ is the alloy scattering parameter. The real part of the complex CPA self-energy gives correction to VCA band structure, while its imaginary part gives lifetime broadening effects.

The complex energy band structure of the ternary alloys $\text{GaAs}_{0.5}\text{P}_{0.5}$, $\text{InAs}_{0.5}\text{P}_{0.5}$, $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$, where the disorder is expected to be maximum, are studied in detail. In addition, the variation of seven important states - Γ_{15v} , Γ_{1c} , X_{5v} , X_{1c} , X_{3c} , L_{3v} and L_{1c} as a function of composition x is studied for all the four ternary alloys in the whole composition range between two end-point semiconductors. It is found that CPA self-energy correction is maximum for cation s-like states. The variation of direct as well as indirect Γ -X and Γ -L energy gaps with composition x is studied within CPA for all these alloys. The calculated variation of these gaps is seen to match well with the available experimental data. The CPA bowing parameter is found to be small for anion substituted ternaries - for $\text{GaAs}_{1-x}\text{P}_x$, the calculated value is 0.177 eV, while for $\text{InAs}_{1-x}\text{P}_x$, it is 0.035 eV. For cation substituted ternary alloys, the calculated bowing is found to be large - it being 0.7 eV for $\text{Ga}_x\text{In}_{1-x}\text{P}$ and 0.79 eV for $\text{Ga}_x\text{In}_{1-x}\text{As}$. These values agree with the experimental data.

A crossover between the direct gap and indirect Γ -X gap has been obtained for the ternary alloys $\text{GaAs}_{1-x}\text{P}_x$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$. The alloy $\text{GaAs}_{1-x}\text{P}_x$ is found to be a direct gap semiconductor for $0 < x < 0.5$ and an indirect gap semiconductor for $x > 0.5$. For $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy, the crossover is obtained at $x = 0.77$, it being an indirect gap semiconductor for $x > 0.77$. Finally, the variation of E_1 -optical gap with composition x is studied for all the ternary alloys, and a good agreement between theory and experiment has been obtained.

The CPA technique has also been applied to enumerate the electronic properties of the quaternary alloy $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$. The complex energy band structure of the quaternary alloy $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}_{0.5}\text{P}_{0.5}$ is studied. The compositional variation of direct as well as the indirect Γ -X and Γ -L gaps has been studied for the quaternary alloys $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ lattice-matched to InP and GaAs. The bowing parameters calculated in VCA as well as in CPA for various values of x and y are presented for both the lattice-matched quaternary alloys. The disorder-induced effects are seen to be larger for GaAs lattice-matched quaternary than for InP lattice-matched one. This is also found to be true for the E_1 -optical gap which has been calculated for the various combinations of x and y . The compositional variation of direct gap and E_1 -optical gap for the InP lattice-matched quaternary is seen to agree with the experimental values.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	
CHAPTER 1 INTRODUCTION	1
1.1 General Background	1
1.2 Electronic Structure of Binary Semiconductors	2
1.3 Mixed Crystals or Solid Solutions of Substitutional Alloys	4
CHAPTER 2 CALCULATIONAL PROCEDURE	11
2.1 Introduction	11
2.2 CPA Formalism	12
2.3 Sampling Procedure	21
2.4 Calculation of E_1 -Optical Gap	26
2.5 Discussion	28
CHAPTER 3 TERNARY ALLOYS: ANION SUBSTITUTION	32
3.1 Introduction	32
3.2 Electronic Structure of $\text{GaAs}_{1-x}\text{P}_x$ Alloy ..	35
3.3 Electronic Structure of $\text{InAs}_{1-x}\text{P}_x$ Alloy ..	46
3.4 Conclusions	50
CHAPTER 4 TERNARY ALLOYS: CATION SUBSTITUTION	54
4.1 Introduction	54
4.2 Electronic Structure of $\text{Ga}_x\text{In}_{1-x}\text{P}$ Alloy ..	59
4.3 Electronic Structure of $\text{Ga}_x\text{In}_{1-x}\text{As}$ Alloy ..	66
4.4 Conclusions	73

CHAPTER 5	QUATERNARY ALLOYS		77
5.1	Introduction		77
5.2	Quaternary Alloy $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}_{0.5}\text{P}_{0.5}$		79
5.3	Electronic Properties of the Quaternary GaInAsP Lattice-Matched to InP		82
5.4	Electronic Properties of the Quaternary GaInAsP Lattice-Matched to GaAs		88
5.5	Summary and Discussion		92
CHAPTER 6	CONCLUDING REMARKS		93
APPENDIX	A		98
REFERENCES			102