$InAs_{1-X}P_X$ Semiconductor Solid Solutions in Modern Electronics

$InAs_{1-X}P_X$ Semiconductor Solid Solutions in Modern Electronics

By

Nodar Kekelidze,
Elza Khutsishvili,
Georgy Kekelidze
and Tengiz Qamushadze

Cambridge
Scholars
Publishing

$InAs_{1-X}P_X$ Semiconductor Solid Solutions in Modern Electronics

By Nodar Kekelidze, Elza Khutsishvili, Georgy Kekelidze
and Tengiz Qamushadze

This book first published 2022

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-8892-0
ISBN (13): 978-1-5275-8892-9

CONTENTS

ABSTRACT

This book is dedicated to the description of a special class of a diamond-like family of semiconductor materials - $InAs_{1-x}P_x$ solid solutions, which have obtained a wide practical application in semiconductor electronics and laser technology. The book is a result of many years of the scientific research implemented under the guidance of Academician Nodar Kekelidze on producing crystals of $InAs_{1-x}P_x$ solid solutions and their multifaceted study, including properties and practical applications. For a complete presentation the results of the research conducted by scientists from countries around the world on $InAs_{1-x}P_x$ solid solutions are also presented. The most promising methods of growth techniques of single bulk crystals and layers of $InAs_{1-x}P_x$ solid solutions are presented too. The basic important theoretical and experimental data on the energy zone structure and physicochemical, electrical, optical and thermoelectrical properties of these solid solutions are likewise presented. The book reveals the features of $InAs_{1-x}P_x$ solid solutions with special emphasis on radiation effects and their application.

The presented book will be useful for physicists, chemists, engineers and PhD students working in the condensed matter physics direction and on the problems of radiation physics, which are connected with the zinc blende crystal structure-like family of the mixed III-V's. The presented book can be considered as an auxiliary textbook in the study of problems associated with the physics of semiconductors.

PREFACE

Semiconductor materials are the main "driving force" of modern electronic technologies and play an important role in the economic strength of any country, national security, global competitiveness, their resilience in times of crisis, and an industry facing numerous challenges. Semiconductor materials are the basis of such new technologies in modern electronics as advanced wireless communications (5G), flexible electronics, artificial intelligence, quantum computing, and other technological innovations. Semiconductors, as an essential component of cutting-edge electronic technologies, play a major role in all areas of the economy and are an important part of individuals' lives. They are used in electronic vehicles, TVs, computers, smartphones, unique medical diagnostic equipment, global e-commerce, and more. Semiconductor-based devices have replaced older technological systems with more sophisticated mobile systems characterized by increased reliability, low cost, unusual lightness, small size, and reduced service personnel.

The rapid development of electronics requires new semiconductor materials different from classical elementary (Si, Ge) and traditional (III-V compounds) semiconductors. A great opportunity in this regard is hidden in the solid solutions of III-V semiconductor compounds. Their continuously variable basic properties allow for the expansion of the group of known semiconductor materials. Such materials include the so-called "pseudo-binary" $InAs_{1-x}P_x$ solid solutions system. Apart from the specific properties of InAs and InP compounds, new original phenomena are found in their solid solutions. $InAs_{1-x}P_x$ solid solutions, as a variant of phosphides and arsenides with fascinating unique properties, allow the selection of materials with optimal properties for specific devices, including modern electronics and laser equipment.

Today, as a result of technological advances, the flow of information on $InAs_{1-x}P_x$ solid solutions has increased dramatically. This has made it possible to describe and present the most important research results obtained in this field in a complete way with new data from the research in the form of a book. The book summarizes the current scientific knowledge on the production, properties and application of $InAs_{1-x}P_x$ solid solutions obtained by a large number of scientists from many countries of the world. The results of the many years of scientific research conducted by

Academician of the National Academy of Sciences of Georgia Dr. Phys-Math. Sci., Professor Nodar Kekelidze *et al.* at Ferdinand Tavadze Institute of Metallurgy and Materials Science (Laboratory of Semiconductor Materials Science) and Iv. Javakhishvili Tbilisi State University (Laboratory of Problems of Radiation Physics of Solid State) are among the principal material treated in this book.

The noted scientific studies were carried out in a full form, from producing the investigated semiconductor materials to their comprehensive study. For the first time a modern technology for the production of InP and InAs binary compounds and their $InAs_{1-x}P_x$ solid solutions was developed. Despite the great technological difficulties of production of phosphide-based materials, their homogeneous single crystals were obtained in laboratories that fully met all the requirements stipulated by the international standard. Modern methods and special devices for studying optical and electrical properties in a wide temperature range of 4.2K-300K have also been developed. Complex and continuous experiments have been conducted over the years.

A creative generalization of the results of existing studies of $InAs_{1-x}P_x$ solid solutions has been carried out in the present book for disseminating and sharing the accumulated knowledge of these solid solutions. In this way the inexhaustible potential of $InAs_{1-x}P_x$ solid solutions will be demonstrated. The book highlights the importance of understanding the physicochemical properties, the energy band structure and dynamics of the crystal lattice, the physical mechanisms that underlie observed transport phenomena, and radiation processes in $InAs_{1-x}P_x$ solid solutions at a fundamental level. The data presented in the book cover concepts from the fundamental physics of the semiconductor material and material science. The book will have a major impact on many applications of $InAs_{1-x}P_x$ solid solutions in modern radiation-hardened electronics. The book will be useful for specialists, undergraduates and young scientists working on the problems in condensed matter physics, particularly, the physics of semiconductors.

