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REDUCTION OF ARSENIC WASTES IN THE SEMICONDUCTOR INDUSTRY

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FOREWORD

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land air and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of our natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge data base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and iprove the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

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E. Timothy Oppelt, Director
National Risk Management Research Laboratory

ABSTRACT

The research described in this report was aimed at initiating and developing processes and process modifications that could be incorporated into semiconductor manufacturing operations to accomplish pollution prevention, especially to accomplish significant reduction in the quantity of arsenic waste generated in that industry. The effort resulted in the development of processes for the recovery of both gallium and arsenic from gallium arsenide semiconductor crystal manufacturing. Recovery of materials from both solid and aqueous waste streams was achieved and the solids recovery process was demonstrated at an operating semiconductor manufacturing plant. The processes developed herein are applicable to other types of III-V semiconductor manufacturing, including indium phosphide, gallium phosphide and indium arsenide manufacturing.

The two processes developed include processes for recovery of materials from both solid and aqueous waste streams. The solid waste recovery process a thermal process for separation of gallium and arsenic from each other and from process contaminants with subsequent thermal refining of the captured gallium and arsenic. The aqueous waste recovery process incorporates sequential precipitation of the arsenic and gallium to allow for their recovery and reuse. This report was submitted in partial fulfillment of the requirements of Cooperative Agreement No. CR 821808-01

TABLE OF CONTENTS

Section	Description		Page
	Notice		ii
	Foreword		iii
	Abstract		iv
	Acknowledgements		x
1.0	Conclusions and Recommendations		1
2.0	Introduction		3
	2.1	Why Arsenic and Other Toxic Elements are Important in Semiconductor Device Manufacturing	
	2.2	"Strategic" Elements Used in Semi-conductor Devices	5
	2.3	General Summary of Manufacturing Processes for Compound Semiconductors	7
	2.4	Summary of Pollution Prevention Processes Developed Under This Grant	13
3.0	Recycling and Recovery of Materials from Solid GaAs Wastes		18
	3.1	Current Disposal/Recycling Methodology	18
	3.2	Recovery Process Development	19
	3.3	Prototype System	21
4.0	Recovery and Recycling of Gallium and Arsenic from Crystal Polishing Wastewaters		30
	4.1	Current Treatment Methodology	30
	4.2	Approach for Metals Recovery	32
	4.3	Methods for Arsenic Recovery	35
	4.4	Methods for Gallium Recovery	39
	4.5	Process for Recovery of Materials from Aqueous Waste	42
5.0	Economic Assessment		43
	5.1	Factors Affecting the Economics of GaAs and Other III-V Material Recovery Systems	
	5.2	Important Economic Factors for Solid and Aqueous Gallium Arsenide Recovery	45

TABLE OF CONTENTS (continued)

Section	Description	Page
5.3	Important Economic Factors for Solid and Aqueous Indium Phosphide Waste Recovery	45
5.4	Important Economic Factors for Recovery of Other III-V Compounds	46
5.5	Economic Factors for Recovery of Wastes from III-V Epitaxial Processes	46
5.6	Summary	46
References		48

LIST OF FIGURES

Figure No.	Description	Page
2.1	Process Flow Diagram for Compound Semiconductor Device Fabrication	8
3.1	Schematic of the Recovery Process for III-V Solid Wastes	21
3.2	Cross-section of Unit Operation 1 – Thermal Separation Furnace	22
3.3	Schematic of Existing Equipment for Low-Temperature Purification of Gallium	23
3.4	Schematic of Existing Equipment for Sublimation /Purification of Arsenic	24
3.5	EDS Analysis of Unreacted GaAs	25
3.6	EDS Analysis of Volatized Material	26
3.7	EDS Analysis of Residue	26
3.8	EDS Analysis of Volatile Material after 2-hour Run	26
3.9	Analysis of Residue from 1-hour Run with Continuous Evacuation	27
3.10	Analysis of Residue from 2-hour Run with Continuous Evacuation	27
3.11	SIMS Analysis of Pure Gallium Fraction Resulting from Thermal, Low-Pressure Recovery of GaAs	28
3.12	SIMS Analysis of Gallium "Slag" Resulting from Thermal, Low-Pressure Recovery of GaAs	29
4.1	Current Treatment Approach for GaAs Polishing Wastes	31
4.2	Comparison of Metal Arsenate Systems	36
4.3	Experimental Residual Concentrations of As as a Function of pH and Metal-Arsenate System at 25°C	37

LIST OF FIGURES (continued)

Figure No.	Description	Page
4.4	Experimental Residual Concentrations of As in Calcium Arsenate Precipitates as a Function of pH and Temperature	38
4.5	Measured Residual Ga Concentrations as a Function of Metal-Arsenate System and pH at 25°C	40
4.6	Measured Residual Ga Concentrations Following Calcium Arsenate Precipitation as a Function of Temperature and pH	41
4.7	Developed Process for the Sequential Recovery of Gallium and Arsenic from GaAs Polishing Wastes	42

LIST OF TABLES

Table No.	Description	Page
2-1	Compound Semiconductors	5
4-1	Arsenic and Gallium Concentrations in a Typical Industrial Filtrate and Filter Cake using Ferric Hydroxide Coprecipitation Methodology	31
4-2	Treatment/Recovery Procedures for As Considered and Tested in Phase I	33
4-3	Treatment/Recovery Procedures for Ga Considered and Tested in Phase I	34
4-4	Comparison of Metal-Arsenate Systems for As and Ga Removal/Recovery from GaAs Polishing Wastewaters at Different Metal-As Ratios	39
5-1	Estimated III-V Raw Material Costs	43
5-2	Estimated Annual Tonnage of Bulk III-V Crystals Produced in 1995 in the U.S.	44
5-3	Estimated Annual Costs of Raw Material Wasted in the Form of Solids from Gallium Arsenide Crystals	45
5-4	Estimated Annual Costs of Raw Material Wasted in the Form of Aqueous Streams from Gallium Arsenide	45
5-5	Estimated Annual Costs of Raw Material Losses in Epitaxial Growth Processes	46
5-6	Total Estimated Annual Dollar Value of Wasted Raw Materials from III-V Semiconductor Growth Operations	47

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1.0 CONCLUSIONS AND RECOMMENDATIONS

Gallium arsenide (GaAs)-based semiconductor devices are used for a multitude of military and commercial applications in the United States and throughout the world, including lasers, light-emitting diodes, and communications. Manufacturing processes devoted to the fabrication of these devices generate large volumes of wastes which contain the toxic metal arsenic, as well as the economically valuable metal gallium. Arsenic is currently regulated under a number of federal and state laws, including legislation that makes generating companies liable for environmental cleanup at waste disposal sites, even if these wastes have been manifested and disposed of in an approved manner. In addition, even though many of the wastes currently being disposed by the industry are unlisted (e.g. solid GaAs), the toxic arsenic contained therein is regulated, should it be released to the environment (e.g., through the action of acids, present in many landfills). Current gallium prices make recovery of wastes containing this metal economically viable if the recovery process is sufficiently low cost. Therefore, recovery of these metals (As and Ga) from GaAs processing wastes is economically advantageous.

One process has been developed for the on-site recovery of both arsenic and gallium from gallium arsenide (GaAs) solid wastes. The process described herein first involves the thermal separation of GaAs solid wastes into their constituent elements (with a minimum of energy input or additional handling). Each of the separated elements is then purified to the required levels for further crystal growth using low-cost procedures. Because of this three-step approach, the developed procedure can accommodate a wide range of input material characteristics. Prior work with GaAs thermal separation and constituent element purification provided a template for the development of this process, and subsequent thermodynamic consideration of each of these unit operations provided a theoretical basis for process optimization.

A second process was developed for the recovery of both arsenic and gallium from gallium arsenide polishing wastes. The economics associated with the current disposal techniques utilizing ferric hydroxide precipitation dictate that sequential recovery of toxic arsenic and valuable gallium, with subsequent purification and in-house reuse of both, is to the benefit of the gallium arsenide crystal grower. The developed process involves first the removal of the majority of the arsenic and suspended polish as a mixed precipitate of calcium arsenate and polish. This first process step is performed at ambient temperatures and at a pH > 11 using NaOH. At these pH regimes, gallium is retained in solution as a sodium gallate species. Precipitation of virtually pure gallium hydroxide is then accomplished in the next process step through pH adjustment to between 6 and 8 with waste acids. The commonly used ferric hydroxide coprecipitation step is retained as a final treatment step, but because of the removal of the majority of the arsenic, gallium, and polish in the two prior steps, far less waste is land disposed. A patent application has been filed with the United States Patent Office.

In summary, the authors recommend that the processes developed under this cooperative agreement be considered for implementation as in-plant pollution prevention techniques. It is believed to be to the ultimate economic advantage of existing GaAs

fabrication companies to minimize or altogether eliminate the amount of toxic arsenic which is disposed of from their manufacturing operations. This not only eliminates "short-term" costs such as manifesting and disposal, but also the much more costly "long-term" liability costs associated with environmental cleanup. Payback for gallium recovery is "immediate", in terms of reduction of operating costs. The payback associated with arsenic recovery is an avoidance of future costs that might be incurred for environmental cleanup. The processes developed will allow recovery and reuse of these materials in a cost-effective and environmentally responsible manner.

2.0 INTRODUCTION

The majority of prior research devoted to pollution prevention in the vital semiconductor industry has focused on the replacement of ozone-depleting chlorofluorocarbon (CFC) precision cleaners and solvents with environmentally-benign chemicals which can function in the same capacity. With the guidance of such entities as SEMATECH (SEmiconductor MAnufacturing TECHnology, a research consortium of the 10 largest U.S. semiconductor manufacturers) and successful development programs by the industrial vendors, a host of proven replacements have been developed and are beginning to be implemented throughout the semiconductor manufacturing industry. Ongoing efforts in this area will undoubtedly continue as further improvements in cleaning processes are tested and marketed.

However, there are ongoing environmental threats in certain types of semiconductor manufacturing that have been largely ignored until the present. For example the toxic element arsenic is widely used as a principle component in important semiconductor substrates such as GaAs and as a dopant for modifying the electronic characteristics of other substrates. At present, much of the waste produced in arsenic-based semiconductor manufacturing goes to land disposal, while arsenic-laden wastewaters produced in some operations are released (at low concentrations) to local POTWs. Arsenic is a relatively low cost material and by itself, offers little economic incentive for the implementation of pollution prevention.

There is, however, an incentive for the development of waste minimization and materials substitution practices because of the ongoing use of certain, relatively scarce materials (e.g., gallium and indium) in arsenic-containing semiconductor device manufacturing procedures. The worldwide scarcity of such materials, as well as the lack of any domestic ores or suppliers, implies that the U.S. semiconductor industry must continue to pay high prices for imported raw materials. A number of very possible political or economic scenarios in foreign countries (or even in the U.S.) could drive the price of these materials to exorbitant levels, or could cause them to become essentially unavailable. Therefore, these materials truly can be classified as "strategic" metals, because of their use in a high technology, defense-related capacity, as well as their overall availability.

