Materials Science Research India Volume **3**(2a), 215-230 (2006)

Ultra high purity gallium and indium for emerging III-V epitaxial nanoelectronics materials technologies: An overview

V. N. MANI

Ultra High Purity Materials Division, Centre for Materials for Electronics Technology, Department of Information Technology, Government of India, Cherlapalli, Hyderabad - 500 051, (India)

(Received: July 27, 2006; Accepted: September 03, 2006)

ABSTRACT

The epitaxial fabrication and assembly of GaAs, GaN, AlN nanostructures into quantum wells and quantum dots based devices and integration into larger scale structures has been the topic of most recent technological developments. Gallium and indium based III-V binary, ternary and quaternary multi-layered structures and devices play a vital role in satellites, super computers, surveillance systems, proximity sensors, because they can send and process information about five times faster, withstand high radiation dosage and operate at higher temperatures and frequencies compared to silicon based devices. This paper, describes our efforts of developing high pure gallium and indium metals, which are required for nano electronics and optoelectronics and specifically in the fabrication and assembly of GaAs, GaN, AlN nanostructures into quantum wells and quantum dots based devices. In this presentation principles and techniques associated with the purification and purity analysis characterization of gallium and indium and also the current trend and future prospects are covered. Results pertaining to the segregation characteristics of metallic impurities associated with gallium and indium metals will be discussed in detail.

Key words: Ultra high purity, Gallium, indium, Nanoelectronic.

INTRODUCTION

Information technology has become the key technology of our time, which made world as a global village. Whatever the major field of social activity or world industry is selected, it will be realized that micro-optoelectronics is playing an increasingly dominant role in it. The invention of the transistor and the laser has provided the starting blocks for incredible developments in technology and application or solid-state electronics. So impressive it was that the last two decades of technological development in the field are often quoted as unique in the whole history of human technological achievements. The long lasting period of development in micro-optoelectronics has produced a wide range of distinct ultra high pure metals, electronic materials, compound semiconductors, single crystals, epitaxial structures and devices where silicon, III-V binary, ternary and quaternary compounds and mercury cadmium telluride are of pivotal importance. Among the process technologies, development of ultra high pure materials, crystal and epitaxial growth represent various building blocks for realizing many device structures. Much progress in micro-optoelectronics technology during the last decade has been based on epitaxial and related device fabrication technologies. The applications and successes of these epitaxial multilayered structures based devices and gadgets have greatly influenced the whole information technology. The success of advanced multi-layered structures and devices in the laboratory and in production depends heavily on the advanced technologies used to purify and grow them and fabricate devices. The various forms

of epitaxial methods are the leading candidates for the fabrication of devices.

The epitaxial fabrication and assembly of GaAs, GaN, AlN nanostructures into quantum wells and quantum dots based devices and integration into larger scale structures has been the topic of most recent technological developments. Much attention is diverted in the areas of a) assembly of nano-structures and their integration across various dimensional scales: nano-structures to functional devices to system architectures to final products and b) study on the material and functionality properties manipulation and control (mechanical, electromagnetic, thermal, biological, and chemical). Different approaches were employed to realize the nanostructures and systems. Major routes include bottom–up-(atom by atom or molecule by molecule) and top-down – start with a full 3–D and "carve" it through nano-crafting via monolithic processing on the nanoscale.

Ultra high pure gallium and indium metals, gallium arsenide (GaAs), gallium nitride (GaN), indium phosphide (InP), indium nitride (InN) and their other related binary, ternary and quaternary multi-layered nano-epitaxial systems are the important building blocks, which find place in state-of-art micro-optoelectronic gadgets. These crucial material systems are essential for fabrication of monolithic microwave integrated circuits (MMICs), high mobility electron transistors (HMETs), lasers, light emitting diodes (LEDs), detectors, solar cells etc. Beneficial features, such as, high speed and efficiency, high sensitivity, radiation selectivity and tolerance of GaAs and InP devices coupled with lattice match and tailorable material properties of GaAs ternary and quaternary based multi-layered epi-structures make them very special candidates in micro-optoelectronics. These features of GaAs and InP devices and MMIC fabrication technology made the dream concept of integrating the electronics device domain with photonics device domain a reality[1]. Ultra high pure (7N) gallium and indium are the primary input materials required for preparation of GaAs and InP bulk single crystals and epitaxial nano system. Epitaxial precursors such as, gallium chloride, trimethyl gallium, triethyl gallium, pure metal forms of gallium and indium based precursors are needed for GaAs, GaN, InP epitaxial growth (Vapour Phase Epitaxy, Metal Organic Vapour Phase Epitaxy, Molecular Beam Epitaxy, Metal Organic Molecular Beam Epitaxy and Atomic Layer Epitaxy) and manufacture of multi-layered devices[2]. Development of cost effective purification processes suiting to the grade and source of input crude gallium, purity test, yield improvement, recycling of impure metal, design and development of automated and modular refining systems are the major current technological problems and challenges. Fig. -1. highlights the role of the micro-optoelectronic gadgets and their impact in modern technology.

Epitaxial Technology

The Backbone of Micro-optoelectronic and Nanomaterials Devices and Systems

After the Second World War, R&D efforts on thin films intensified and during the last twenty years, a strong impulse has come from semiconductor technology. Vacuum, ultra high vacuum techniques, surface analysis, evaluation and fabrication methods have played a major role in understanding of the intimate and intricate mechanisms of epitaxy, growth, evaluation and fabrication aspects. A better understanding of epitaxial growth revolves around the following concepts: a) nucleation and phase stability on substrate (thermodynamics), b) non-equilibrium situations of deposits and sequential processes in crystalline thin film growth (kinetics), c) growth of layers with tailored properties (band-gap engineering). Excellent reviews covering all the above issues on epitaxy have been reported[1-4]. The most spectacular advances have been in the field of multi-layered structures, super lattices and multiple quantum well and dot structures comprising hundreds of alternating layers of differing compositions, individual layers being only a few tens of Angstroms thick. The physics of such devices is completely new and offers exciting prospects in terms of faster, even smaller electronic components.

Low-dimensional structures (LDS) have become the essential elements in modern device technology. Epitaxial layers as thin as 10 Å or less with excellent physico-chemical and electro-optical properties, homogeneity and purity are now required. Major challenges in solid state technology