INTRODUCTION

At the time when technical development processes mean semiconductor materials are used in almost all areas of modern technology, it is crucial to find new semiconductor materials, which differ in their properties from classical elemental semiconductors and the group of III-V semiconductor compounds. Although these traditional semiconductors occupy the leading place in modern semiconductor technology, modern electronics is waiting for new materials with new properties. The diamond-like family of the semiconductor ternary III-V's with unlimited solubility of components and continuously variable combinations of their basic properties enable this move.

The range of properties of these solid solutions is also expanded by the fact that their characteristic parameters in some cases are not always additive values with respect to the properties of the starting components. Such substances include the so-called "pseudo-binary" system of $InAs_{1-x}P_x$ solid solutions. Their starting components InAs and InP have always attracted the attention of researchers due to their unique electronic, optical, and radiation properties. The main advantage of the ternary solid solutions is the fact that they may change properties within the limits of their binary constituents. In spite of the specific properties that InAs and InP compounds preserve to a certain extent in their triple analogues, in addition to the known, new original phenomena are found in solid solutions. $InAs_{1-x}P_x$ solid solutions, as a variant of phosphides, and having fascinating unique properties, have always attracted researchers too due to the possibility of merging the desirable and eliminating the undesirable properties of InAs and InP.

The first semiconductor systems to reveal the solid solubility properties of Ill-V compounds were $InAs_{1-x}P_x$ and $GaAs_{1-x}P_x$ solid solutions as reported by Folberth [1]. However, at that time, and due to the discovery of the semiconductor injection laser and the need for visible-light emitting devices, $GaAs_{1-x}P_x$ solid solutions received a much wider attention as materials owing visible-light emission properties. Although stimulated emission from $InAs_{1-x}P_x$ was obtained as early as 1964, little effort was invested in preparing these solid solutions epitaxially. Due to the high vapor pressure of the As and P, the technology for producing $InAs_{1-x}P_x$ solid solutions has been very complex and received very little attention.

However, the possibility of their widespread use in electronics technology was a strong stimulus for the development of their production technology. There was a need to develop methods of homogenization, which were not needed when working with binary III-V compounds. The search began for methods that made it possible to obtain homogeneous phases immediately after synthesis. The great technological difficulties in producing of $InAs_{1-x}P_x$ solid solutions can be considered as almost overcome today.

So a renewed interest in this solid solutions system has arisen because of an application of new crystal growth techniques. In parallel with the development of technological methods that make it possible to obtain ever more pure and perfect $InAs_{1-x}P_x$ solid solutions crystals, their physical properties have been intensively studied. Furthermore, unlike other semiconductor solid solutions, the $InAs_{1-x}P_x$ system revealed full miscibility of components and was characterized by thermodynamic stability. Besides $InAs_{1-x}P_x$ solid solutions characterized by low solubility in water and the resistance to oxidation in moist air, the deviation from a stoichiometric composition was not found.

The development of theoretical concepts was of particular importance too, because it allows a direct analysis of experimental data and the prediction of unexplored properties. Overcoming difficulties in this direction was helped by excellent theoretical works, which are presented in the given book along with experimental works [2-11].

The need of practice is always ahead of the real possibilities of using materials. This happens because a long and thorny path is between the establishment of the fundamentally possible applicability of a substance in a given area of semiconductor technology and its actual use in a device. The problem is associated with the purification of a substance, the development of a technology for its preparation, the elucidation of the characteristics of properties and with many factors familiar to device developers. That is why sometimes $InAs_{1-x}P_x$ solid solutions were underestimated. Eventually this system of $InAs_{1-x}P_x$ solid solutions has become one of the most important materials for many electronic devices, including lasers after many years.

Initially, $InAs_{1-x}P_x$ solid solutions received considerably more attention since they offered potential applications in a variety of devices such as high efficiency Hall probes [12] and high field transferred electron devices [13]. At the initial stage of studies of $InAs_{1-x}P_x$ solid solutions, the rates of their studies lagged behind the more experimentally available other semiconductors. Afterwards $InAs_{1-x}P_x$ solid solutions were widely studied and their electronic and optical properties have aroused great interest, because of their direct band gaps for all compositions, sharp absorption edge, high refractive indices, high electron mobility, high radiation resistance, etc., which make it possible to manufacture practically all fundamental devices of micro-, opto- and nanoelectronics. The possibilities of using $InAs_{1-x}P_x$ solid solutions are very wide. In addition to obtaining the entire gamut of intermediate properties, it is possible to use the exceptional properties of one of the components without changing too much the properties of the other component selected as the basis. For example, increasing the band gap with a small addition of a wider-gap compound will heal the defects of the base component without changing valuable properties, etc. [14]. In $InAs_{1-x}P_x$ solid solutions, some properties of one of the components that are unfavorable for technical use may be improved.

There has been a renewed interest in the $InAs_{1-x}P_x$ solid solutions in the last few years, because of the availability of new data on their unique radiation properties. The quasi-binary $InAs_{1-x}P_x$ solid solutions have great potential for creation of radiation-resistant materials on their basis, which withstand large fluence of hard radiation [14, 15]. This opens an important opportunity for applying devices on the basis of $InAs_{1-x}P_x$ solid solutions in the innermost tracking systems, in the Large Hadron Collider, in thermonuclear experiments, in space, and in the radiation contaminated territories of Chernobyl and Fukushima-type active zones.

The study of $InAs_{1-x}P_x$ solid solutions is important for a fundamental point of view too. By now, as a result of the progress of technology, a large amount of information on InP_xAs_{1-x} solid solutions has accumulated. A sharp increase in the progress of the information flow technology devoted to $InAs_{1-x}P_x$ solid solutions has enabled to summarize the most important works in the main areas, which will be reflected in this book.