This report includes an introduction to the current status of the U.S. semiconductor industry from a materials-related pollution prevention standpoint. The U.S. Environmental Protection Agency (U.S. EPA) has an interest in the minimization of wastes (such as arsenic) from semiconductor manufacturing operations, while at the same time doing so in a way that will not hamper this important industry. Under the subject project, the University of Dayton Research Institute (UDRI) has conducted specific research into pollution prevention and waste minimization methods for this industry from a materials recovery perspective.

2.1 WHY ARSENIC AND OTHER TOXIC ELEMENTS ARE IMPORTANT IN SEMICONDUCTOR DEVICE MANUFACTURING

Silicon (Si) has been, and will continue to be, the dominant material used for the overwhelming majority of semiconductor device applications. Silicon itself is environmentally-benign, and is toxic only when in the form of gaseous silane or as certain organosilanes. In the last ten to twenty years, however, there has been a tremendous upsurge in the use of compound semiconductors (i.e., semiconductors whose crystalline structure contains two or more elements) for both commercial and military applications, as these materials have moved from the laboratory to specific applications. The usage and demand for compound semiconductors will continue to increase, in much the same way that the demand for silicon-based devices has continued to increase. Many of these compound semiconductors utilize chemical elements or precursor materials that exhibit varying degrees of toxicity (e.g., arsine, phosphine, stibine, etc.) For this reason, compound semiconductors present an opportunity to perform pollution prevention and waste minimization on a materials recovery and reuse basis.

2.1.1 Compound Semiconductors in Use Today

Table 2-1 presents a very general summary of the compound semiconductors which are in use today, or which are rapidly approaching widespread acceptability. Arsenic, as a group V element, is used in the manufacture of certain so-called III-V compound semiconductor materials (i.e., semiconductors composed of elements from group III and group V of the periodic table). The last three "families" shown in Table 2-1 have not as yet made a significant impact on the U.S. semiconductor industry, but should be expected to do so within the next ten to twenty years. The first three compound semiconductor families already are in widespread use.

The III-V semiconductors are used in a multitude of device applications, including light-emitting diodes (LEDs), lasers, detectors, and communication devices. For example, every cellular phone presently utilizes a gallium arsenide (GaAs) chip because the transfer of electrons through GaAs results in microwave oscillations. Because III-V pnictides can be readily alloyed with one another, it is possible to fabricate light emitters or detectors capable of functioning from far-infrared through green spectral wavelengths. And, with the continuing development of nitride-based devices (e.g. GaN, AlN), it will very soon be possible to fabricate solid-state devices that can function well into the ultraviolet.

The majority of II-VI semiconductors have traditionally been used for photovoltaic applications, wherein light energy is converted into electrical current. Mercury cadmium telluride (HgCdTe), when cooled to liquid nitrogen temperatures, is an excellent detector for use in the far-infrared spectral regime, and as such, is used on satellites for weather or spy applications. The IV-VI chalcogenides such as lead sulfide (PbS) are also utilized as infrared detector devices.

Table 2-1
Compound Semiconductors

Compound Family	Semiconductor Examples	U.S. Production/Usage
III-V	GaAs, InP, InSb, GaP, GaN	Large
II-VI	CdS, CdSe, HgCdTe, ZnSe	Large
IV-VI	PbSe, PbS	Medium
IV-IV	SiC, Si-Ge	Small
I-III-VI2	CuInSe2	Small
II-IV-V2	ZnGeP2	Small

2.1.2 Toxic Elements and Precursors Used in Compound Semiconductor Fabrication

Lead, mercury, and cadmium have been targeted by the Pollution Prevention Act as being among seventeen chemicals for which waste reduction options must be attempted for those manufacturing entities that utilize them. Therefore, fabricators of cadmium- and mercury-based II-VI compounds, as well as lead chalcogenide devices, are required to seek methodologies to reduce emissions of these chemicals.

In addition to these three chemical elements, arsenic and selenium are currently regulated under such legislation as the Drinking Water Act. Therefore, disposal of wastes containing lead, cadmium, mercury, arsenic, or selenium carries the potential for future legal liabilities. Somewhat less toxic species such as antimony, copper, zinc, or tellurium also may be regulated on a state or local basis. Finally, it must be remembered that dopant or epitaxial sources may also be regulated. An example of the former includes beryllium; examples of the latter include phosphine (PH3), ammonia (NH3), silane (SiH4), or hydrogen sulfide (H2S). Many of these epitaxial sources are among the most toxic substances known to man. For example, the dopant and epitaxial source arsine (AsH3) is instantly lethal in concentrations of only 250 parts per million in air. Lower concentration exposures result in chronic effects and often subsequent death.

2.2 "STRATEGIC" ELEMENTS USED IN SEMICONDUCTOR DEVICES

The U.S. semiconductor industry currently imports the majority of its silicon from Australia, due to the high purity reserves that are present in that country. If needed, the industry could turn to lower-grade, domestic reserves for its source of silicon. There are, however, three chemical elements that must be classified as "strategic" because of the current lack of domestic reserves or suppliers, their worldwide scarcity, and their important use in U.S. defense-related applications. These are gallium, indium and germanium. Of these, gallium and indium are currently utilized almost exclusively in III-V semiconductor applications, although the future will also see their use in I-III-VI2 semiconductors. Germanium was one of the first semiconductors used for communications; its use in “cats-whisker” crystal radios even predated our understanding of semiconductors. However, newer semiconductor applications (e.g. gallium-doped germanium, silicon-germanium, and II-IV-V2 compounds) are causing a revival of its usage. It must also be remembered that these three chemical elements have other, albeit

specialized applications - gallium in magnesium gallate phosphors for photocopying, germanium in bismuth germanate scintillators for astral sensor devices, and indium for specialized plating applications. A true appreciation of the relative scarcity of these materials and the precarious U.S. supply situation can only be realized by quickly reviewing the sources (or lack thereof) for each of these three chemical elements.

Gallium (Ga) Sources

In terms of its abundance in crustal rocks, gallium is not that rare a chemical element, being 30th in terms of abundance at an average concentration of 19 ppm. However, what makes gallium so rare in terms of availability is that it is very uniformly distributed throughout a large number of rocks at these concentrations. Thus, there are no concentrated ores from which gallium can be extracted, as is often the case with many chemical elements which are present in lower concentrations in crustal rocks, such as silver, gold, or the platinum metals. There are no gallium-containing minerals of any economic significance. The few minerals that do contain appreciable concentrations of gallium (e.g. germanite and gallite) are so rare that they can be considered nothing more than mineralogical curiosities.

Contacts made with semiconductor manufacturers indicated that the U.S. semiconductor industry obtains most of its high-purity gallium from either Japan or Germany. Gallium is concentrated as a result of the processing of other materials whose ores contain low concentrations of gallium and thus is derived from wastes of other industrial processes, such as flue dusts from the zinc industry or sludges from the aluminum industry. For example, bauxite (the primary aluminum ore) typically contains 0.003 to 0.01% Ga. Concentrations in zinc ores (e.g. sphalerite) are comparable. Because of such scarcity, industry sources say that the price of semiconductor grade gallium recently has ranged from $0.50 to $1.50 per gram.

Indium (In) Sources

Like gallium, there are no indium minerals of any economic significance. Those indium minerals that do exist in nature (e.g. roquesite, indite, and dzhalindite) are exceedingly rare. Indium is one of the rarest of the commonly-used compound semiconductor constituents in terms of its crustal abundance (61st in abundance at an average concentration of 0.24 ppm). However, from a practical standpoint, it is more readily available because it occurs not only in zinc and tin ores, but also in association with lead, iron, and copper sulfide. Therefore, indium can be derived from the flue dusts and sludges of these industries. High purity indium for semiconductor fabrication is most often obtained from Germany or Japan, at an average cost of $50 to $150 per kilogram, depending on purity.

Germanium (Ge) Sources

Germanium is also a rare element in the earth's crust, being 53rd in order of abundance at an average concentration of 1.5 ppm. As with gallium and indium, no

significant ores or minerals exist for commercial mining, and germanium minerals (e.g. germanite, argyrodite, argutite, renierite, and briartite) are merely collector items. At present, germanium is principally derived from flue dusts from the zinc or tin industries, and, according to manufacturers, its cost approaches $300 per kilogram in raw, unpurified form. One of the highest natural concentrations of germanium is in coal (0.01%), and coal ashes can contain up to 1% germanium as GeO2. Some work was conducted by the British in the 1950s and 1960s to develop methodologies for the extraction of germanium from coal ash, but there are no such sources being used in the U.S. at present.

2.3 GENERAL SUMMARY OF MANUFACTURING PROCESSES FOR COMPOUND SEMICONDUCTORS

The ultra-precise manufacturing steps involved in fabricating semiconductor components from raw materials represents one of the greatest achievement by materials science and chemistry to date. In order to achieve materials with the final desired electrical characteristics and properties, a large number of manufacturing steps are necessary. Although the exact manufacturing steps are largely governed by the final desired properties of the material, as well as the initial starting materials, a general overview of the manufacturing steps can be summarized (Figure 1.1). These include:

- Growth of bulk substrate crystals;
- Cutting, polishing, and etching of substrates;
- Epitaxial growth of circuit constituents on substrate (if desired);
- Multisequenced masking and doping of atoms into substrate (if desired);
- Metallization;
- Alloying/annealing; and
- Final lapping and separation of individual semiconductor "chip" devices.

Typically, the first three operations are performed at facilities that grow the initial crystal of semiconductor material. These crystal growers are referred to as semiconductor "foundries" and they provide the basic substrates on which specific devices can be "grown" in a controlled manner. Subsequent operations are then carried out by one or more specialty device manufacturing houses until semiconductor "chips" are prepared for the final user market.