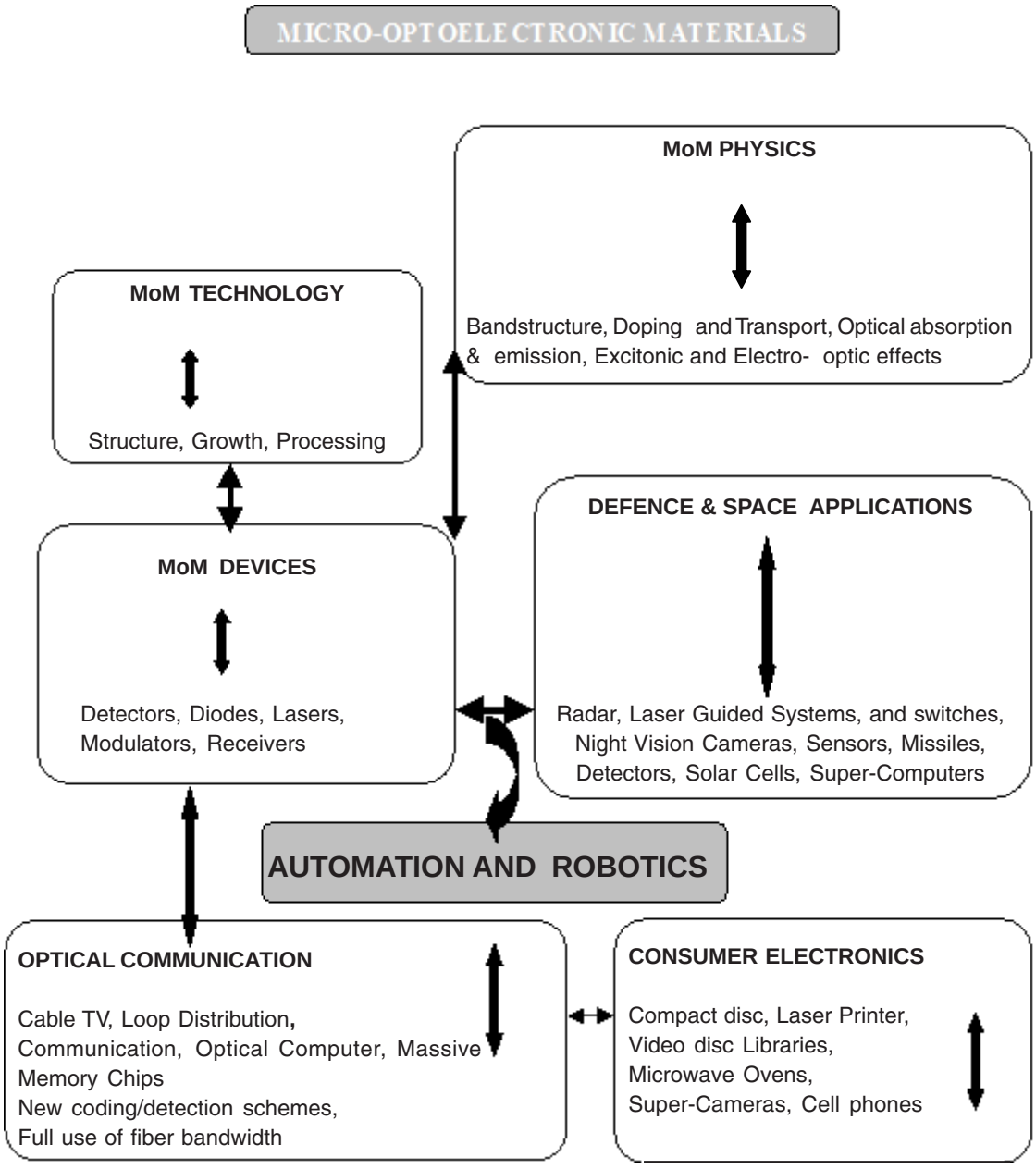


Fig. - 1: Role of the micro-optoelectronic gadgets and their impact in modern technology

is the perfection of materials and substrates in which charge carriers have long time, low scattering, high mobility and controlled densities, such materials have allowed the development of micro-optoelectronics. Significant recent developments in epitaxial technologies have substantially altered the existing situation and offer exciting and potentially revolutionary prospects for the future. It was not long ago that quantum wells were only figured in textbooks. Molecular beam epitaxy (MBE) has not only brought the experimental quantum physics to the class room but has continued to lead the fields of epitaxial growth and device fabrication by exploring new physics, chemistry, materials

science and engineering, and by fabricating novel microwave and optical devices. Materials artificially structured with MBE have extended the imagination of Device Physicists and Engineers to design a whole new generation of devices with 'band structure engineering' concept.

Epitaxial growth techniques have largely superseded bulk crystal growth techniques for electronic circuit fabrication, because the devices to be fabricated require only micron dimensions. The use of epitaxial growth, therefore, reduces growth times, wafering costs and eliminates waste due to ingot slicing losses. Epitaxial materials have better properties than the bulk ones, as far as structural and electro-optical properties are concerned. This is mainly due to the fact that in epitaxy, independently of the particular method used, the growth is carried out at temperatures, which are several hundred degrees lower than the melting point of the compound or alloy. The lower temperature growth accounts, at least in part, for the concentrations both of chemical and crystalline defects, which are lower in epilayers, than in materials grown from a nearly stoichiometric melt. At the same time, the lattice vacancy concentration is expected to decrease. The above considerations clearly underline the prominent role of the epitaxial processes in the semiconductor technology. Fig. - 2. show various purification, crystal growth, substrate preparation, and epitaxy and device fabrication schemes.

GaAs, GaN, InP Epitaxial Nanosystems and Devices

Formation of active multi-layers by epitaxial growth provide several advantages over ion implantation, leading to devices with improved operating characteristics, such as better noise and gain performance. But until recently the cost of epitaxial technology, especially MBE and MOVPE, has limited its use mainly to R&D and the production of small area devices, such as discrete FETs and HEMTs. However, a combination of increasing demands on device performance and price reduction in epi-material enabled by multi-wafer systems, has resulted in the expanded use of epitaxy for the manufacture of GaAs integrated circuits. III-V Epitaxial films are used to create semiconducting, optical and micro-optoelectronic structures. Vapor phase or chemical beam epitaxial processes were among the first to incorporate in-situ surface preparation steps, diagnostic tools (LEED, RHEED, SIMS, Auger) and to focus on interface issues. Multi-layered structures have gained an increasing interest both in optoelectronic and in microwave devices. The importance of double heterostructures in lasers and LEDs, single heterostructures in solar cells and in detectors is well known.

Epitaxial Processes

Metal Organic Vapor Phase Epitaxy

In MOVPE, organo-metallic compounds such as trimethyl gallium (TMG) are used as the source of gallium, and arsine is used as the source of arsenic. The organo-metallic gas sources, plus dopant gases, are carried in a hydrogen gas stream and combined with arsine and phosphine in the chamber. An MOCVD reactor consists of a glass or steel cylinder, which contains the heated wafer holder, with single or multiple wafers. The chemical process that occurs in the growth chamber on the heated wafer holder is the pyrolysis or thermal decomposition of the metal organic and the hydrides. The presence of low levels of H_2O, as well as other volatile species, poses serious problems of purity and composition control. Currently, the complex chemistry and source purity are active areas of research. Reaction mechanism in the organometallic vapor phase growth of GaAs has been reported.

Molecular Beam Epitaxy (MBE)

MBE is an ultra high vacuum (UHV) deposition technique. Background pressure of the order of 10^{-11} torr is maintained and an ultra pure layer with very slow growth velocity as small as one monolayer (ML) per second is grown. The wafer is placed in a high vacuum and heated from effusion cells or cracking furnaces and travel in a straight line to the substrate due to an ultra high vacuum. Here the elemental materials (Ga, As, Al etc.) are the sources are materials that are heated and evaporated to high temperature in an effusion cell to provide fluxes of the compound semiconductor (GaAs). The beam flux, which is controlled by the cell temperature, is directed at the heated sample. This process is the most recognized technology for producing super lattices and quantum dots and wires with abrupt interfaces and