The presented book contains the results of experimental and theoretical studies of the issue of obtaining $InAs_{1-x}P_x$ solid solution systems and the investigation of their properties currently known from the literature from 1955-2022, including works by Kekelidze and staff at the Ferdinand Tavadze Institute of Materials Science and the Ivane Javakhishvili Tbilisi State University.

Chapter 1 “Physicochemical properties” summarizes results of investigation of the phase diagram, the lattice parameter, thermochemical properties and other physicochemical properties of $InAs_{1-x}P_x$ solid solutions. The material presented is considered in comparison with the analogous properties of InAs and InP starting components. This allows the full assessment of the position of the $InAs_{1-x}P_x$ solid solutions among the diamond-like family group of semiconductors.

Chapter 2 “Production of $InAs_{1-x}P_x$ solid solutions” focuses on the most promising synthesis methods and growing single bulk crystals and single crystal layers of $InAs_{1-x}P_x$ solid solutions. These methods include techniques based on crystallization of stoichiometric melts of $InAs_{1-x}P_x$ solid solutions using high pressure equipment, as well as epitaxial deposition of layers from the gas and liquid phases.

Chapter 3 “Optical properties and energy band structure” reviews key features of the optical absorption at the fundamental edge, refractive indices and optical dielectric constants and optoelectronic properties of $InAs_{1-x}P_x$ solid solutions under different temperature and pressure conditions. The emphasis is on the electronic band structure of $InAs_{1-x}P_x$ solid solutions at the lowest and highest energy band structures.

Chapter 4 is devoted to the infrared spectra of $InAs_{1-x}P_x$ solid solutions associated with the dynamics of the crystal lattice. To this end lattice reflection spectra are considered here.

Chapter 5 is devoted to the electrical phenomena in $InAs_{1-x}P_x$ solid solutions. Much attention is paid to the peculiarities of current carriers scattering in crystals of $InAs_{1-x}P_x$ solid solutions.

Chapter 6 outlines the thermoelectrical properties of $InAs_{1-x}P_x$ solid solutions. Chapters 7 and 8 provide data on the radiation effects on electrical and optical properties of $InAs_{1-x}P_x$ solid solutions, which determine the principles of operation of all semiconductor devices. The revealed changes in the properties of the $InAs_{1-x}P_x$ system during irradiation are much more marked than in the Group IV of semiconductors Si and Ge.

Chapter 9 carefully compiles all the currently available experimental data on the use of $InAs_{1-x}P_x$ solid solutions. The scope of these solid solutions is huge: lasers in the wavelength range of 0.9µm-3.1µm, optical filters, and thermoelectrical elements. There is also the potential for widespread applications in the fabrication of high-efficiency solar cells, in quantum electronics, in infrared spectroscopy and in other fields of semiconductor technology.

The book is accompanied by two attachments with appropriate tables, which provide the numerical computation of charge carrier mobility due to scattering by optical vibrations of the lattice in the III-V's and data of the Fermi-Dirac integrals and the chemical potential with high reasonable accuracy, with an error rate of <<1%.

CHAPTER 1

PHYSICOCHEMICAL PROPERTIES

Semiconductor elements or compounds do not always form solid solutions with each other. For example, Ge only forms substitutional solid solutions with Si over the entire composition range, in which the properties of germanium transfer into the continuously changing properties of silicon. One of the reasons that prevents the formation of solid solutions between other couples of semiconductor elements of Group IV is the difference in their atomic size.

To form solid solution crystals, the following three conditions are required: the maximum similarity or common chemical type of the solid solution's components (chemical elements or compounds); identity of their crystal lattice structure; and close interatomic distances in their lattices (the difference should not exceed 15%). However, there is another requirement - close ionicity values, in order to prevent lattice distortions. This requirement plays an essential role only when considering the properties of semiconductors (e.g. InAs and InP) where the electronic bonds have a significant ionic component.

InAs and InP binary compounds are generally characterized by a number of common crystal-chemical data: the same nature of the chemical bond, identical stoichiometric composition, the same crystal structure (ZnS type), the proximity of lattice periods (the difference is 4%), and close ionicity values [1]. So they can form relatively easily an $InAs_{1-x}P_x$ pseudo-binary system with a continuous series of solid solutions. The $InAs_{1-x}P_x$ solid solutions system (together with $GaAs_{1-x}P_x$) was the first system to exhibit the solid solubility properties of III-V compounds.

1.1. Crystal structure and lattice parameters

The existence of full miscibility of the most III-V compounds, among them in $InAs_{1-x}P_x$ solid solutions, was first discovered by Folberth [2]. Folberth found that Debye-Scherrer images showed lines of ZnS-type structure for $InAs_{1-x}P_x$ solid solutions, as well as for InAs and InP.

According to Folberth $InAs_{1-x}P_x$ solid solutions are crystal-chemical analogs of Si and Ge and crystallize mainly in the zinc blende crystal structure, which corresponds to the space group T_d. Being also electronic analogues of elements of Group IV, InAs, InP and their $InAs_{1-x}P_x$ solid solutions have 4 valence electrons for each atom, which determine the commonality of their properties. Each In atom has four atoms of Group III (As or P) as their nearest neighbors, and vice versa.

On the other hand, the presence of two different types of As and P atoms in the unit cells of InAs, InP and their $InAs_{1-x}P_x$ solid solutions is the reason for the lesser symmetry of their crystal lattice and the appearance of an ionic bond fraction to the main type of covalent bond and finally distinctive properties from the elements of Group IV.