Of course, each one of these general processes may involve numerous preparation and handling steps. Also, all of these steps may not be necessary for the fabrication of a specific electronic component, or the order in which they are carried out may be varied. Each of these manufacturing steps is summarized below, with a particular emphasis on the types of input materials used, as well as waste products that are typically generated. Finally, it should be remembered that the conclusion of each of these manufacturing steps represents a quality control checkpoint from the standpoint of meeting product quality

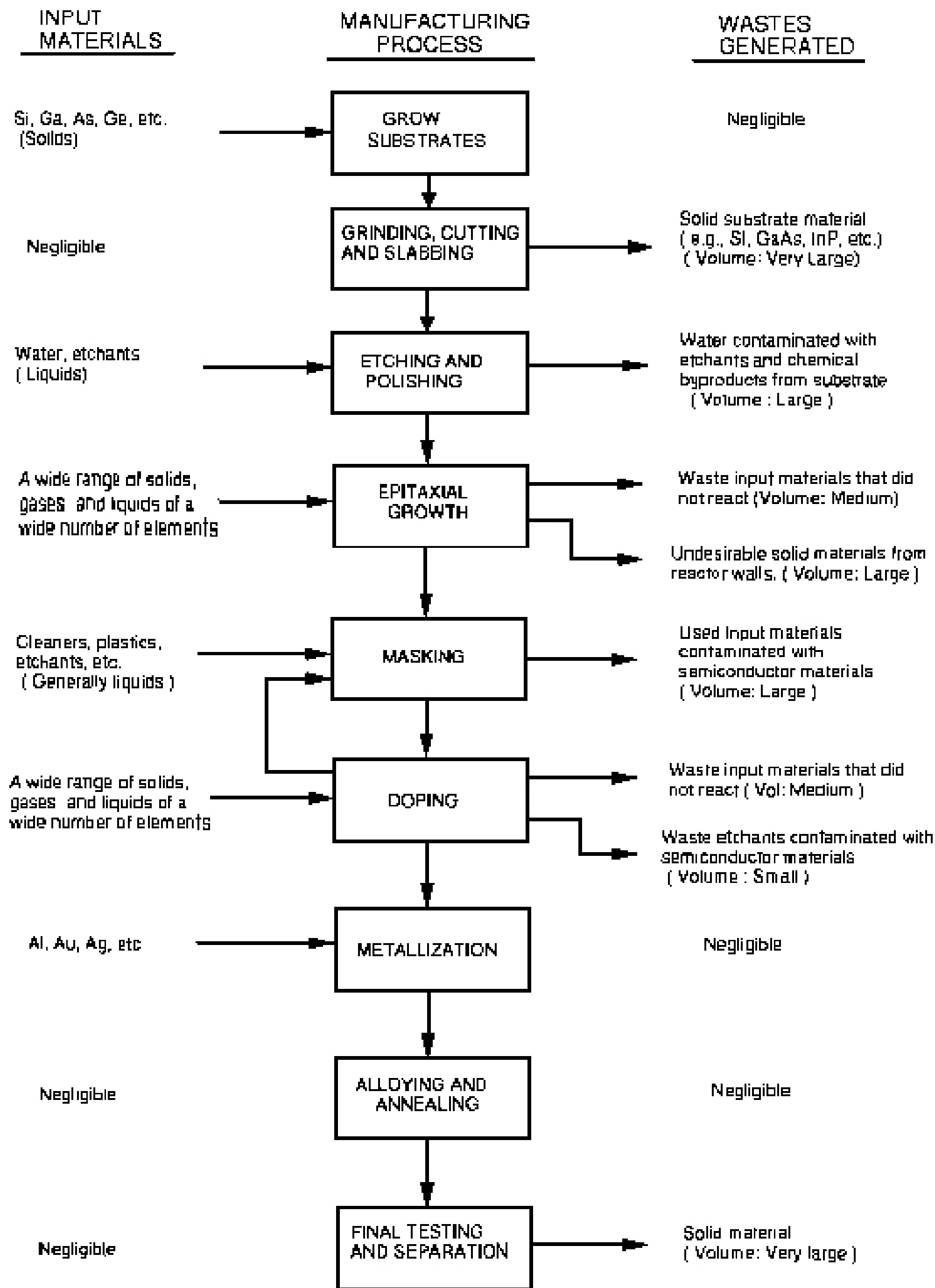


Figure 2.1 - Process Flow Diagram for Compound Semiconductor Device Fabrication

(Note-volume descriptors are relative and specific to a particular semiconductor)

objectives. Any devices that do not meet specifications at each of these points will be discarded. Such discards are a significant contribution (at least at the present time) to the overall semiconductor waste stream.

2.3.1 Growth of Bulk Substrate Crystals

The quality of bulk substrates is an important aspect of electronic device design. Significant improvements have been made in the areas of bulk crystal growth with regard to uniformity, reproducibility, thermal stability, diameter control, and impurity and dopant control. Substrate crystals of silicon or germanium have conventionally been prepared by either the Czochralski or float-zone methodologies. However, compound semiconductors, because they involve the joining of two or more elements, must use more sophisticated techniques. Although many different methodologies are currently being used in the industry today, two examples stand out as being representative of these methodologies. The horizontal gradient freeze technique is a static technique where the melt is gradually solidified by movement of a temperature gradient along the melt. Vertical Bridgeman furnaces utilize a similar temperature gradient movement (in a vertical direction, however) to achieve controlled crystal growth. Average growth rates using these methodologies are from 1 to 5 mm per hour. Typical crystal dimensions produced by these methodologies range from one to six inches in diameter, and from two to thirty inches in length.

The actual growth of bulk crystals (also called boules or ingots) generates very little waste, since starting materials are fed into the system in exact quantities. Should excess starting materials result, then they are almost always reused in the production of other crystalline boules. While a defective boule would represent a significant mass of waste materials, their incidence of occurrence is very low, and even if a defective boule were to be generated, usable portions of the material are frequently salvaged.

2.3.2 Cutting, Polishing, and Etching of Bulk Crystals

The semiconductor boule obtained has a generally cylindrical shape with somewhat conical ends. After removing the ends (which, since they have smaller diameters than required are usually wasted), the first operation is often surface grinding. This process is used to precisely define the diameter of the material and is accomplished using a rotating cutting tool (i.e., a lathe) that makes multiple passes down the rotating boule until the desired diameter is obtained. A flat is then ground along the entire length of the ingot, and the surface orientation is determined by cutting several slices and measuring their crystalline orientation using an x-ray diffraction method. The cutting saw is then reset so that the proper orientation (i.e., the desired crystal faces) is achieved for subsequent cutting of wafers.

Upon proper orientation, the crystal is cut into thin slices called wafers. The slicing is accomplished using either of two common wafer sawing procedures. In one procedure, the inside diameter of a ring-shaped saw blade made of stainless steel with diamond impregnated on the inner rim. Newer, more efficient methods, utilize a series of

rapidly moving abrasive-coated steel wires over the ingot, so that multiple cuts can be performed simultaneously. Both such cutting processes are liquid cooled, and a volume of material is lost during this process equal to the width of the saw blade or wire. In fact, approximately one-third of the total crystal mass can be lost as sawing fines during the cutting process. This waste stream is in the form of fine powders suspended in an oil or water matrix (depending on the coolant liquid used for the cutters.) The sawing operation also leaves a damaged layer of about 20 to 50 microns thick on the wafer that is later removed by lapping and etching.

2.3.3 Wafer Lapping, Etching and Polishing

The final operation performed at a crystal foundry is polishing. The wafers are mounted onto large circular stainless steel polishing plates (lap plates), and either wax or vacuum is used to hold them in place. These plates are then mounted on a polisher, and the wafers are pressed against a tough polishing pad. A polishing agent such as alumina and an etchant that contains a chemical oxidizer are used simultaneously, and the surfaces are continuously flushed with water as they are polished. The etchant (oxidizer) is used to aid in polishing by slowly dissolving some of the semiconductor material from the surface being polished. Either one or both sides of the wafer are polished to a mirror-like finish. After a thorough cleaning and subsequent inspection, the wafers are ready for device fabrication. Device fabrication usually is performed at specialty job-shops, while only the early stages of semiconductor manufacturing (i.e., boule growth, wafer cutting and polishing) are performed at semiconductor foundries.

The high percentage of wastes associated with foundry operations makes their wastes the largest mass of waste for the compound semiconductor industry. Toxic wastes from these operations can be loosely categorized into two forms:

1. liquid wastes that contain dissolved metal ions from the etching and polishing operations, and

2. solid wastes, i.e., large pieces and cutting fines from the cutting and shaping operations.

The wastes from crystal polishing consist of the flushant wastewaters containing dissolved substrate materials with suspended polishing agent. For example, the polishing wastewaters from GaAs manufacturing contain dissolved arsenic and dissolved gallium at concentrations of between 200 and 400 ppm. These wastewaters are difficult to treat because of stringent arsenic discharge limits and because of the difficulties introduced into any sludge dewatering operations by the extremely fine, suspended polishing agent particles.

Solid wastes from cutting can range in size from whole segments of ingots (e.g. 6" diameter wafer pieces) to fine powders of a few microns in size suspended in the saw's coolant liquid. Out-of-spec wafers (along with the discarded boule ends and ingot segments) compose another form of solid wastes generated at semiconductor foundry

operations. These latter solid wastes are physically large and are of high purity. Thus, they have been the only part of a foundry's waste stream that has been captured for recovery and reuse. Often, these wastes are sent to off-site contractors who process the waste for recovery of gallium alone (with any arsenic being wasted). No effort has previously been made to recover materials from the sawing fines or from the polishing wastewaters.

2.3.4 Epitaxial Growth

Epitaxial growth is the means whereby ultrathin layers of exact chemical composition are laid down on substrate wafers that have been prepared by the methodologies described above. In particular, this is a useful means to prepare semiconductors that are to be used for laser or LED applications. There are four general means by which epitaxy can be achieved. These are:

- Liquid-phase epitaxy (LPE);
- Vapor-phase epitaxy (VPE);
- Organometallic vapor-phase epitaxy (OMVPE); and
- Molecular beam epitaxy (MBE).

LPE was the first commercially used epitaxial growth process and it involves the growth of an epitaxial layer on a single crystal substrate from a solution saturated or supersaturated with the material to be grown. VPE utilizes vaporized metal chlorides or hydrides that are transported under controlled conditions (e.g., temperature, pressure, flow rate) to the metal substrates. Unlike the LPE processes, smooth surfaces are attainable, and several processing runs can be performed in an eight hour day. Unfortunately, the toxicities associated with the hydride species used are always high. OMVPE is an improvement over VPE because the reactions are irreversible and this allows very abrupt transitions in composition of epitaxial structures. Such structure is a necessity for the fabrication of digital or analog alloy systems. Another advantage is that lower temperatures can be used for the growth processes and this minimizes the effects of interdiffusion. Additionally, the organometallic substances used in OMVPE are less toxic than hydrides resulting in lower toxicity starting materials and waste products alike. MBE is the process of depositing epitaxial films from molecular or atomic beams on a heated substrate under ultrahigh vacuum (UHV) conditions. The beams are thermally generated from elemental feedstocks in Knudsen-type effusion cells. The thermal beams travel in rectilinear paths to the substrate where they condense and grow under kinetically controlled growth conditions.

With the exception of LPE, the wastes generated from epitaxial growth processes are gaseous or solid in nature. The gaseous wastes are the "exhaust" vapors that are drawn off from the epitaxial reactors. These are either passed through "hot boxes" where they are mixed with oxygen and burned, or are oxidized using often proprietary catalyst materials. Typically, the oxidized gases are scrubbed out of the effluent gas stream and added to the plant's wastewaters for treatment. These waste materials are disposed of with little or no effort directed towards recovery. It is reported that epitaxial growth

processes utilize only 20 to 25 percent of the input materials for final product fabrication. Such process "efficiency" is dependent upon both the design of the reactor and the product being fabricated. For example, existing nitride fabrication systems utilizing ammonia feedstocks frequently operate at only 1% efficiency in terms of input ammonia.

Solid wastes constitute those materials that are deposited on the epitaxial system's reactor walls. It is frequently necessary to remove these wastes prior to the next fabrication run because their presence could interfere with achieving the requisite partial pressures necessary for each constituent in the subsequent run. In fact, fully 50 percent of the labor hours associated with such epitaxial growth processes is devoted to cleaning waste solids off of walls and other reactor parts. This material is not currently recycled back into the overall manufacturing scheme partly because it is usually contaminated with dopant and maskant materials.

2.3.5 Masking and Doping

For establishing specific circuits on a chip, it is common to add dopant atoms into the substrate or to add epitaxial layers in specific configurations in order to produce regions of controlled electronic behavior. This is done by first masking those regions for which no dopant atoms are desired, and then using doping techniques for the regions that are still exposed.