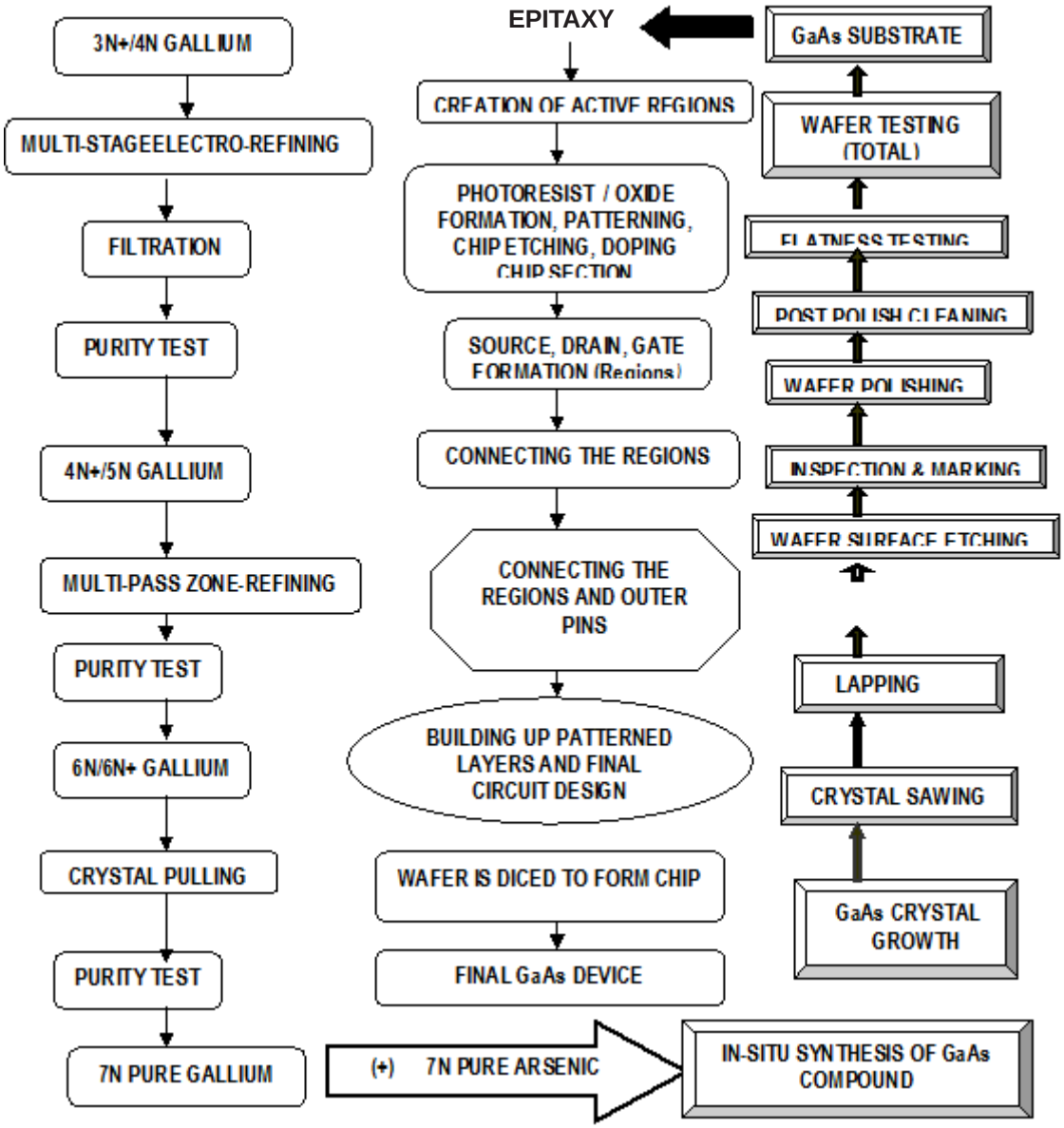


Fig. -2: Purification, crystal growth, substrate preparation, epitaxy and device fabrication schemes

controlled properties. Interruption of the beams of material that arises from the effusion cells facilitates abrupt composition and /or doping transitions. Strengths and limitations of epitaxial processes are outlined in Fig. -3. III-V materials and their related ternary, quaternary VPE growth modeling has been well reported[5-19].

Recent advances in epitaxial growth

The growth of epitaxial layers began over fifty years ago and the technology has now diversified due to the following material requirements for micro-optoelectronics: a) growth over patterned substrates, b) selective area epitaxy, c) high degree of reproducibility, d) large area

uniformity-uniform thickness: uniform doping, e) control of absolute thickness, f) control of absolute doping, g) low defect density, h) range of available compositions, i) growth of ultra thin layers (<<100Å) for quantum wells and, j) strained layers for micro-optoelectronics. Most of the epitaxial crystal growers and device engineers are aiming towards the development of novel or superior devices. Device structures are increasingly complex, frequently many semiconductor layers are required, sizes are shrinking in all dimensions and very exacting purity levels are demanded. The evolution of the epitaxial

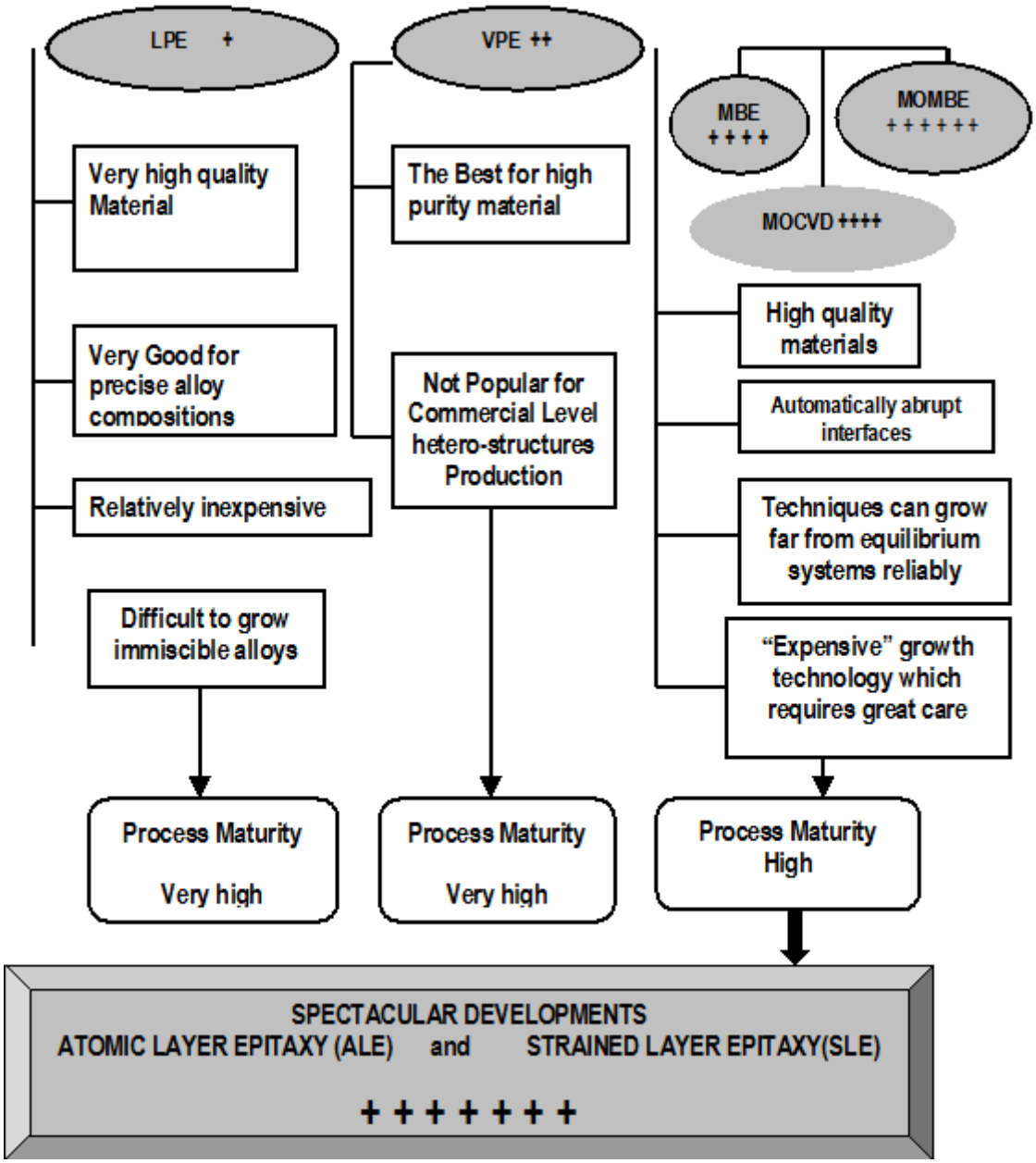


Fig. - 3: Strengths and limitations of epitaxial processes

technology has led to highly sophisticated growth methods and to complex multilayered device structures of gallium arsenide and related III-V materials. The deposition temperature is controlled to eliminate surface decomposition, while at the sane time allowing desorption of the excess elements. The layer-by-layer growth used in ALE represents an elegant means of growing exceedingly uniform and high quality materials. Because of its uniformity, ALE is currently studied at numerous laboratories worldwide. The principal limitation of this process is its slow growth rate. In a MOVPE or MBE process, growth rates of 0.1 to 10μm per hour can be achieved. In the case of ALE, we are talking in terms of only a few nanometers. Atomic layer epitaxy of III-V semiconductors has been extensively reported[20].