As is known, the chemical bond in InAs and InP compounds is of a mixed character, but as a result of the dominating role of the covalent bond, the chemical bond system is electrically neutral. The presence of a definite shift of electrons from atoms of Group III to those of Group V adds some ionic character to the chemical bond in InAs, InP and $InAs_{1-x}P_x$ solid solutions. At the time the type of covalent bond predominates in InAs, InP and their $InAs_{1-x}P_x$ solid solutions. The fraction of the ionic bond component is greater for InP and InP-rich solid solutions than for InAs and InAs-rich solid solutions [3]. Due to the additional contribution of the ionic bond component in InAs and InP compounds and $InAs_{1-x}P_x$ solid solutions the chemical bond is stronger than that of the Group IV elements.

The measurements of the lattice parameters (a) of $InAs_{1-x}P_x$ solid solutions were made using the Debye-Scherrer technique with a 57.32-mm-radius Straumanis-type camera and nickel-filtered radiation (Fig. 1.1 and Table 1.1) [4]. A trigonometric extrapolation was used to obtain the precision lattice constants [5]. The samples gave back reflections, which sharply resolved the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines. The solid line in Fig. 1.1 has been drawn through the experimental points, while the dashed line represents a linear variation between the values for the compounds.

Thomson *et al.*'s results [4] confirmed the data of Folberth [2], which showed a lattice parameter varied approximately linearly with the composition. The lattice parameter of $InAs_{1-x}P_x$ solid solutions varies monotonically from the ones for InAs to the ones for InP, with the largest deviation from additivity in the middle of the system. The deviation (Δ) from Vegard's law (a linear function of lattice parameter on the composition of the components) [6] is small. This is the case which demonstrates positive deviation from Vegard's law:

$$\Delta = a_{InAsP} - \{a_{InP} + (a_{InAs} - a_{InP})c_{InAs}\}, \qquad (1.1)$$

where a_{InAsP}, a_{InAs} and a_{InP} are the lattice parameters of InAsP, InAs and InP respectively, and c_{InAs} is the mole fraction of InAs.

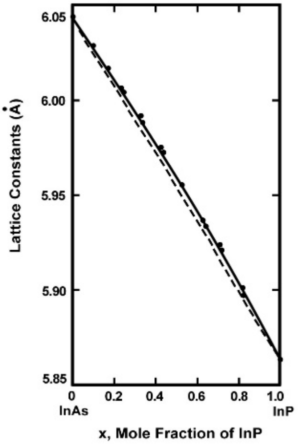


Fig. 1.1. The dependence of the lattice parameter on the composition of $InAs_{1-x}P_x$ (300K) [4].

Table 1.I. The lattice constants of InAs, InP and $InAs_{1-x}P_x$ (300K) [4]

mol%InP	a_0, Å	Δ a_0, Å
0 (InAs)	6.0587	+0.0004
0 (InAs)	6.0587	+0.0004
0.10	6.0416	+0.0022
0.20	6.0220	+0.0018
0.20	6.0232	+0.0029
0.30	6.0109	+0.0094
0.30	6.0107	+0.0092
0.30	6.0049	+0.0034
0.30	6.0045	+0.0030
0.40	5.9866	+0.0042
0.40	5.9904	+0.0080
0.50	5.9707	+0.0070
0.50	5.9731	+0.0094
0.60	5.9540	+0.0093
0.60	5.9535	+0.0088
0.70	5.9303	+0.0048
0.70	5.9305	+0.0050

0.80	5.9125	+0.0057
0.80	5.9092	+0.0024
0.90	5.8892	+0.0015
0.90	5.8897	+0.0021
1.00 (InP)	5.8692	+0.0004
1.00 (InP)	5.8689	+0.0002
1.00 (InP)	5.8691	+0.0003

The small deviation of the lattice parameter from Vegard's law points to the proximity of $InAs_{1-x}P_x$ solid solutions to the ideal system. Since the starting components of $InAs_{1-x}P_x$ solid solutions crystallize in the same structure, it seems natural that the lattice parameter in this system varies with the composition according to Vegard's law. This is typical for solid solutions with unlimited solubility of components. The strict implementation of Vegard's law is a reliable indicator of the homogeneity of $InAs_{1-x}P_x$ solid solutions. So the composition and quality of homogeneity of $InAs_{1-x}P_x$ solid solutions may be determined by the measurements of the lattice constants.

1.2. Phase diagram

The phase diagrams of the binary In-As and In-P systems are the same type (Fig. 1.2) [7]. The only one congruently melting chemical compound of InAs and InP with an atomic ratio of 1:1 is formed in these binary systems of In-As and In-P accordingly. The melting points of the InAs (942^0C) and InP (1062^0C) compounds lie significantly higher than the melting points of the source components. The equilibrium pressure of the As vapor is ~0.35 atm, while the equilibrium pressure of the P vapor is ~60 atm.

The pseudo-binary phase diagram of the $InAs_{1-x}P_x$ system of solid solutions is presented in Fig. 1.3. The data of a pseudo-binary phase diagram has been established by Thomson and Wagner in [8] in the following manner. The starting composition of the melt was calculated and the composition of the first-to-freeze portion of the ingot was determined by the X-ray powder diffraction technique.

Koster and Ulrich [9] investigated the liquidus and solidus points by the usual method of taking cooling and heating curves (dotted lines). The data (points-3, Fig. 1.3) obtained by Koster and Ulrich [9] are much lower than solidus, which is probably due to the use of inhomogeneous samples and would be expected with the application of a one-temperature melting technique.