Masking can be divided into two distinct processes, both of which are necessary for the successful transfer of an image to the surface of a semiconductor wafer. These processes include the generation of the "mask", whose image is transferred to the wafer; and the process of transferring the image from the mask to the surface of a wafer through the use of a sensitized layer called a photoresist. Masking results in aqueous streams that may have measurable concentrations of metals that had been deposited on the photoresist when the photoresist is subsequently removed from the substrate wafer with chemical agents.

Doping involves the emplacement of dopant atoms into selected regions of a semiconductor crystal and this is accomplished using either diffusion doping or ion implantation. Diffusion doping involves two distinct processes: predeposition, wherein a carefully controlled amount of dopant is placed onto the surface of the semiconductor; and drive-in, which uses a thermal process to cause diffusion of the dopant into the overall crystal bulk. Today, most doping is effected using a technique called ion implantation. This process takes ions of a desired dopant, accelerates them using an electric field, and scans this "ion beam" across a wafer to obtain a uniform predeposition with subsequent thermal drive-in. Older doping operations generated wastes similar to those described under epitaxial deposition. Ion implantation techniques generate far less wastes.

2.3.6 Metallization/Alloying/Annealing

After the devices have been fabricated, they must be connected together to perform electronic circuit functions. The process of implanting electrical connections is called metallization. Alloying and annealing involve a low temperature heating to ensure low-resistance contact between the deposited metal and the fabricated electronic devices. These processes generate little toxic waste.

2.3.7 Final Lapping and Separation

The backside of a wafer may have to be altered in order to prepare it for subsequent processing steps. Backside lapping of a wafer is used to remove diffused layers that interfere with the electrical properties, to thin the wafer, or to prepare the backside for subsequent metal deposition. When lapping the backside of wafers, approximately ten thousandths of an inch of material is removed from each wafer. This results in fine powders in a water carrier. Currently, these powders are filtered or settled out of solution, and are subsequently land disposed.

The wafers are now ready for final quality control testing. To determine their acceptability, the wafers are placed on a probe and each microchip device on the wafer is tested. Those devices on the wafer that function properly are left alone; those that fail are typically marked with a spot of ink. Separation into individual devices is then achieved with a wafer scribe. This ultrathin saw or laser separates the substrate material into square or rectangular components. Any device that does not function properly is discarded. Finally, there is a large wastage of edge material from each wafer. Because each wafer is round (from the crystal growing process), and because the devices themselves are square or rectangular, there will be some solid waste generated when the devices are separated, even if all devices contained on it pass performance inspections.

2.4 SUMMARY OF POLLUTION PREVENTION PROCESSES DEVELOPED UNDER THIS RESEARCH EFFORT

It can be seen that in its current state, the U.S. semiconductor industry offers a multitude of opportunities for waste reduction. Indeed, although the industry itself is perceived as "clean", due to the ultrahigh purity required of input materials and processing equipment, the amount and nature of the waste materials are "dirty" in comparison to many other manufacturing industries. The semiconductor manufacturing industry has devoted most of its resources to building better devices and electronic circuit components, and not to minimization of wastes. Because of the high value of part of their waste streams, combined with the environmental threats posed by other parts of their wastes, U.S. semiconductor fabricators have a very real (but currently unrecognized) economic incentive to implement pollution prevention and waste minimization strategies.

Current Superfund and RCRA legislation makes generating companies liable for environmental cleanup at waste disposal sites, even if wastes have been manifested and disposed in an approved manner. In addition, even though many of the wastes currently

being disposed are unlisted (e.g., GaAs is not a specifically regulated waste except in California) and usually will pass a TCLP test, the toxic metals contained therein still can constitute an environmental threat. In such circumstances, disposal of wastes that contain toxic metals can carry with it potential legal liabilities for environmental cleanup, even if the wastes themselves are unlisted. Finally, shipment of wastes to off-site “recyclers”, wherein "strategic" metals are recovered, but toxic species are not, still leaves some legal responsibility with the generating, semiconductor manufacturer should any uncontrolled release (e.g., of unrecycled arsenic) subsequently occur.

The industry's process lines are currently geared towards the manufacture of ultra-precise, miniaturized components, but not towards the recovery of waste fractions. The industry generally views the many processing steps associated with device fabrication (as well as the procedures necessary for environmental compliance) as a cost of doing business, and this cost is passed on to the customer. When compared to other U.S. manufacturing schemes, the overall process efficiencies are terribly low. For example, just in the first three unit operations shown in Figure 1.1 (the crystal foundry operations), total material wastage is approximately 50 percent of the original input material.

At the device fabrication operations (i.e., unit operation four and beyond in Figure 1.1), only about 17% of their input materials (wafers) will ultimately be usable as final devices. In other words, for the entire process, from original crystal growth to final device testing and separation, only approximately 8.5% of the input materials will be used in final electronic components. The remaining material (nearly 92 percent) is currently discarded as wastes.

In spite of the very large apparent paybacks associated with implementation of pollution prevention and waste minimization in the industry, there are certain characteristics unique to U.S. semiconductor manufacturing operations that need to be addressed. These characteristics set the industry apart from other manufacturing operations in the U.S.

2.4.1 Material Substitution Difficulties

In many manufacturing operations, substitution of environmentally-benign materials for toxic or harmful materials has been and is being conducted. Indeed, the successful replacement of CFC precision cleaners by other agents or processes in the semiconductor industry has resulted in a significant decrease in regulated emissions. However, replacement of "toxic" semiconductors (e.g. those compounds containing lead, cadmium, mercury, arsenic, or selenium) or "strategic" semiconductors (e.g. those containing gallium, germanium, or indium) with less toxic or lower-cost semiconducting compounds would be a far more time-consuming process than for other manufacturing operations. For example, it is theoretically possible that the III-V compound semiconductor material aluminum antimonide could be grown and doped to perform many functions of more expensive and more toxic equivalent III-Vs, but there are difficulties associated with such material replacement concepts.

The development period for semiconductor compounds and devices is far longer than for most products developed by other manufacturing industries. For a given semiconductor compound, the development period is measured in terms of years (e.g., twenty years) as opposed to months for most other manufactured products. And, because the semiconductor industry is so interconnected in terms of small companies (see below), validation of the effectiveness of replacement compounds and devices would be needed across a number of manufacturing firms.

This is not to say that materials substitution is not possible in terms of replacement compounds. Rather, it is the opinion of the authors that one of two scenarios would be necessary in order to overcome the development time necessary to bring a new product on-line, and to gain industry acceptance. In one such scenario, if a replacement product already had a long history of development work having been performed on it, this would significantly shorten the development time necessary for device development, and may also help to foster industry acceptance. An example would be the material aluminum antimonide mentioned above. Conceivably such material could replace higher-cost, higher toxicity III-V materials such as GaAs and InP for some device applications, and aluminum antimonide does have a long history of development work associated with it. Under a second scenario, if the materials to be replaced were still "new" in terms of their industry implementation, then waste minimization efforts could more readily be incorporated into production schemes. An example would be the III-nitride wide band gap devices that are just beginning to see large-scale industrial application. Because this industrial sector is still so "new", it is still possible to implement good waste minimization and pollution prevention practices without seriously affecting the industry's concepts about "proper" manufacturing methods.

2.4.2 Difficulties with Small Company Size

A further impediment to implementing pollution prevention in the U.S. semiconductor industry is the fact that unlike many other manufacturing schemes, the entire processing operation is not done under a few, relatively large roofs. Rather, the industry consists of many small "fab-shop" companies performing one or two of the manufacturing steps shown in Figure 1-1, and then selling their products to companies which are involved in additional fabrication operations further down the overall manufacturing scheme. Pollution prevention implementation must therefore enlist the cooperation of several companies in order to be effective for the whole industry.

Because of the small size and operating budgets of such small firms, economic resources simply don't exist to perform research on a company-by-company basis in order to improve process efficiencies, design new environmentally benign or lower-cost products, etc. The cost of environmental compliance is simply passed onto the next customer rather than implementing pollution prevention steps that would eliminate or reduce compliance costs.

2.4.3 Purity Concerns

Recycling in the semiconductor industry entails different concerns than for other manufacturing industries. This is because the purity standards for most input materials to the various process unit operations are extremely rigid. For example, materials with a purity less than 99.999% will generally not be tolerated because they will result in manufactured products that will not meet performance specifications. For most other manufacturing industries, recycled wastes with a 99% purity is exceptionally good, and materials of 90% purity can usually be reused. The question is now being raised in the semiconductor industry, however, as to what material purity is really necessary if the material is being recycled back into its generating process. For example, "wastes" of GaAs consist of nearly 50 percent gallium atoms and the same number of arsenic atoms, with minor amounts of other impurities that may be picked up during the processing steps. If the other, minor impurities are successfully removed, does the purity of the gallium have to be 99.999% with absolutely no arsenic present, provided that the material is to be reused for the growth of GaAs? Would 99.9% be sufficient? Such questions can only be answered by growth and testing of semiconductor compounds and devices using recycled materials in which some residue of the related material is present.

2.4.4 Material Recovery Processes Developed

At the initial stages of the research effort, it was our intent to first address the waste resulting from vapor phase epitaxial growth processes (both VPE and OMVPE). These wastes are in the form of highly toxic chemicals (e.g., arsine, phosphine, organoarsine, etc.) which is usually treated on-site by oxidation in a “hot box” with the oxidized materials scrubbed from the effluent using a water scrubber. This results in generation of wastewaters that must undergo treatment for arsenic removal prior to release to a POTW. However, as our research efforts progressed, it soon became obvious that there were two major reasons for focusing on waste streams other than the wastes from epitaxial growth operations. First, other waste streams, specifically those from foundry operations, constituted a larger and more important “target” for pollution prevention efforts. Second, the development of recovery techniques for the foundry wastewaters also would result in methods for recovery and reuse of materials dissolved in the epitaxy hot-box’s scrubber waters. In that way, adoption of a technique with broad applicability in the semiconductor foundries could also allow recovery of epitaxial wastes through an add-on process to the existing waste control methods.

Focusing on the large quantities of arsenic-bearing wastes generated in the III-V foundries, we have developed two processes that can be implemented at foundry sites for the recovery and in-plant reuse of both the very valuable gallium and the highly toxic arsenic that are presently wasted. The first process developed was a thermally-based 3-unit operation process for recovery of both gallium and arsenic from the solid wastes. The wastes processable with this technique include both the large-sized wastes such as boule ends and waste wafers, but also the difficult-to-treat saw fines. Together, these two waste streams account for two-thirds of the arsenic wasted at semiconductor foundries

(approximately 30 to 35% of the arsenic wasted in all of the GaAs semiconductor industry.)

The other process that was developed under this grant is a method for capturing and recovering both gallium and arsenic from the polishing wastewaters. Through use of specific reagents, combined with careful pH and temperature control, the process sequentially removes arsenic from the waste stream and then gallium. Upon conversion back to metallic arsenic and gallium, the recovered wastes can be further treated for purification using the process developed for the solid waste streams. In fact, the same process used for recovery of oxidized gallium and arsenic from foundry wastewaters can be applied to vapor phase epitaxial scrubber waters. Both of these recovery processes for foundry wastes are described in detail in following sections of this report.