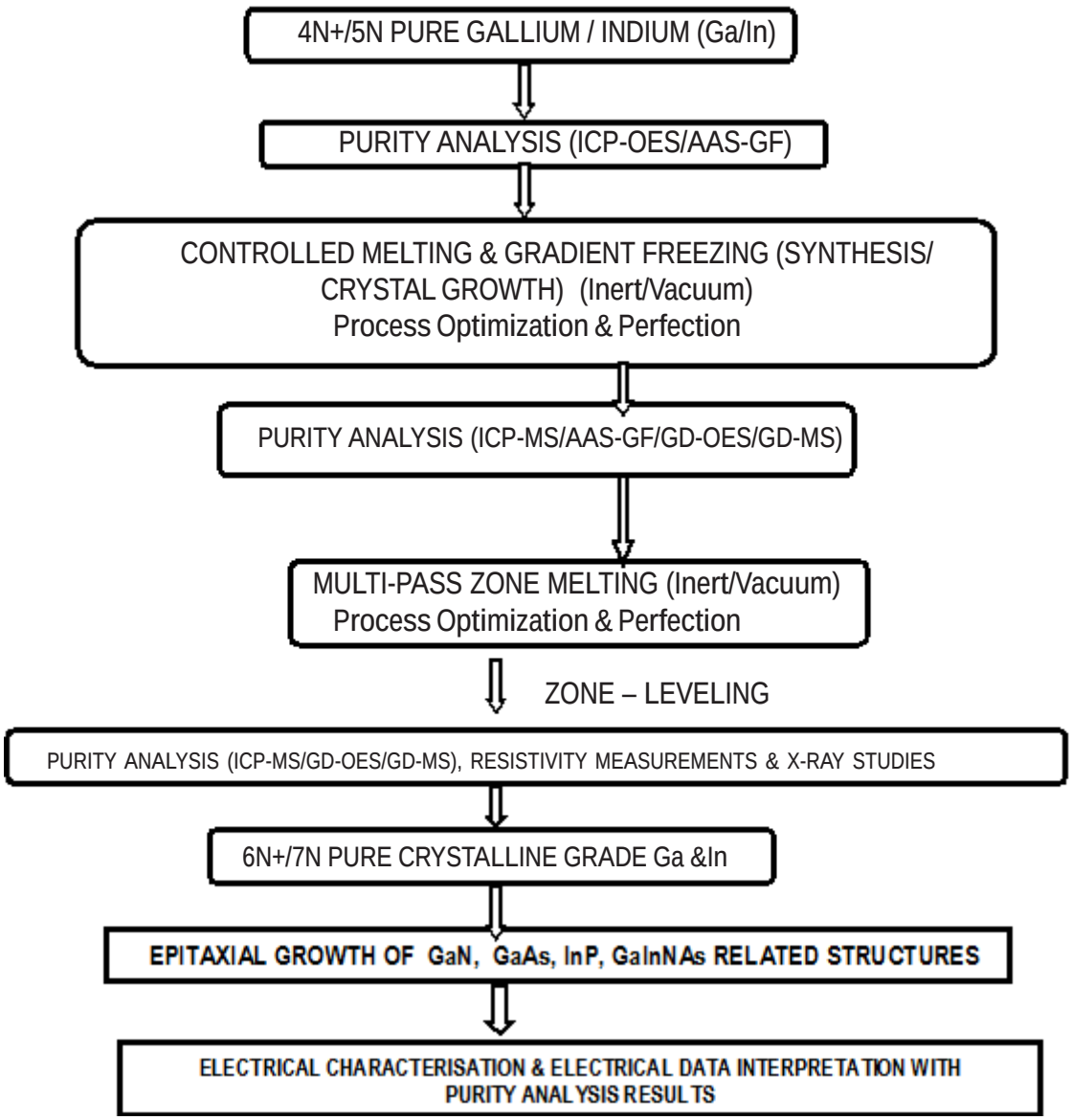


Fig. - 4: Purification processes and purity testing scheme

Technology Trend

In MOVPE, a major replacement effort for the highly toxic As- and P- sources and perfection of safety issues has been underway for some time, but hydride sources remain dominant due to cost considerations. Oxygen contamination remains an important concern for AlGaAs epitaxy. Replacement of the AlGaAs emitter with InGaP in HBTs is under investigation and shows promise. Both MBE and MOVPE compete strongly for strained AlGaAs/InGaAs/GaAs pHEMTs. GaN technology is raising hopes for specialized LED applications with affordable cost. MOVPE dominates the production of heavily carbon-doped AlGaAs/GaAs HBT, and MBE is focused on further refinement of Be-doped devices. Currently most of the developmental efforts and funding is directed towards modeling of the growth processes, development of fully automated and computer controlled growth systems, precise control of growth parameters, study and control of strain and defect, device modeling & fabrication, yield improvement, susceptibility to extreme conditions, safety aspects with a view to achieve for repeatable and re-producible results. The evolution of multi-layer growth technology can be divided in to six time periods 1966-1977-Early manufacturing implementation; 1978-1984-Expanding and refining the technology; 1985-1987-New growth chambers; 1988-1998- New technology, diagnostic tools; 1999-2005-Experiments under micro-gravity conditions and the future.

Future and Foreseen Developments in Nano Epitaxial Technology

Multi-layer hetero-epitaxy is a very challenging and active research area where progress is rapid. Because of the importance of low growth temperatures to almost all advanced multi-layered structures, there is a continuing trend towards lower temperature. Even conventional vapor phase epitaxy (chloride & hydride processes) has been revolutionized by the recently developed low-pressure deposition techniques. Further, this technology is being extended to the growth of epitaxial layers on insulation substrates by means of a variety of lateral seeding approaches. More established epitaxial techniques; particularly MBE and MOVPE are undergoing almost continuous improvement and enhancement. Models are sought that will predict the most favorable substrate orientation for a given film deposition. The technology of choice in the future will undoubtedly be dependent upon the required growth of the sophisticated devices in an environment that achieves the quality, uniformity, and the yield of the wafers required for the manufacturing processes. Each technology requires a unique set of conditions.

A series of models and physico-chemical methods have been used to investigate the growth mechanism of III-V vapor phase or chemical beam epitaxy. The interesting results show clearly the importance of fundamental research focused on an applied problem. Crystal Growers and Solid State Device Engineers can take advantage of scientific and engineering issues of the investigation namely thermodynamics, nucleation, chemical kinetics, mass transport, heat transfer, fluid flow, reactor design, defect control, physico-chemical and electro-optical properties of the grown structure. These issues will greatly help in attack the problems that limit the deposition of device quality epitomical layer. However, to effectively accomplish this task, epitaxial crystal grower and device engineer must broaden their knowledge base and closely co-operate to include the growth mechanism, concepts of crystal growth and process modeling and tailoring the properties of materials and device fabrication. This will help in improving the yield and performance of the devices.