The slight difference between the liquidus of [8] and that of [9] is probably due to the different pressures and non-stoichiometric conditions used. The theoretical work by Steininger [10] shows the liquidus-solidus separation derived in [8] to be reasonable.

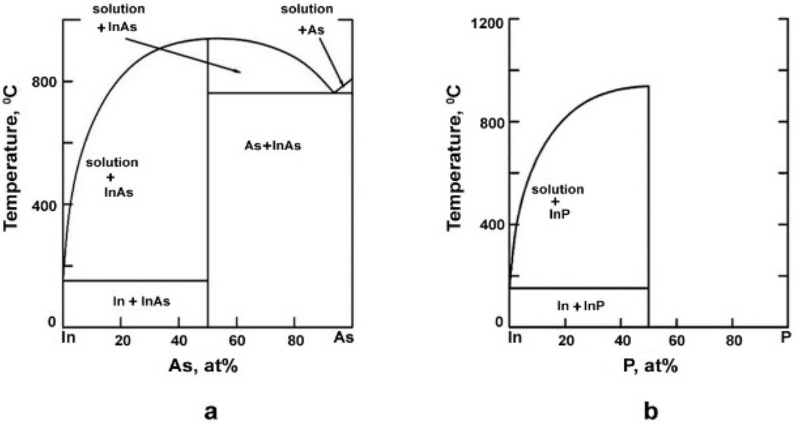


Fig. 1.2. Phase diagrams of In-As (a) and In-P (b) systems [7].

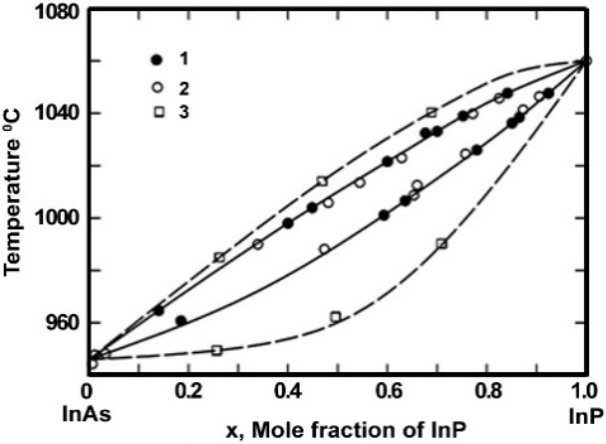


Fig. 1.3. The pseudo-binary phase diagram of the InAs$_{1-x}$P$_x$ system [8]. Data obtained by: 1-liquid encapsulation and 2- sealed system [8]; 3-one-temperature melting [9].

The pseudo-binary phase diagram of the $InAs_{1-x}P_x$ solid solution system (Fig. 1.3) exhibits complete miscibility of components in the liquid and solid phases and presents a particularly simple phase diagram characterized by monotonic variations in liquidus and solidus temperatures with composition.

A significant number of binary and pseudo-binary solid solution systems, exhibiting complete miscibility in liquid and solid phases, present particularly simple phase diagrams characterized by monotonic variations in liquidus and solidus temperatures with composition. In general, such types of homogeneous and monotonic systems are not ideal, and the enthalpies and excess entropies of mixing in the liquid and solid phases are not negligible. However, according to [10] the complete miscibility and the absence of minima or maxima in the liquidus and solidus curves in the pseudo-binary phase diagram of the $InAs_{1-x}P_x$ solid solution system suggest that the deviations from ideality in two phases are relatively small and of comparable magnitude. Steininger [10] has found that for these conditions an ideal form of the liquidus-solidus equation can be used to relate the equilibrium liquidus and solidus compositions at a given temperature for the $InAs_{1-x}P_x$ solid solution system.

It is seen (Fig. 1.3) that no superstructure is formed and there is no stratification phenomenon in this system. The phase diagram confirms that the $InAs_{1-x}P_x$ system can be considered as a pseudo-binary solid solution (alloy) of two components' – $(InAs)_{1-x}$ and $(InP)_x$ – compounds, which dissolve continuously in each other in any proportion, both liquid and solid.

So InAs and InP form a continuous series of substitutional solid solutions (alloys) and are denoted by $InAs_{1-x}P_x$, where x is the mole fraction of InP in the solid solutions (or $InAs_xP_{1-x}$ where x is the mole fraction of InAs). Any composition of the InAsP system is a single-phase and homogeneous solid solution. The phase diagram of the $InAs_{1-x}P_x$ system presents the first type temperature-composition phase diagram according to Roozeboom's classification [11, 12], i.e. a typical phase diagram for systems of solid solutions with unlimited solubility of components.

1.3. Chemical and thermal stability

Understanding the chemical and thermal stability of a material is an important aspect of material design and study, especially when it comes to decaying semiconductor materials such as InAs, InP and $InAs_{1-x}P_x$ solid solutions. The powerful and robust tools to explore a material's chemical and thermal stability, namely, degradation reactions, phase transitions determining the suitability of the material used in a given temperature range, and so on are mass-spectrometric, thermogravimetric, and differential thermal analyses.

1.3.1. Thermochemical properties

The calculation showed that the mixing energy of the $InAs_{1-x}P_x$ solid solutions system is positive and equal to 4000 kcal/mole [13]. A positive value of the mixing energy means that in InAsP solid solutions the interaction between the atoms of the same name is stronger than between the unlike atoms.