3.0 RECYCLING AND RECOVERY OF MATERIALS FROM SOLID GaAs WASTES

Due to the economic value of gallium, a number of recovery methodologies have been developed and tested over the years, but none have been applied for in-plant pollution prevention. The first step in these processes is typically to separate the gallium and arsenic. A well-documented method to accomplish this separation is to contact the solid waste stream with an aqueous solution or a heated bath, allowing a chemical reaction to facilitate separation. These separation media consist either of an oxidizing species such as hydrogen peroxide [1-2] or nitric acid [3-6], or of molten sodium hydroxide.[7] Once in solution or the heated bath, the gallium is then sequentially removed using a number of additional methodologies. While these practices have been demonstrated as workable, they all involve the introduction of a very large volume of an additional media in order to effect separation. This larger-volume media then must itself be treated (e.g., to preclude the release of toxic arsenic or to recover gallium). Thus, rather than merely separating the constituent elements from one another, these approaches result in the requirement for further processing (for metal recovery) from a much larger waste stream.

3.1 CURRENT DISPOSAL/RECYCLING METHODOLOGY

On a material weight basis, approximately 50% of solid GaAs wastes generated by semiconductor foundries are currently disposed of, and 50% are treated off-site for recovery of the gallium fraction. Because GaAs is not (at this time) a listed hazardous waste, disposal usually implies that the waste materials are placed into 55-gallon barrels, and disposed of in landfills. When GaAs wastes are sent to the only existing U.S. recycler, only gallium is presently being recycled and arsenic is presently not recycled.

One major problem with the existing disposal approach is that GaAs may be converted to the insidious gaseous toxin arsine (AsH_3) under acidic conditions. (Arsine gas is immediately lethal in concentrations as low as 250 ppm; lower concentrations result in chronic effects. The LD_{50} for arsine is 0.5 ppm.) It is well documented that landfills are typically anaerobic (reducing), with the simultaneous formation of organic acids such as acetic and formic acids. Therefore, GaAs exposed to typical landfill conditions could theoretically be easily converted to arsine gas. Even under less catastrophic circumstances, such as the oxidation of the released arsenic to the trivalent or pentavalent state, aqueous-phase arsenic will still represent a measurable toxic threat.

The prevailing attitude within the GaAs bulk crystal industry is that the existing disposal and recycling approaches are satisfactory. Under existing U.S. environmental laws, the original GaAs crystal grower is liable for any future environmental cleanup costs related to releases of the arsenic into the environment, with or without recycling of the gallium from the waste stream. Perhaps the only reason why such costs have not begun to be incurred by today's crystal growers is because the industry is only approximately twenty years old, and so arsenic contamination that is directly attributable to GaAs production has not yet been observed. Judging from the large monetary sums currently being awarded to localities (for liabilities) and environmental contractors (for

cleanup) from disposal of arsenic-containing wood preservatives, it is safe to predict that the future holds some very unpleasant economic surprises for today's GaAs crystal growers if disposal approaches are not altered to allow for arsenic recovery and reuse. Therefore, recycling of both gallium and arsenic from GaAs manufacturing wastes offers both short-term (gallium recovery) and long-term (minimizing arsenic-related liabilities) economic benefits

3.2 RECOVERY PROCESS DEVELOPMENT

Thermal processing of GaAs solid wastes to recover gallium has also been demonstrated in the past. While thermal separation under air has been achieved for GaAs, that procedure results in the formation of arsenic and gallium oxides.[11,12] These oxide "slags" require an additional processing step (reduction) to obtain reusable metals. Therefore, from an in-plant pollution prevention approach, separating under an inert atmosphere or under vacuum is more desirable in order to minimize the number of processing steps (and thus the overall cost of the recovery operation). This too has been attempted, and many of the processes described are very exact with respect to necessary conditions to achieve thermal separation.

Initial studies of the effects of high temperature conditions (above 950°C) showed that thermal cracking of the GaAs takes place until the partial pressure of arsenic vapor in the head space prevents further sublimation of arsenic. Thus, a conceptual process was proposed in which the GaAs solids would be subjected to high temperatures at reduced pressure with a continual draw-off of released arsenic vapors. Continued operation of such a process would ultimately result in removal of most of the arsenic leaving a residue that would be high in gallium, and which would contain any unmelted (or high-boiling) contaminants. However, it was expected that such thermal separation alone would not produce gallium or arsenic products of sufficient purity for reuse in semiconductor crystal growth. Further processing steps would be required whereby the arsenic-rich vapors and the gallium-rich residue could be further purified to acceptable levels for reuse.

3.2.1 Purification Thermodynamics of Arsenic

Processes for recovery and purification arsenic are not as well developed as those proposed for gallium. In fact, no recovery/purification of arsenic is attempted in any of the gallium arsenide recovery processes. This is the case in all reported thermal separations - liquid gallium is recovered, but condensed arsenic is disposed of, presumably due to its low raw material cost.[8-12]

Arsenic purification has been achieved through the zone refining of such arsenic compounds as arsenic trioxide,[13,14] arsenic trichloride,[15] or arsine gas,[16] followed by reduction to the elemental state with a number of reducing agents, including hydrogen[17,18] or metallic species such as aluminum and calcium.[14] Arsenic has also been purified through a zone refining process whereby the arsenic is heated to 814°C at a pressure of 36 atmospheres, so as to achieve a solid-liquid transition.[19] Using any of these concepts within a GaAs recovery process would mean that the compound purification processes

would require three processing steps (conversion of elemental arsenic to a compound, followed by purification and then re-reduction to the elemental state). Such an approach also would present inherent toxicity concerns (since the only truly successful reduction is that using hydrogen gas, of which arsine is a thermodynamically-feasible byproduct). The high-pressure approach to arsenic purification also bears significant hazards for in-house recovery operations.

Purification of arsenic using sublimation mechanisms has been achieved in the past,[20,21,22,23] and because it is a one-step process with minimal energy or toxicity (only metallic arsenic is involved and not the more toxic oxides or hydrides) concerns, this approach was chosen for incorporation into the overall recovery scheme. The prior art suggests that the use of an inert carrier gas (e.g., nitrogen) aids in the separation of arsenic from impurities.

3.2.2 Purification Thermodynamics of Gallium

Gallium purification requires a significantly different purification methodology than those traditionally applied to other semiconductor materials (e.g. silicon or germanium) because gallium is present in the liquid phase at ambient temperatures and pressures. For this reason, gallium purification has been attempted in a multitude of fashions. The methodology that was used for a number of years involved the conversion of (impure) gallium to gallium trichloride (which is a solid), followed by zone refining of the gallium trichloride, and reduction to pure metallic gallium.[24-30] This methodology was not considered further for our recycling process because, like arsenic purification utilizing arsenic trichloride, it is a three-step process which requires material addition. Additional purification methodologies that were rejected because they involve a three-step purification process included electrolysis,[31-33] hydride reduction,[34] and nitride separation.[35] A one-step physical separation process of gallium from its impurities was desired.

Because gallium has a large liquidus range (b.p. = 2403°C), a considerable amount of energy would be required to separate gallium from other metals and from refractories (e.g. diamond) utilizing a liquid-vapor separation methodology. Therefore, a separation based on liquid-solid phase transitions is required, of which three procedures are documented in the literature: single crystal lifting process, fractional crystallization, and zone melting. The single crystal lifting process achieves purification by contacting a seed crystal with a gallium melt, with gradual lifting,36,37 but due to its low productivity, this physical separation methodology was rejected. Fractional crystallization exhibits a similarly low productivity and was also rejected.

Zone melting of gallium appears to offer a reasonable and cost effective method for purification of gallium from a thermal separation process, provided that the initial separation results in a gallium-rich stream that is better than 90% pure gallium. At such a purity level, the gallium-rich product should have a melting point close to the melting point of pure gallium (approximately 35°C). Under such conditions, the gallium-rich product would be a solid at room temperature and a low-energy heat source could easily

raise the product temperature to the melting point allowing for an inexpensive zone refining operation.

3.3 PROTOTYPE SYSTEM

Based on the initial studies, a conceptual recovery process was developed that could conceivably be operable in a small space and at reasonable costs. The proposed process also seemed likely to achieve product purities sufficient to recycle the recovered materials back into the semiconductor crystal growing operation. The process was envisioned to include an initial thermal separation of GaAs into an arsenic-rich vapor stream and a gallium-rich residue. These product streams would then undergo further processing for purification to necessary levels.

A major result of the research performed under the subject grant has been the development of a three unit operation procedure in which the solid wastes are thermally separated into their constituent elements (with a minimum of energy input or additional handling). Then each of the separated elements (gallium and arsenic) is purified to the required levels for further crystal growth. Prior work with GaAs thermal separation and constituent element purification provided a template for the development of this "optimum process", and subsequent thermodynamic consideration of each of these unit operations provided a theoretical basis for implementation into the developed process.

Figure 3.1 shows a schematic of the developed process for solid III-V materials as it currently exists. As a result of this research, it is now known that the lowest cost means

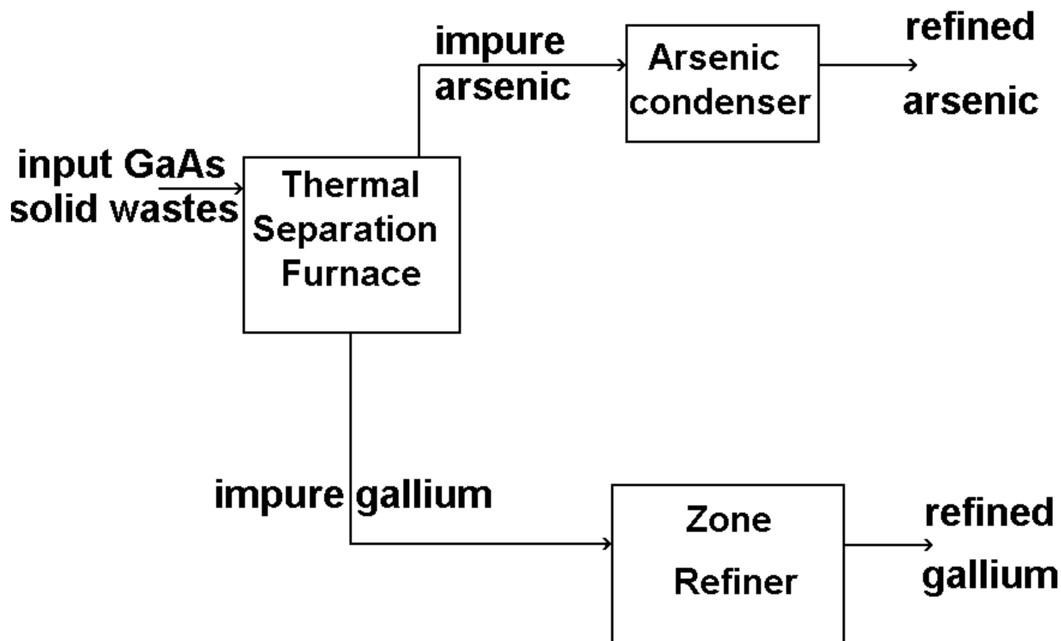


Figure 3.1 - Schematic of the Recovery Process for III-V Solid Wastes

to separate III-V solids is through the low-pressure, high-temperature process shown as the first unit operation in Figure 3.1. It is also now known that some further processing of recovered gallium or arsenic is necessary in order to maximize the quantity of recovered material for reuse.