Characterization of Epitaxial layers

Presence of impurities and extended crystal defects with in III-V heteroepitaxial structures used in micro-optoelectronic and microwave applications adversely affect the device performance and reliability. The defects and impurities introduce deep traps in the band gap and behave as non-radiative recombination centres. Different types of crystal defects may form inside the heterolayers during growth. Since layer and substrate have the same crystal structure but different lattice parameters, the accommodation at the interface may occur either by elastic deformation of the layer until cell or by the formation of misfit dislocation parallel to the interface itself. The complex phenomenology of the misfit dislocations, including the crystallographic nature, the asymmetric distribution on the interface plane, the

location in depth and the influence of the substrate misorientation are the current active areas of research. In addition to the misfit dislocations, other extended crystal defects namely threading dislocations, micro cracks twins and stacking faults both single and arranged in tetrahedral pyramids may be present with in epilayers.

Optical characterization technique is quite useful to investigate compositions, impurities, defects and surfaces of epitaxial layers. Optical technique has been widely used because of its advantages of high sensitivity, nondestructive and contact less nature etc. IR analysis is one of the most powerful techniques to assess the light element impurities in semiconductors. The method utilizes the optical excitation of localized vibration mode (LVM) of impurity atoms whose excitation energy is in the IR region. Although PL has long been used to study the electronic and optical properties of semiconductors, it has been mostly limited to the qualitative analysis[21].

Trends of Epitaxial Technologies and III-V Materials Systems and Devices - R& D and Industry

Epitaxy is extensively used in R&D, but for GaAs device production, its role until recently has been limited mainly to discrete device manufacture. With growing demand for performance levels, which can be achieved with heterostructure devices, the influence and use of epitaxy in GaAs ICs manufacture is steadily increasing. VPE, although widely used in the micro-optoelectronics industry, has significant applications in electronics. It is successfully used to grow and fabricate thick layer based power FETs and MMICs and has the advantage of being a reasonably low cost technology. But the inability to grow AlGaAs heterostructures, and poor flexibility, limits its use in GaAs electronics. For MESFET devices, epitaxial technology readily offers abrupt doping transitions compared to ion implantation, resulting in far better device characteristics. MBE is used for production of discrete microwave devices, such as power FETs. Recent advances in MOVPE have made inroads and eroded this position to some extent. Particularly in Japan, the use of MOVPE is increasingly used for the production of power FETs. Production of discrete HEMTs, one of the biggest markets for MBE material, is also coming under increasing pressure from advances in MOVPE and MOMBE. For GaAs ICs, the main heterostructure devices under investigation are HEMTs, HBTs and HFETs. MBE has dominated production of HEMT devices which are based on GaAs/AlGaAs or InP/GaInAs structures devices devices. There is an increasing interest in strained, or pseudo-morphic, devices fabricated by growing a thin InGaAs layer between the AlGaAs and the GaAs buffer. In such pHEMTs, the superior transport properties of the InGaAs channel, and improved sheet charge, lead to higher transconductance and improved RF power densities. MBE has dominated the pHEMT sector. However, MOVPE presents a strong challenge and devices with noise and gain comparable to MBE have been fabricated. In recent years considerable attention and R&D on both material preparation and device fabrication using newly developed Atomic layer epitaxy (ALE) and MOMBE technologies on the above and GaN based devices were diverted and the field is in infancy stage.

MOVPE has dominated the HBT sector where the typical GaAs/AlGaAs device structure played significant role. The HBT requires a heavily doped p-type base region between the emitter and collector and is produced by MBE using beryllium as dopant (acceptor). Alternatively this has been realized by heavily doping with carbon during MOVPE growth, which enables reproducible high doping levels and negligible doping diffusion. An effort is presently underway to replace the carbon tetrachloride source, which is an ozone-depleter. Much attention has been focused on refining and use of Be in MBE for the development of HBT devices. Be incorporation and using high As/Ga flux ratios and low substrate temperatures controls diffusion. High reliability HBTs with Be-base doping has been realized by MBE. But Be is highly toxic and still alternatives are being sought. Both MBE and MOVPE are now attempted to grow alternative wide gap emitters, such as GaInP, in place of AlGaAs. GaInP offers improved current gain and improved stability over the GaAs/AlGaAs system, due to the elimination of oxygen contamination associated with using aluminum. It also simplifies fabrication, since many wet and dry etches are available with high selectivity between GaAs and GaInP. Thus from a technical standpoint MBE and

MOVPE each have several advantages and drawbacks. From a cost perspective to some extent both are evenly balanced. MBE is traditionally perceived as more expensive, but the availability of multi-wafer and barrel systems has almost eliminated the differential. For high volume runs there is no significant difference in price between MBE and MOVPE in the market place today. Both technologies typically offer products at prices ranging from 5-8 times that of the semi-insulating substrate.

Gallium and Indium– An Uncommon and Important Metals

High purity starting and input materials such as Ga, In, As, P, etc. are needed to prepare and produce GaAs, GaN, GaP, InAs, InP and related single crystals, substrates and epitaxial structures. 90% of World's production of ultra high pure (7N/ 8N) gallium metal is consumed in the manufacture of GaAs, GaN, GaP bulk crystals, substrates and wafers and remaining 10% is consumed for synthesizing the precursors (trimethyl gallium, triethyl gallium, molecular and atomic level) for VPE, MBE, MOVPE, ALE epitaxial growth. High purity gallium oxide is also used in preparing single crystal garnets for special optical applications. Gallium gadolinium garnet (GGG) substrate is required for fabrication of bubble memory devices. Gallium gadolinium garnet (GGG) crystals used construct bubble memory devices. Gallium-scandium-gadolinium garnet (GSGG) rods are the potential laser host materials. Researches are underway to fabricate super-conductor components using ultra high pure gallium.

Prospects of ultra high pure gallium and indium

Use of GaAs and InP based micro-optoelectronic devices in the laser, compact disc players, light emitting diode based television, information and communication technologies is generating substantial amount of business for GaAs, InP, GaN devices. But then silicon technology is already well established and its production cost kept affordable, which stage has not yet been reached for GaAs, InP, and GaN devices. But GaAs, InP IC integrated circuits with over 50,000 transistors, which are mass-produced, find their way in supercomputers, telecommunications, and military, space instrumentation. The Japanese, European manufacturers and US have been leading in the commercial production of GaAs, InP, GaN devices and components. The GaAs programmable logic devices are prevalent in the logic that surrounds the microprocessors in super-computers. The most dramatic impact on the computer market had occurred in the early 1990's. However, technology is maturing now for large-scale manufacture of GaAs, InP computer chips at costs competitive with silicon. To conclude and forecast, there is a steady future for Gallium and Indium metal and GaAs, InP devices.

Purity Requirements for Nano GaAs, GaN, InP, InN Nanomaterials Technology

Ultra high pure (8N/7N) gallium and indium are used for GaAs and InP micro-optoelectronics and also for manufacture of semi-insulating GaAs and InP substrates and devices. MMIC applications demand stringent purity requirements. Particularly the metallic impurities namely, Ag, Sn, Te, Cd, Mg, Al, Si, Fe, Ni, Cu, Hg, Pb, Zn, V, etc. should be in the range of ppb levels and as also the other unwanted atmospheric, organic, gaseous, oxide impurities at desirable low levels. Purity analysis with consistent batch results; clean environment and class clean air station(s) for purification, processing, packaging and purity certification are the very major segments of gallium and indium purification and production. Data sheets for batch scale operation, yield improvement, quality and purity tests are the backbones of process perfection and development of technology package. As far as 6N and above pure gallium and indium testing is concerned, the following purity testing scheme is meticulously followed. a) Using GD-MS, neutron activation methods, the analytical procedures, developed, mastered and standardized and purity of the high pure metals is tested. b) Residual resistivity ratio concept is also used to arrive at the impurity content. c) Using 7N/ 8N pure gallium and indium samples as input materials, GaAs, GaN and InP epi-structures are also grown and their electrical resistivity is measured. Feed back from the resistivity data (reverse engineering approach), impurity data is generated and correlated with GD-MS, neutron activation analysis data. For process development, optimization, fine-tuning and perfection, the above feedback is finally used for experimental modeling

of the whole process and the required quality output with consistent results is achieved.