H. Gutbier [14] implemented mass-spectrometric studies of the evaporation processes of InAs, InP and the $InAs_{0.44}P_{0.56}$ solid solution in the temperature range up to 1000K. Some thermochemical quantities were calculated and experimentally determined for InAs, InP and the most interesting composition-equimolar $InAs_{0.44}P_{0.56}$ solid solution.

It was found that InAs, InP and the $InAs_{0.44}P_{0.56}$ solid solution thermally decompose upon evaporation in vacuum at 1000K, and the components of the Group V evaporate partially in the form of four- and diatomic molecules. Molecules arising from the evaporation of the $InAs_{0.44}P_{0.56}$ solid solution contain all possible combinations between P and As atoms. No radicals containing simultaneously atoms of Groups III and V were observed. In vacuum, phosphorus and arsenic evaporate in the form of different molecules like P_4, P_5As, P_2As_2, PAs_3 and As_4 with different activation energies, which were determined both experimentally and by calculation. The enthalpies of the formation (ΔH) of InAs, InP and the $InAs_{0.44}P_{0.56}$ solid solution were calculated from the temperature dependence of the rate constant of the evaporation process. For $InAs_{0.44}P_{0.56}$ $\Delta H=25.5$kcal/mole (at 1000K) and $\Delta H=19.7$kcal/mole (at 298K). The process follows:

$$InAs_{0.44}P_{0.56solid} \rightarrow In_{liquid}+0.56\cdot 1/4P_{4Gas}+0.44\cdot 1/4As_{4Gas} \qquad (1.2)$$

On the other hand, in studies of pure elements as phosphorus (red) and arsenic (rhombohedral), there were found practically only X_4 type molecules (X=As, P) as sublimation products in the temperature range from 500K to 800K. The composition of molecular particles practically corresponds to the state of the thermodynamic equilibrium in the evaporation processes under consideration. According to the measurement results [14] the liquid phase surrounding the substance acts catalytically on the formation of As_4 or P_4 molecules. The enthalpy of formation of the

$InAs_{0.44}P_{0.56}$ solid solution, as expected, lies between the corresponding values of InP and InAs (Fig. 1.4).

It is interesting that the measured enthalpy of creation of the $InAs_{0.44}P_{0.56}$ solid solution is located between the values for InAs and InP on the line. Enthalpy was calculated (dashed line) by the specified method developed by Pauling [15] using the so-called electronegativities of the elements. Vapors of dissociated compounds are almost entirely composed of molecules of amorphous components.

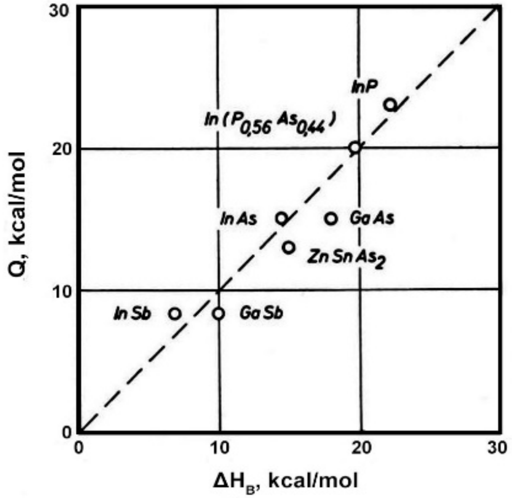


Fig. 1.4. Comparison of the calculated and measured enthalpies of the III-V’s [14].

1.3.2. Thermogravimetric and differential thermal analyses

Presented here are data that are important for the technology of producing InAsP solid solutions type crystals, but they can also be incorporated into solving other problems. By accurately monitoring the weight of InAs, InP and $InAs_{1-x}P_x$ solid solutions, while heating at a constant rate, it is possible to measure changes in their mass on the different stages of the heating process, and attribute the process to the response of these materials to a thermal stress (Figs. 1.5-1.8) [16].

To protect from oxidation at elevated temperatures, the heating of InAs, InP and $InAs_{1-x}P_x$ solid solutions in air has been carried out under a protective layer of the unique flux of boron anhydride. Boron anhydride satisfies requirements of chemical stability up to the melting points of

InAs, InP and $InAs_{1-x}P_x$ (942^{0}C-1062^{0}C): the smaller density than for InAs and InP compounds, and immiscibility with a melt of InAs and InP. Thermogravimetric (TG, curves 1) and differential thermal analyses (DTA, curves 2) were implemented in the 25^{0}C-900^{0}C temperature range (Figs. 1.5-1.8). The descending TG thermal curves for all samples indicate a mass loss occurred.

InAs. Experimental curve 1 (Fig. 1.5) shows clearly, that the mass gradually decreases while heating from room temperature up to 600^{0}C. According to the derivative of thermogravimetric data in the 25^{0}C-900^{0}C temperature range the mass loss occurs in three stages. The maximum mass loss makes up 1.49% in the 273^{0}C-314^{0}C temperature range. The biggest exothermic effect is fixed at 463^{0}C (Fig. 1.5, curve 2). At 888^{0}C the sample is sharply oxidized and destroyed.

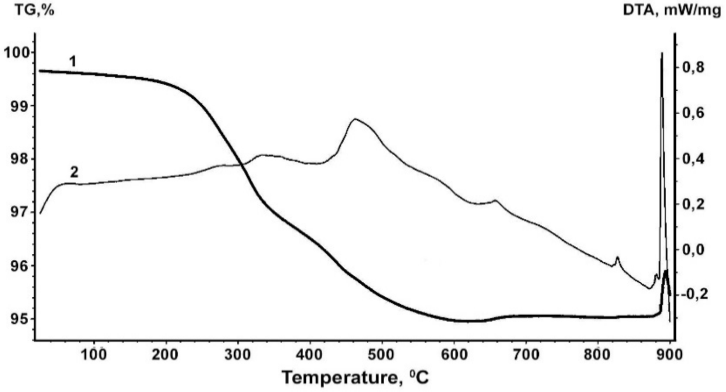


Fig. 1.5. Thermogravimetric (1) and differential thermal analyses (2) at heating of InAs at 10K/min rate in the temperature range of 25^{0}C-900^{0}C.