3.3.1 Unit Operation 1 – Thermal Separator

The first and most critical operation in the developed recovery process is the thermal separation furnace. Figure 3.2 shows a cross-section of the thermal separation furnace that was constructed for laboratory and field trials of the proposed concept. The unit can be operated at temperatures above 950°C and at reduced pressure with an inert atmosphere. The off-gases are continually pumped through a series of condensers for capture of the arsenic-rich vapors. The residue in the reactor contains the gallium-rich fraction mixed with a separable slag of other contaminants.

It was known that thermal separation alone could not achieve product purities great enough to allow for immediate reuse of the recovered products. In addition to contaminants introduced into the waste stream, some contaminants could be intentionally introduced into the crystals as dopants for specific control of the crystal's electronic characteristics. Dopants commonly found in GaAs include Si, Zn, and C or Cr. These dopants typically occur in concentrations of about 10^{18} atoms/cc. Some of these dopants (e.g., C at about 10^{15} atoms/cc) are utilized to make GaAs semi-insulating, and some are utilized to make GaAs semiconducting n-type (Si) or p-type (Zn). The physical characteristics of each dopant are important because they will dictate where the dopant

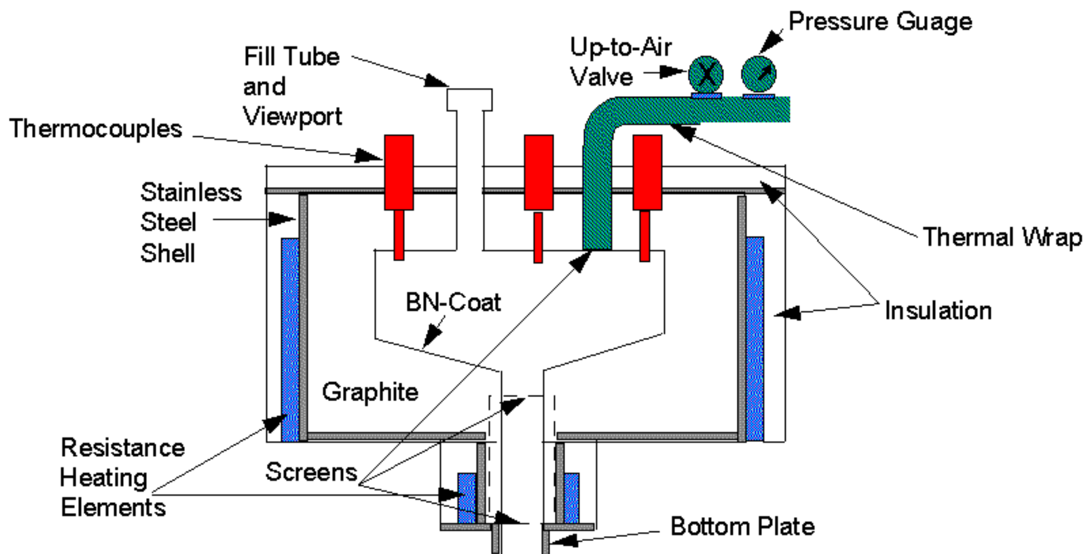


Figure 3.2 Cross-section of Unit Operation 1 – Thermal Separation Furnace

will likely occur in the product streams resultant from the thermal separation. For example, silicon and iron are very soluble in liquid gallium, and so these elements can be expected to remain with the gallium, forming an impure “slag”. Simultaneously, “volatile” dopants such as sulfur and selenium are expected to partition into the arsenic fraction. For this reason, further processing steps were incorporated into the process for purification of the gallium-rich and arsenic-rich product streams.

3.3.2 Unit Operation 2 - Low-Temperature Zone Refining of Gallium

Because the impurity levels in the product gallium from doped GaAs sources are expected to be fairly low (because dopant concentrations are relatively low), then the melting temperature of the “impure” gallium should approach that of pure gallium (i.e., ~ 35°C.) UDRI has developed a system for the purification of nearly pure gallium with small concentrations of impurities (Figure 3.3). Specifically, it involves chilling the gallium with ice water or refrigerant to 0°C or less, and then using a controlled heat

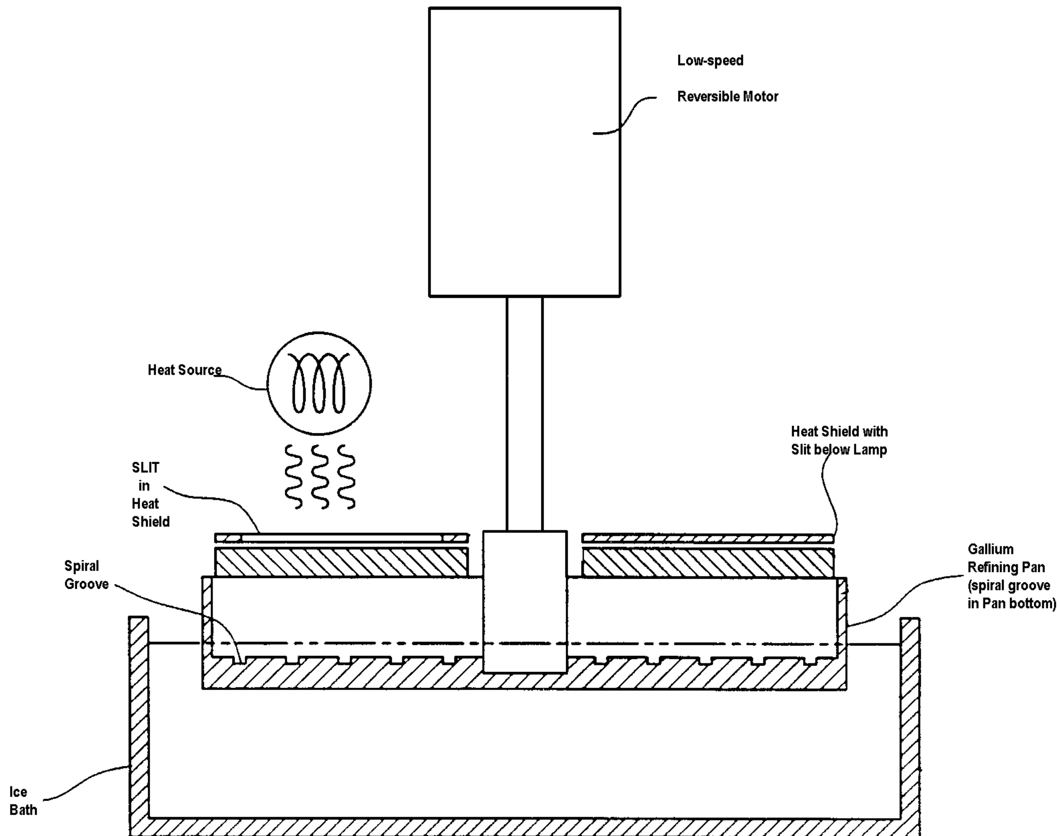


Figure 3.3 - Schematic of Existing Equipment for Low-Temperature Purification of Gallium

source (heat lamp) to heat specific zones of the gallium sample. (Note: Although gallium is a solid at ambient temperatures of 20-25°C, this is not a sufficiently cold temperature for efficient zone refining due to supercooling effects. In other words, zone refining from ambient room temperature will not be successful because the temperature difference between solid and liquid will not be sufficient to effect impurity segregation.) The molten zone is allowed to pass through the gallium by slowly rotating the pan containing the gallium. Based upon the segregation coefficients of each of the contained "impurities", the dopant elements will segregate to both ends of the spiral groove in the gallium refining pan shown in Figure 3.3 and can then be removed.

3.3.3 Unit Operation 3 - Sublimation Refining of Arsenic

As noted previously, the arsenic fraction can be contaminated with the more volatile dopants, especially carbon. UDRI has achieved some purification of arsenic through the use of a repeated sublimation/condensation process as is shown in Figure 3.4. Specifically, the arsenic in the first condenser (e.g. evolved from the low-pressure, high-temperature process in Figure 3.2) is heated to slightly above the sublimation temperature of arsenic (610°C) in an inert gas stream such as nitrogen, and recondensed in a second condenser. This thermally separates the arsenic from impurities due to differences in partial pressure and volatility. Further processing can be achieved through additional sublimation/condensation (e.g., heating from condenser 2 into condenser 3, etc.).

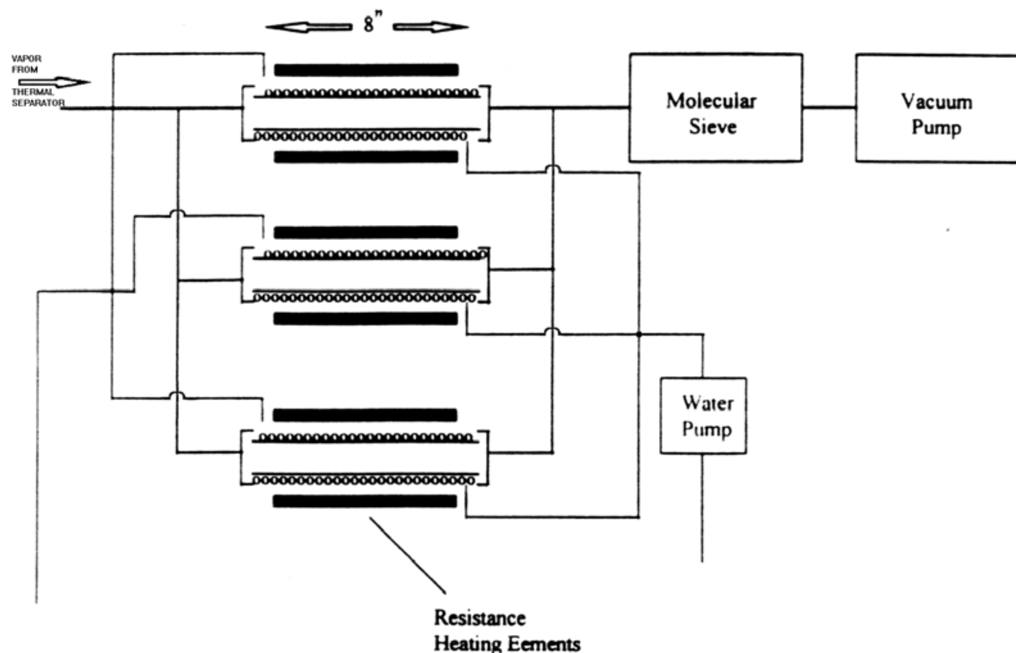


Figure 3.4 - Schematic of Existing Equipment for Sublimation /Purification of Arsenic

3.3.4 Analytical Results

Initial studies were performed to evaluate the basic thermal separation concept that ultimately was incorporated as unit operation number 1 in the concept process. Analyses of samples were conducted using Energy Dispersive Spectroscopy (EDS). This surface analysis technique is capable of detecting the presence of atomic constituents in solid samples down to the parts per million (ppm) level. Thus, EDS will show the presence of unacceptable contaminants at the ppm level and was suitable for initial assessments of the performance of the recovery processes. However, EDS is not a truly quantitative technique and it was known that a more sensitive technique would ultimately be required in order to demonstrate that the recovered material has sufficient purity for reuse.