Emerging Techniques for Purification of Gallium and Indium (7N to 8N Purity Level)

Crystal growth and chemical vapor transport concepts are attempted and employed for refining of certain selective metals and compounds relying on the fact that, if the solid is a single crystal rather than a ploy crystal, then effective segregation takes place. Following crystal growth and gradient freezing techniques aided by class clean processing, testing and packaging environment produces ultra high pure gallium and indium. Few companies have mastered these technologies and marketing 7N/8N gallium and indium in the form of crystalline ingots/rods under special sealing. Very limited details on this topic can be found in some patents. Gallium is boiled and transported through a carrier agent and thus gallium crystals are grown. To remove the atmospheric oxygen, nitrogen impurities as also for suppressing the formation of oxides and nitrides from and in the vicinity of the melt, vacuum induction melting techniques using suitable crucibles is practiced. Growth of single crystals of gallium, vacuum refining, maintenance of the crystalline state in gallium, purity testing, sealing by means of special cooling, packaging and their instrumentation aspects are very challenging areas and very little disclosed information is available on these topics.

Zone Refining and Segregation of Impurities in Gallium and Indium

In multi-pass zone refining, the optimal zone length in each pass and their corresponding maximum fraction of solute removal were obtained normally with distribution coefficient and number of passes at a temperature above melting point. A narrow liquid (or molten) zone travels through a relatively longer charge (or ingot) of solid carrying with it to a position of the solute impurities in the charge, since, the concentration of the impurities in the solid crystallizing from the molten zone is different from that of the remaining in the liquid, the impurities are swept to one end of the sample. The final segregation (distribution) of impurities mainly depends on the segregation (distribution) of impurity in the original charge and on an intrinsic property of the impurity known as the segregation (distribution) coefficient. The zone-refining process ensures the driving (segregation) of many of the impurities, by and large, through thermo-physical cum thermo-dynamical activated processes to one end of the sample, which results in yielding the starting material in a pure and crystalline form. Factors that are affecting the refining process include (a) direction and rate of zone movement, (b) zone size and length of sample, (c) diameter, thickness, conductivity and compatibility to extreme temperature of the sample tube, (d) temperature gradient, (e) thermal conductivity of phases, (f) latent heat of fusion, (g) density differences between the solid and liquid, (h) speed of crystal formation, (i) surface tension of the liquid and (j) tendency of the liquid to super-cool. In practice, using a narrow zone and increasing number of passes leads to efficient refining effect.

EXPERIMENTAL

Zone refiner used for purifying gallium is of different, very complex type, fraught with variety of instrumentation and operation problems, when compared to the systems used for other high melting point metals such as Ge, Cd, Te, In, Si etc. This is due to the fact that, the gallium is liquid at room temperature and hence, creation and their maintenance of narrow solid and liquid regions become more difficult. Typical compatible crucible has to be used and experimental conditions and parameters such as coolant flow rate, coolant and zone temperature, with reference to ambient temperature, sample tube dimension, thickness and conductivity, direction and rate of traverse speed have to be established and optimized at both the pre and final stages of refining. Upgraded Zone Refiner (AT, USA) has been used in the present study for zone refining of 4N/5N pure gallium and indium. The instrumentation and other technical details of the system including heaters, coolant and drive assembly and processing were discussed elsewhere[22-24]. Process flow sheet and photographic view of the zone refiner is shown in Fig. -4 and Fig. -5.

4N/5N pure gallium was chemically treated with supra pure acids, homogenized and loaded into a cleaned tube of 10 mm i.d., 12 mm

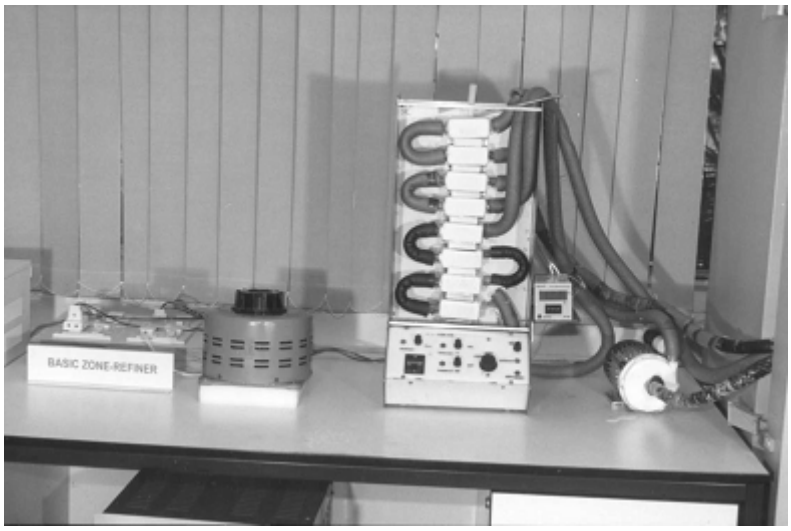
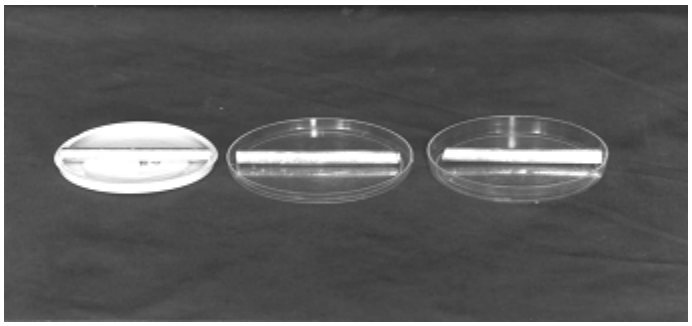


Fig. - 5: Vertical zone refiner



A B C

Fig. - 6: Top (a), Middle (b) and Bottom(c) regions of zone-refined and frozen gallium ingot

o.d. and 500 mm length. Further the sample was super-cooled to (-) 70 ^{0}C and kept for 180 hours. This super cooled and solidified sample was again subjected to further homogenization by following a re-melting (80^{0}C)-cooling (-10^{0}C)-super-cooling (-70^{0}C) scheme using the climatic chamber. A pre-stage fifteen-pass cycle (each pass of three hours duration) zone refining experiment with circulation of coolant at (-8^{0}C) has been carried out in order to sensitize the system parameters and establish the suitable experimental conditions and narrow zone(s). In the second stage refining, to further narrow down the liquid region, a twenty-five–pass cycle zone refining experiment with circulation of coolant at a temperature of -28^{o}C was carried out. After each stage the sample was solidified and kept in solid form. In third stage, a twenty-five pass zone-leveling experiment on the sample was conducted with coolant temperature at –25^{o}C.

Zone-refining experiment on the pre-stage zone refined and zone-leveled sample was conducted by following the pre-calibrated experimental conditions and parameters. Coolant flow with required flow rate and temperature range of (-) 20^{0}C to (-) 40^{0}C was maintained. Temperature profile for each set of passes was optimized set with reference to heater-coolant–ambient temperature. Drive mechanism then started at a first cycle and the sample tube was allowed to traverse. The zone length of 30 mm and width of 15 mm was maintained and experiment continued to complete sixty-five refining cycles. Each completed cycle was recorded through a cycle counter. The sample tube

containing the refined metal has been stored at 4^0C. Experiment of each 65 pass was repeated on three batches of 300-g sample of same 4N/5N pure material lot. At the end of each batch, the ingot was cut into three portions every time analyzing the top, middle and bottom end portions separately for the trace impurities content. The sample tubes, storage containers used for sample homogenization, preparation for analysis and were cleaned with ultra pure acids aided by class clean room (1000) and clean benches (100) environment.