InP. Experimental curve 1 (Fig. 1.6) shows clearly, that the mass gradually decreases while heating from room temperature up to 500^{0}C. According to the derivative of the thermogravimetric curve in the 25^{0}C-900^{0}C temperature range the mass loss occurs in three stages. The maximum mass loss makes up 1.65% in the 25^{0}C-270^{0}C temperature range. The biggest effect is fixed at 444^{0}C (Fig. 1.6, curve 2). At 884^{0}C the sample is sharply oxidized and destroyed.

$InAs_{0.70}P_{0.30}$ solid solution. Experimental curve 1 (Fig. 1.7) shows clearly, that the mass gradually decreases while heating from room temperature up to 700^{0}C. According to the derivative of the thermogravimetric curve in the 25^{0}C-900^{0}C temperature range the mass loss occurs in four stages. The maximum mass loss makes up 0.08% (319^{0}C-545^{0}C). The biggest exothermic effect is fixed at 282^{0}C (Fig. 1.7, curve 2). At 755^{0}C the sample is sharply oxidized and destroyed.

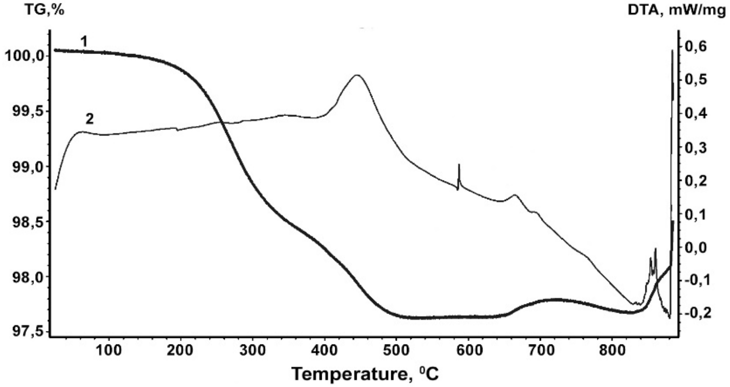


Fig. 1.6. Thermogravimetric (1) and differential thermal analyses (2) of InP at heating at 10K/min rate in the temperature range of 25^{0}C-900^{0}C.

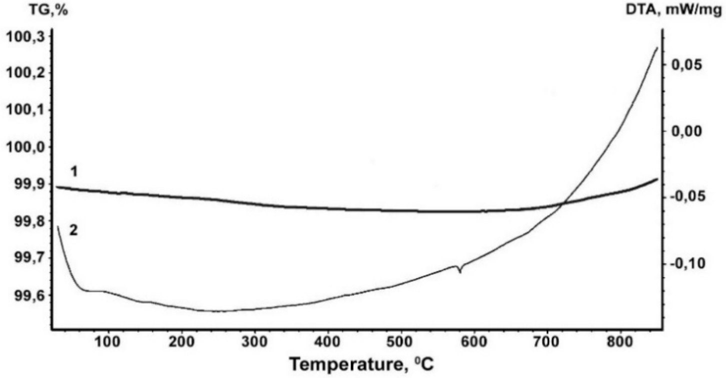


Fig. 1.7. Thermogravimetric (1) and differential thermal analyses (2) of $InAs_{0.70}P_{0.30}$ at heating at 10K/min rate in the temperature range of 25^{0}C-900^{0}C.

$InAs_{0.30}P_{0.70}$ solid solution. Experimental curve 1 (Fig. 1.8*)* shows clearly, that the mass gradually decreases while heating from room temperature up to 700^0C. According to the derivative of the thermogravimetric curve in the 25^0C-900^0C temperature range the mass loss occurs in four stages. The maximum mass loss makes up 0.08% (259^0C-470^0C). The biggest effect is fixed at 580^0C (Fig. 1.8, curve 2). At temperatures above 580^0C the sample is sharply oxidized and destroyed.

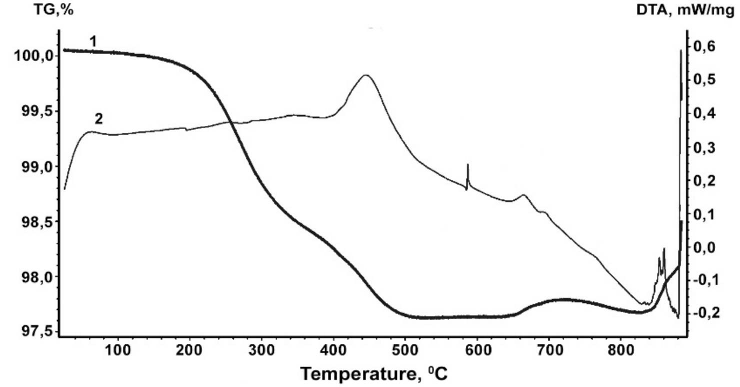


Fig. 1.8. Thermogravimetric (1) and differential thermal analyses (2) of $InAs_{0.30}P_{0.70}$ heating at a rate of 10K/min in the temperature range of 25^0C-900^0C.