Figure 3.5 shows an EDS analysis of a slab of unreacted GaAs solid waste typical of the feed material used in subsequent studies. Initial studies of the thermal separation concept were performed under an inert atmosphere (N_2) but at atmospheric pressure. It was soon realized that as the sample released volatile arsenic, the partial pressure of arsenic rose until further arsenic sublimation stopped. Continued operation at high temperature allowed other, less-volatile materials to escape with no real increase in the arsenic removal

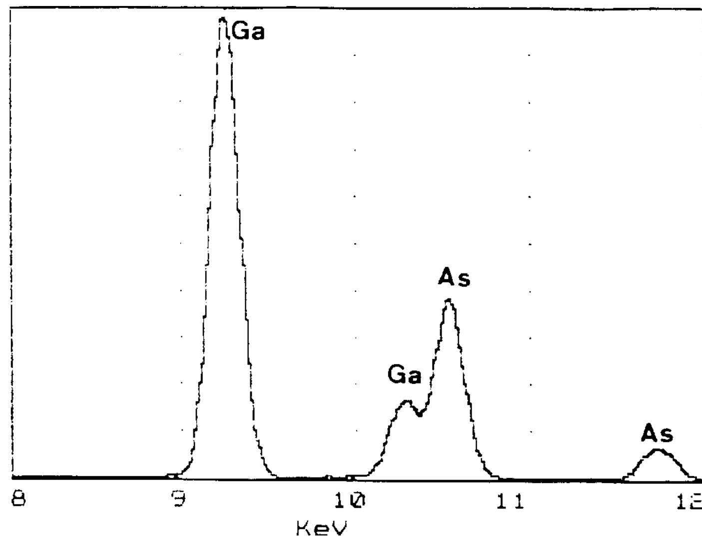


Figure 3.5 EDS Analysis of Unreacted GaAs

rate. Figure 3.6 shows the EDS analysis of a recondensed solid sample of the volatile fraction resulting from a 30 minute run at approximately 1000°C. The presence of an indium peak results from a low-level (< 0.3%) of indium dopant present in the original material. Figure 3.7 shows that, for such operating conditions, high levels of arsenic remain in the residues. In fact, continued operation at high temperature and at

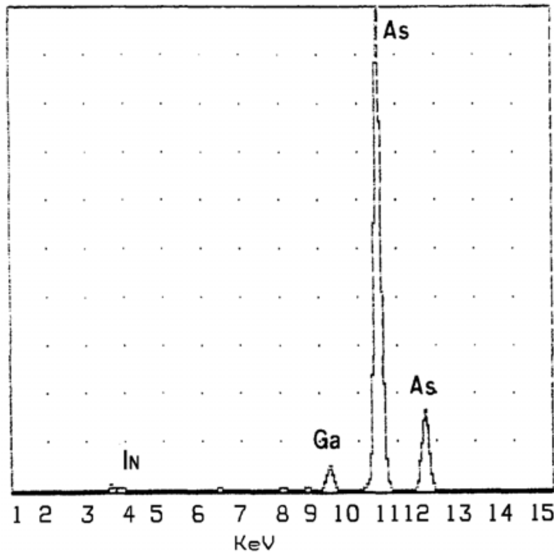


Figure 3.6 EDS Analysis of Volatiized Material

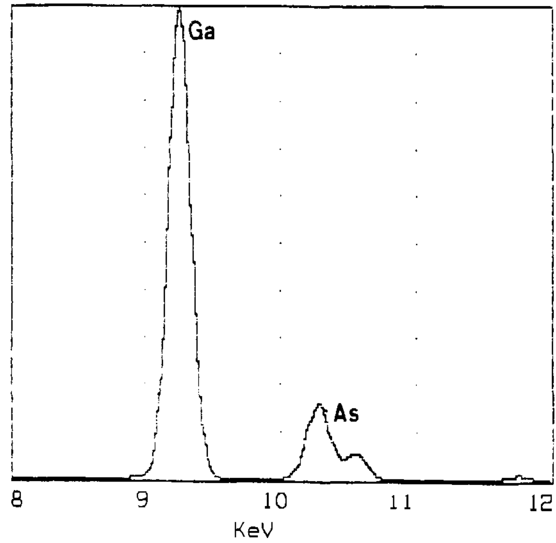


Figure 3.7 EDS Analysis of Residue

atmospheric pressure and above can result in the eventual volatilization of gallium so that the recondensed solid will contain significant proportions of gallium as a contaminant in the arsenic-rich fraction (Figure 3.8).

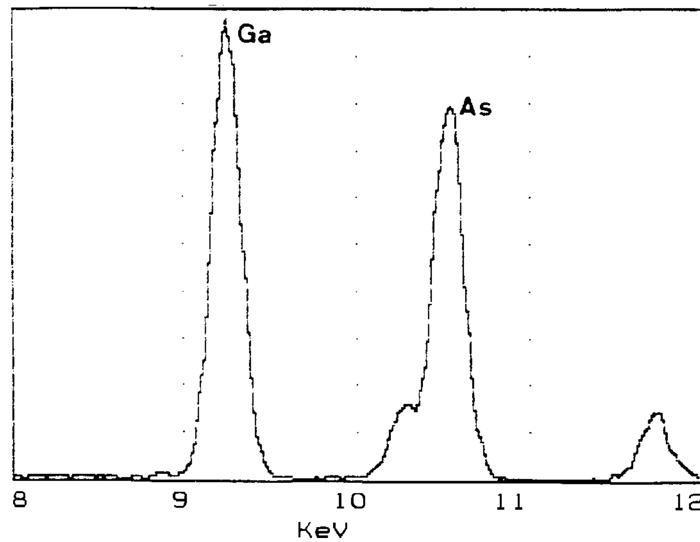


Figure 3.8 EDS Analysis of Volatile Material after 2-hour Run

At this point, it became obvious that, for the process to achieve effective separation of the gallium and arsenic fractions, the evolved arsenic must be continuously removed and recondensed outside of the thermal separation reactor. A thermal reactor was developed that could be continuously evacuated through condenser units for capture of the evolved arsenic. The EDS analysis results on the residual solids are shown in

Figures 3.9 and 3.10 for two runs wherein the evolved gases were pumped out through cooled condensers. In each of these samples, some low level of unvolatilized arsenic is shown (the small "knee" to the right of the smaller gallium peaks in each figure) indicating that the gallium-rich residue would probably still require further purification.

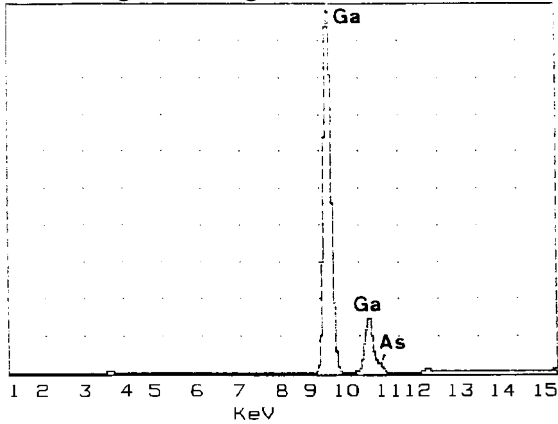


Figure 3.9 Analysis of Residue from 1-hour Run with Continuous Evacuation

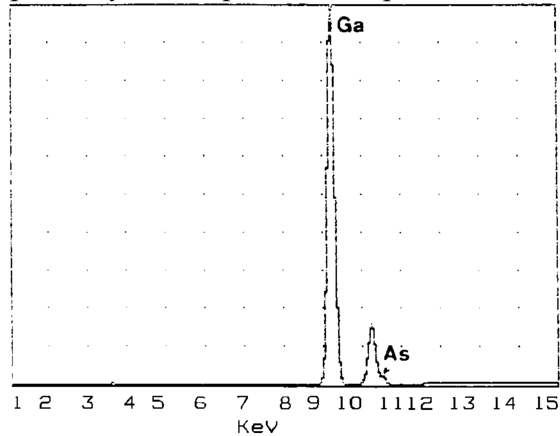


Figure 3.10 Analysis of Residue from 2-hour Run with Continuous Evacuation

Because of the presence of the low levels of arsenic (approximately 3 to 4%) in the residue after thermal separation, it was decided that an additional process step would be required to achieve adequate gallium purity for its reuse. Thus, a low-temperature zone refiner was chosen as the probable best method for purification of the residual gallium-rich material. Similarly, because the volatile fraction could contain materials other than arsenic, it was decided that a sequence of condensation steps followed by volatilization steps would purify the arsenic-rich fraction evolved in the original thermal separation. That logic resulted in the development of the concept process shown in Figure 3.1 at the beginning of this section.

2.3.5 Field Trials at a Semiconductor Foundry

The process for recovering reusable materials from solid GaAs wastes was tested at the AXT Fremont facility in August of 1996. While the primary goal of the field testing was to establish that the proposed recovery process could be effected without disturbing normal GaAs foundry operations, a secondary objective was to establish the purity of the recycled materials.

Waste GaAs kerf and wafer pieces were subjected to the low-pressure, low-temperature thermal process utilized as the first unit operation in the recovery process for solids. Specifically, batches of waste material were placed into a graphite/SiC crucible within the recovery reactor, the pressure reduced to < 1 torr, and the temperature raised to > 1050°C. The waste material was processed for 2-3 hours under these conditions, and arsenic separated out as a condensable vapor, leaving a gallium-rich residue in the crucible. The arsenic and gallium fractions were collected and it was seen that the residue was composed of two different gallium-rich fractions. The purity of the two different gallium fractions from this process is shown in Figures 3.11 and 3.12 which

present SIMS (Secondary Ion Mass Spectrograph) analyses of the product streams. Figure 3.11 is a SIMS analysis of a low-melting fraction that results from this first unit operation. As can be seen, the resultant material is virtually pure gallium. Figure 3.12 shows the purity of a higher-melting “slag” that typically forms around this pure gallium. As can be seen, this material contains substantial amounts of iron, silicon, and other detrimental elements, which account for the higher melting temperature of this fraction.

Equivalent quantities of arsenic were recovered from the condenser as a finely divided powder. No reliable method of measuring the purity of arsenic to the four-9s level was available for the study. The only reliable method to measure the purity of recovered arsenic, is by using it in combination with gallium of certified purity to grow crystals of gallium arsenide. The purity of the recovered arsenic can then be determined by measuring the characteristics of these crystals.

Because of the extremely hjigh purity of the gallium fraction and the difficulties of measuring arsenic purity, the arsenic purification step and the gallium zone refining step were not performed during the field test of the process. Discussions with the foundry operator indicated their desire to participate in future development activities aimed at a commercial process for in-plant pollution prevention.