RESULTS AND DISCUSSIONS

Three ingots sliced from the refined gallium bar are shown in figure.6. Purity test results are shown in table 1 and 2, which confirms the movement trend. From interpretation of the results

Table - 1: Purity test results of zone refined gallium # top region of the total length of the bar different locations- batch-1and zone leveled sample.

Impurity	Top region (in ppm)					(in ppm) Zone leveled	Raw Material
Element	TR1	TR2	TR3	TR4	TR5		4N
Zn	<0.10	<0.10	<0.10	<0.10	<0.10 (0.10*)	0.08	55(61.8*)
Pb	0.345	<0.10	0.261	<0.10	<0.10 (0.10*)	<0.03	2.1(2.16)
Fe	<0.10	<0.10	<0.10	<0.10	<0.10 (0.10*)	NA	<00.500
B	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.502
Mn	<0.10	<0.10	0.078	<0.10	<0.10	NA	1.00
Cr	<0.10	<0.10	0.022	0.52	<0.10	NA	NA
Ag	<0.10	<0.10	<0.10	<0.10	<0.10	NA	NA
V	<0.10	<0.10	<0.10	<0.10	<0.10	<1.00	68.00(48*)
Cu	1.01	<0.10	<0.10	1.38	0.15 (0.10*)	<0.50	12.00
Al	<0.10	0.12	0.33	<0.10	<0.10	0.13	<0.50
Ni	<0.10	<0.10	0.038	<0.10	<0.10	3.00	NA
Hg	<0.10	<10	<0.10	<0.10	<0.10 (0.10*)	<0.50	NA

ICP-OES – Detection limit 0.10 ppm; <0.10 - Not Detected (Below Detection Limit); NA- Not Analyzed; * - Repeat Analysis

it was also observed that, most of the impurities have gone below detection limit as far as purest top region of gallium bar is concerned. It was seen that, there was a significant improvement in purity of the refined sample (6N-top region) with respect to targeted major metallic impurities as compared to starting 4N/5N pure gallium.

The movement trend of selected impurities segregation along the zone-refined bar(s) has also been mapped and the results will be discussed. It was observed that most of the impurities traveled along the melt-interface direction (towards ingot bottom portion), thus, leading to top portion in purest form. Sampling and analysis were also repeated for bottom, middle and top portions for the three batches of the zone-refined bar. The segregation trend and consistency of the purity test results respectively, were thus ascertained and confirmed. Effect of experimental conditions such as, number of passes, zone width and interdependence of ambient, heater and coolant temperature, coolant coil and box dimension, coolant flow rate on the zone refining of gallium was studied in those crucial criticality test experiments. The inferences lead to suggest that these parameters and pre and post stage sample cutting, cleaning procedures and environmental conditions play role in reducing the impurity and contamination levels. Selected impurities in gallium and indium were all segregated much more successfully by crystallization from the melt, if the solid was a single crystal rather than a

Table - 2: Purity test results of zone refined indium # top region

Element	ICP-OES (in ppm)	ICP-MS (in ppm)	Raw Material - 4N pure(in ppm)
Ag	N. D	2.20	1.00
Al	5.54	ND	2.60
Cu	N.D	0.66	3.10
Fe	7.15	0.70	5.60
Sn	N.D	NA	9.58
Ga	0.98	0.40	NA
Zn	0.795	0.06	NA
Ge	N.D	ND	NA
Hg	NA	ND	NA
Pb	NA	ND	4.20
Cd	ND	NA	

ICP-OES – Detection limit 0.10 ppm;
N.D- Not Detected (Below Detection Limit);
NA- Not Analyzed;

poly crystal and that the rejection of impurities during single crystal growth is substantially high. This is due to the fact that the pre-stage refining and zone leveling of sample creates conducive nucleation environment for effective crystallization. As the sample becomes more and more pure, the material was to get transformed (fractional crystallization) into well-defined and separated crystallites or grains and thereby increasing the atomic order and rejecting foreign atoms other than gallium. Each grain would exhibit crystalline features of the sample. To figure out the extent of crystalline phase formation in the 65-pass cycle zone-refined sample, X-ray diffraction (XRD) study on the sample was carried out and the results are shown in Fig. - 7. SEM and SEM-EDAX results (Fig. -8) imply that the sample contains carbon contamination

In this study we have mainly concentrated on the segregation aspects of major metallic impurities, taking into account of the recovery,