So, unlike InAs and InP, $InAs_{1-x}P_x$ solid solutions reveal less mass loss while heating under the flux of boron anhydride. The InAs-rich $InAs_{0.70}P_{0.30}$ solid solution reveals the highest chemical and thermal stability, while heating under a protective layer of boron anhydride. What is more, the $InAs_{0.70}P_{0.30}$ solid solution reveals radiation resistance (Chapter 7).

1.4. Microhardness

Mircohardness is one of the physicochemical properties of solids, and the microhardness test is a simple means of characterizing their mechanical behavior. Hardness not only characterizes the state of the material under load with dependence on the previous history of a sample, but also gives information on some deeper specific features of a material such as, for example, brittleness and the character of the chemical bonding. The microhardness for $InAs_{1-x}P_x$ solid solutions has been reported in [17, 18]. The results of investigations shown in Fig. 1.9 show an effect of composition on the brittle properties of the $InAs_{1-x}P_x$ solid solutions system.

Microhardness depends on the value of the load. It is seen that curve 1 does not possess a maximum at the load of 40g, and curve 2 shows that microhardness of solid solutions, depending on the composition, passes through a weak maximum at the load of 20g. The revealed regularity of microhardness dependence of $InAs_{1-x}P_x$ solid solutions on composition differs from the law observed for solid solutions of metal systems. In the observed dependence for the InAsP solid solutions system, there is no clear maximum in the middle of the system, which is typical for metal solid solutions. This is expected, because $InAs_{1-x}P_x$ solid solutions, as with numerous others of the mixed III-V's, are materials with pronounced covalent chemical bonds and characterized by high brittleness.

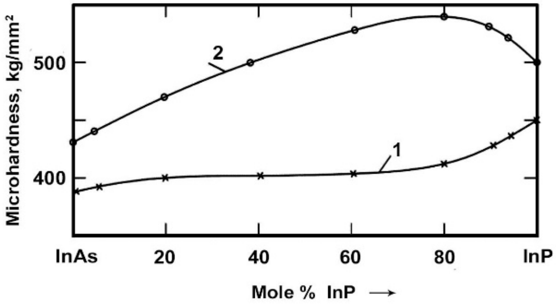
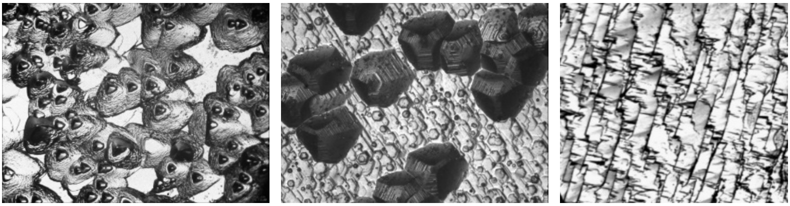


Fig. 1.9. The dependence of the microhardness of the $InAs_{1-x}P_x$ system on the composition under the load of: 1 - 40g and 2 - 20 g [17, 18].

The microhardness dependence of $InAs_{1-x}P_x$ solid solutions on the composition correlates with their band gap width and the melting temperature dependences on the solid solution composition. This confirms the conclusion of [19] on the correlation between microhardness and band gap width and the melting temperature in semiconductor solid solution systems with a diamond-type structure.

1.5. Microstructural analysis

The images of dislocation structure of single crystals of InAs, InP and $InAs_{1-x}P_x$ solid solutions of composition from the middle of system are presented in Fig. 1.10.



a b c

Fig. 1.10. Dislocation structure of single crystals on the (111) plane (x250) for: a) InAs; b) $InAs_{1-x}P_x$; c) InP [20].

Microstructural investigations clearly show, that InAs and InP sublattices retain their identity in $InAs_{1-x}P_x$ solid solutions. At the same time the material retains the crystal structure without amorphous inclusions and metallic phases. The preservation of individuality of sublattices of InAs and InP in $InAs_{1-x}P_x$ solid solutions, has been confirmed by studies of electrical and optical properties [Chapters 4, 7 and 8) [20, 21].

CHAPTER 2

PRODUCTION OF $InAs_{1-x}P_x$ SOLID SOLUTIONS

The research of physical properties has led to a deep understanding of the physics of substitutional $InAs_{1-x}P_x$ solid solutions. This progress was made possible thanks to significant advances in $InAs_{1-x}P_x$ solid solution production technology. Several methods have been used to produce $InAs_{1-x}P_x$ solid solution crystals. The variety and type of growth methods of $InAs_{1-x}P_x$ solid solution crystals are limited and determined by the nature of their phase diagram, pressure-composition and temperature-pressure dependences.

The production of semiconductor materials with well-defined properties has two aspects: the growth of the material as a single crystal and the regulation of its defect structure, often by a post-growth annealing. At present, $InAs_{1-x}P_x$ solid solutions are mainly obtained by two methods: crystallization from the melt or from the vapor phase. Each of these methods has a number of variants and is characterized by different parameters of technology processes (temperature, vapor pressure, and speed of crystal growth), type of chemical reaction, etc.

2.1. Features of crystallization processes of ternary continuous solid solutions

In the process of obtaining homogeneous ternary bulk decaying semiconductor crystals, among them $InAs_{1-x}P_x$ solid solutions, by directional freezing with complete mixing in the melt, like Czochralski pulling or the horizontal Bridgman technique, two main problems arise: segregation of components and their high vapor pressure.

2.1.1. Directional crystallization

The first and toughest of these problems is the control of a composition variation along the length of the bulk crystals, which is due to the depletion of solute elements in the melt during crystal growth. The whole