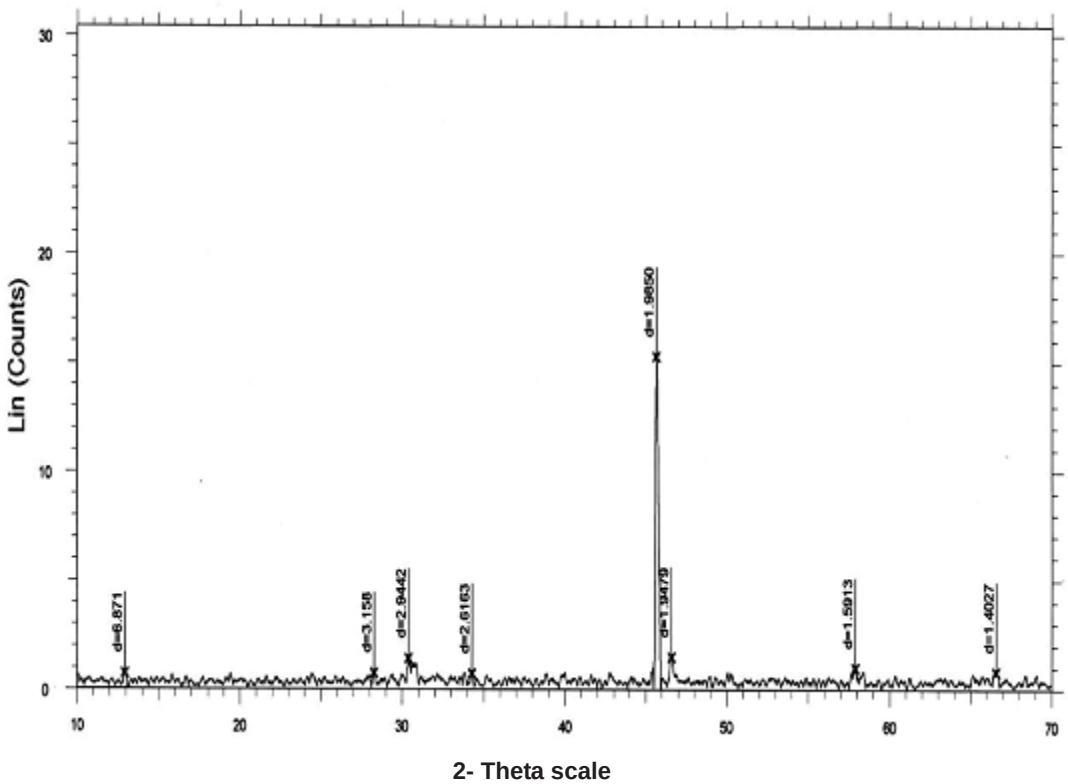


Fig. - 7:.XRD pattern of zone refined 5N+ pure gallium

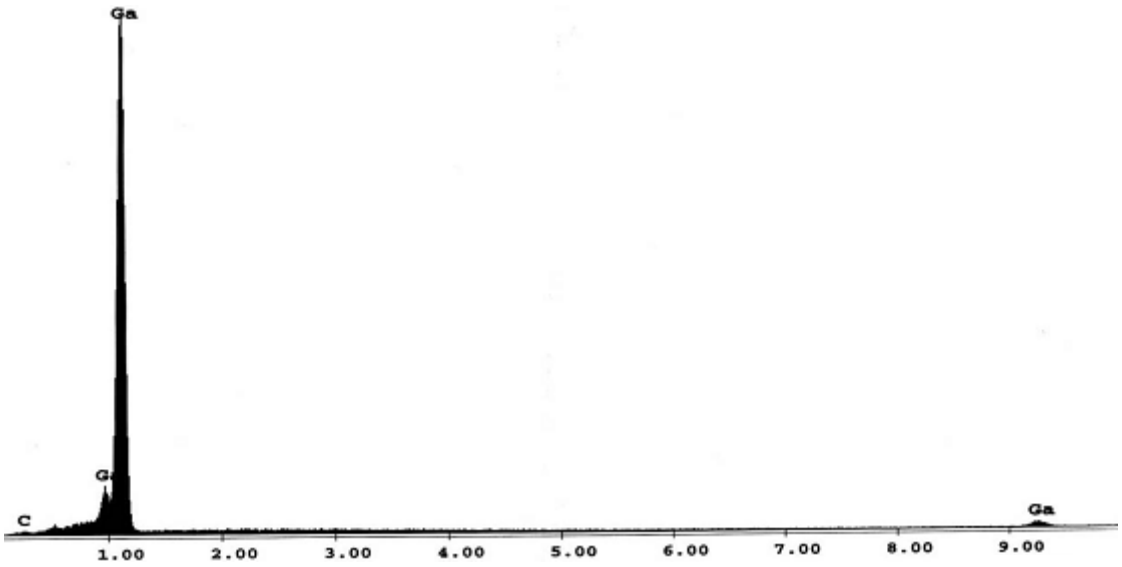


Fig. - 8: SEM-EDAX Spectrum of zone refined 5N+ pure gallium

extraction processes of Indian source 4N/5N pure gallium. Purity control and test aspects with specific reference to O, N, C elements and other gaseous impurities by oxidation, heating under vacuum and using exclusive CHNOS analyzer needs to be further researched. Origin of these impurities attribute to the contamination that took place while treating, cutting, preparing the samples with acid media and the overall effect of sample handling environment. Taking in to account of the zone-refiner system's complexities and limitations used in this study, as also the sample quantity and sample tube dimension, the purer portions (middle and top) portions of 1st and 2nd pre-refining stage samples were again melted and zone-leveled (15 pass) to make uniform distribution of impurities and homogenization of the sample to begin with. This zone-leveled (reverse of zone refining process) sample bar has been used for the subsequent zone refining in an effort to change the atomic ordering and allow the impurities to free and flow themselves to the maximum extent by the so-called thermo-physical cum activation process. This study reveals that for ultra purification of Indian 4N/5N pure gallium, no single method is adequate and oxidation, heating under vacuum and crystallization seems to be good combination of processes. Keeping the Indian climatic conditions, removal of oxygen or oxides and other gaseous impurities should be withheld until the final step of packaging in class clean environment and after treating the metal under vacuum heating and then be protected by an inert atmosphere.

Conclusion

Current trend and future prospects of advanced epitaxial techniques associated with the preparation, evaluation of gallium based epitaxial structures and techno-economic aspects of gallium based multi-layered devices have been discussed. Principles and techniques associated with the purification and purity analysis characterization of gallium and indium, and their single crystal and epitaxial layer growth current trend and future prospects were outlined. Findings of an investigative study on the segregation characteristics of metallic impurities associated with gallium and indium metals are discussed.

ACKNOWLEDGEMENTS

The author thank Prof. P. Ramasamy, CSIR Distinguished Emeritus Professor and Prof. R. Dhanasekaran UGC-Inter-University Centre for Crystal Growth, Anna University, Chennai, for introducing him the fields of GaAs materials crystal growth, epitaxy and gallium and indium purification research. Interaction and discussions with Prof. J.

Kumar, Anna University, Smt. P.K.Girija, C-MET ; Prof. S. Dhar, Calcutta University, Dr. R. Muralidharan and Dr. L. Durai, SSPL, Delhi, Prof. R.Cadoret, LPCM, CNRS, Clermont Ferrand, Prof. Yves Monteil, LMI, CNRS, Lyon France and Prof. Li-Shing Hsu, NCUE, Chang Hua, Taiwan at different stages were also quite useful. The project(s) and fellowship(s) support received from DST, MIT, DRDO and UGC, CSIR, IFCPAR Delhi is acknowledged. Analytical and other technical help received from Dr. M.R.P.Reddy, K.Balaraju and K.Ghosh is acknowledged. The author also thanks C-MET authorities for all the required logistic support provided for implementing the projects.

REFERENCES

1. Pashley, D.W., *Epitaxial Growth Part A,* (ed. Matthews J.W.), Academi Press, New York, (1975).
2. Pashley, D.W., *Advances in Phys*., Vol. **5,** pp. 173-240, 1956.
3. Markov, I ., *Materials Chem. and Phys.,* Vol. 9, 1983, , 93-116,
4. Franchi, S., Margadonna, D. and Pelosi, C., *' Materials Chemistry,* Vol. **4,** 1979, 529-548
5. Anderson T.J., *'Microelectronics Processing,* (Ed. Jensen D.F.), American Chemical Society, Washington DC 1989, pp.105-171.
6. Greene, P.D., *"Advanced Crystal Growth',* (Eds. Dryburgh, P.M., Cockayne B. and Barraclough K.G.,) Prentice Hall, New York pp. 221-242, (1987).
7. Korec, J., and Heyen, M., *J.Cryst. Growth* 1982, 60, pp 297-306,
8. Nishizawa, J., and Kurabayashi, T. *J. Electrochem. Soc*., 1983, 130, pp.413–417
9. Kern, R., *Epitaxial Electronic Materials* (Eds: Balderschi, A., and Paorici, C), World Scientific Publishers, Singapore, 1988.
10. Mani, V.N., Dhanasekaran, R., and Ramasamy, P., *Semicond. Sci. Technol.,* **2,** 73-77 (1987).
11. Mani, V.N., Dhanasekaran, R., and Ramasamy, P., *Thin solid films*, **163**, 437-441 (1988).
12. Mani, V.N., Dhanasekaran, R., and Ramasamy, P., *Journal of crystal growth,* 99, 333-340 (1991).
13. Mani, V.N., Dhanasekaran, R., and Ramasamy., P., *J. Appl. Phys.,* **69,** 1399-1407 (1991).
14. Mani, V.N., *Bull.Mater.Sci.,* **17,** 469-478 (1994).
15. Stringfellow, G.B., *Crystal Growth: A Tutorial Approach* (Eds. Bardsely, W.,
16. Hurle, D.T.J., and Mullin, J.B.), North Holland, Amsterdam, 217-239 (1979).
17. Joyce B.A., *'Advanced Crystal Growth* ', (Eds. Dryburgh P.M., Cockayne B., and Barraclough, K.G.,) Prentice Hall, New York, 337-382 (1987).
18. *Epitaxial Electronic Materials*, (Baldereschi, A., Paorici, C.,)World Scientific, Singapore, 124-163 (1988).
19. Nishinaga T. MBE Growth Process in Procs.Intl.School on Advanced Electronic Materials (1995) .
20. Dapaskus, P.D. , Den Baars, S.P., Chen, Q., Jeong, W.G., and Maa, B.Y., *Prog. Crystal Growth and Charact*. **19,** 137-147 (1989).
21. Franzosi, P. Characterisation of Epitaxial Layers in Procs.Intl.School on Advanced Electronic Materials (1995).
22. Mani, V.N., Proceedings of the International Workshop on Preparation and Characterization of Technologically Single Crystals, NPL, New Delhi, Feb. 26-28, 451-458 (2001)
23. Mani, V. N. and K.Balaraju Physics of Semiconductor Devices Vol.2 pp.1142-1146 Eds. Vikram Kumar etal, Allied Publishers, New Delhi (2001).
24. Mani, V. N. and K.Balaraju Physics of Semiconductor Devices Vol.**1,** 203-205 Bhatt K.N. *et al.,* Allied Publishers, New Delhi (2003).