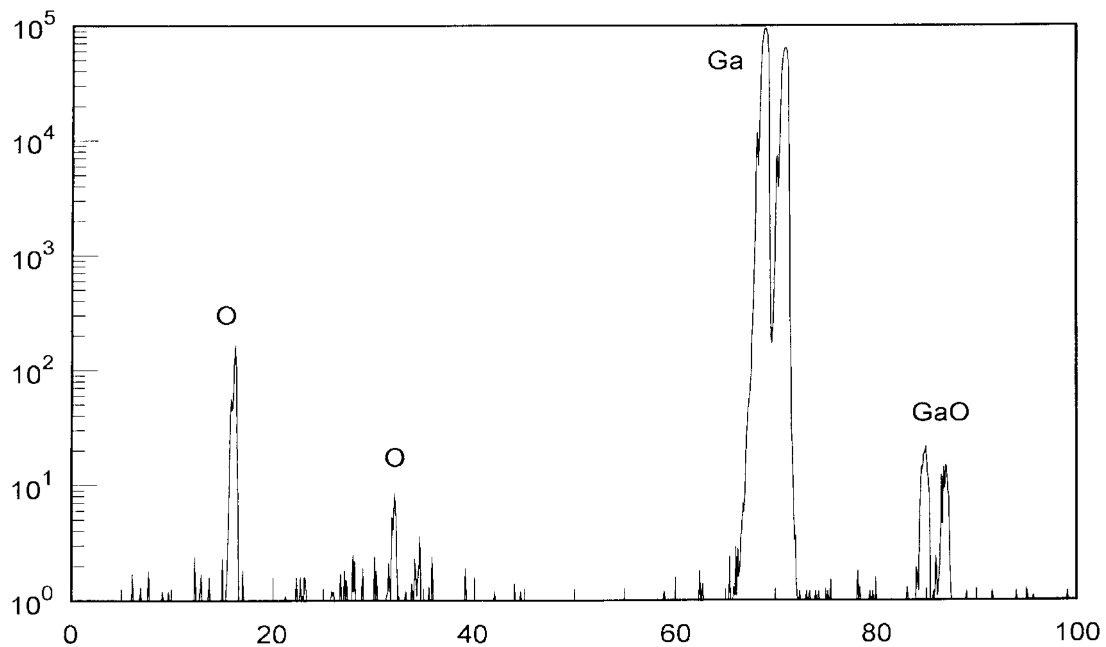


Figure3.11 - SIMS Analysis of Pure Gallium Fraction Resulting from Thermal, Low-Pressure Recovery of GaAs

(note - presence of oxygen and GaO peaks results from use of oxygen as primary ion source)

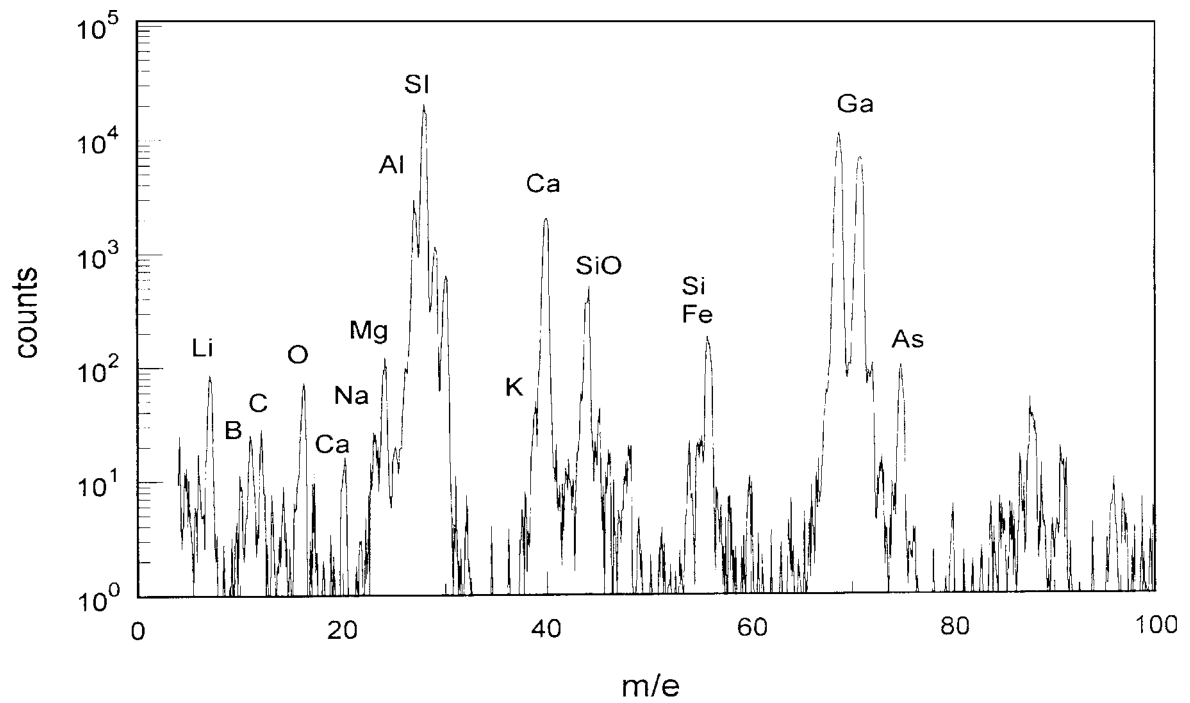
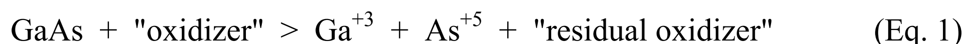


Figure 3.12 - SIMS Analysis of Gallium “Slag” Resulting from Thermal, Low-Pressure Recovery of GaAs

4.0 RECOVERY AND RECYCLING OF GALLIUM AND ARSENIC FROM CRYSTAL POLISHING WASTEWATERS

Facilities that grow bulk crystals of GaAs perform a number of subsequent processing steps wherein the boules (or "ingots") are slabbed into wafers, and etched and lapped to remove surface damage. The final operation performed by these facilities is polishing, to achieve a mirror finish on one or both faces of the wafer. The wafers are mounted onto large circular stainless steel polishing plates (lap plates) and either wax or vacuum is used to hold them in place. These plates are then mounted on a polisher and the wafers are pressed against a tough polishing pad. The polishing is done “wet” in which a very fine polishing agent such as alumina and a mild etching agent that contains an oxidizing species are used to remove surface materials through a combination of mechanical and chemical action.

Use of an oxidizing species as the polishing etchant results in solubilized metal ions according to the following general reactions:



$$GaAs + \text{"oxidizer"} > Ga^{+3} + As^{+5} + \text{"residual oxidizer"} \qquad \text{(Eq. 1)}$$

A number of chemical oxidizers have been used as polishing etchants in the laboratory and in industry to polish the respective metals[38,39,40]. In general, it is desirable to utilize chemical species which will aid the polishing operation by oxidizing arsenic to the water-soluble +5 valence state, because the use of acids (without oxidizer) will lead to the in-plant generation of toxic arsine (AsH_3) gas. The most commonly used oxidizer species are hydrogen peroxide, chlorinated compounds (especially hypochlorite), and nitric acid. Typical concentrations of oxidizer are 30% in water, depending on oxidizer species.

The wet polishing process results in an aqueous wastestream that contains from 200 to 400 ppm of each dissolved metal, as well as residual oxidizer concentrations of from 3 to 10%. At such concentrations, those wastestreams require subsequent treatment for arsenic removal prior to discharge of the water. The polishing wastestream itself has a "milky" appearance, due to the large concentrations of very fine polish (e.g. < 0.5 micron) suspended within it. Although some of this suspended polish will settle after time, most remains suspended; hence the white appearance. The pH of these solutions is dependent upon the initial oxidizer solution used; but the resultant wastestream is generally more basic than the initial solution, due to a number of factors (e.g. presence of oxide polish, generation of soluble gallium, etc.). Any process for precipitation and removal of the arsenic concomitantly will also remove the suspended polishing agent.

4.1 CURRENT TREATMENT METHODOLOGY

The current treatment approach for GaAs polishing wastes is shown in Figure 4.1. A soluble ferric iron species (e.g., ferric chloride or ferric nitrate) is added to the polishing wastewaters, and the pH is adjusted so as to precipitate insoluble ferric

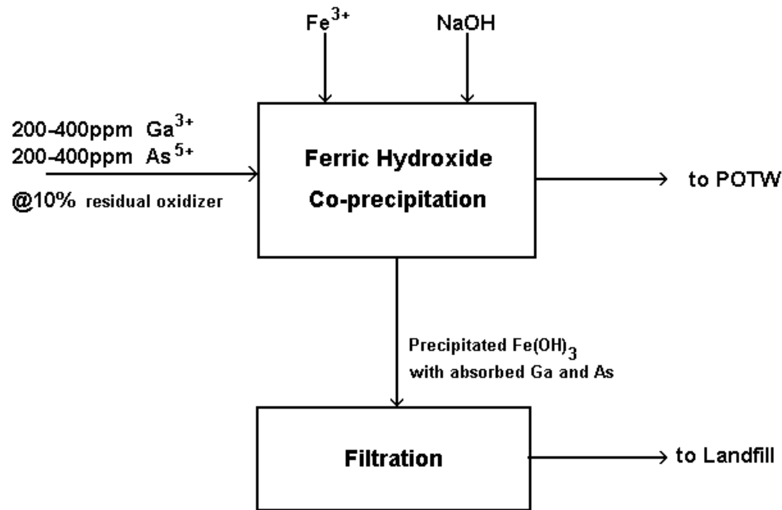


Figure 4.1 - Current Treatment Approach for GaAs Polishing Wastes

hydroxide. The toxic arsenic is "coprecipitated" with the ferric hydroxide. Coagulating and flocculating agents are added to aid in the physical removal of the resultant precipitate.

Table 4-1 shows the resultant arsenic (and gallium) concentrations for a typical industrial filtrate and filter cake using this approach. It is immediately obvious from inspection of the appearance of the filter cake that a tremendous excess of ferric iron is necessary on a weight-to-weight basis with respect to arsenic. This results in a large volume of waste solids which must be disposed, and which could readily leach toxic arsenic. The colloidal nature of the polishing

Table 4-1
Arsenic and Gallium Concentrations in a Typical Industrial Filtrate and Filter Cake using Ferric Hydroxide Coprecipitation Methodology

	Filtrate Discharge*	Filter Cake**
Arsenic (ppm)	1.8 - 2.5	10.3 - 24.6
Gallium (ppm)	8.5 - 10.5	7.5 - 18.4

* Filtrate concentrations determined following methods described in EPA 600/4-79/020[41]. Samples taken from industrial discharge in August 1996.
** Metal concentrations determined using a technique in which weighed, pulverized sample of filter cake was placed into 25.0 ml of 70% nitric acid solution and allowed to sit in this solution for 24 hours at ambient temperature, but with no agitation. Metal concentrations in the extracting acid were determined using Perkin-Elmer Model 3030B AA Spectrophotometer, and measured concentrations correlated back to filter cake concentration.

agent adds difficulty to the physical separation process (as will be discussed later). For this reason, it is difficult to obtain consistent arsenic concentrations in the discharged filtrate on a day-to-day basis.

An additional concern for the disposed filter cake, from a materials recovery standpoint, is that the two materials for which recycling is desirable (arsenic and gallium) are now intimately mixed with a tremendous excess of a third material (iron). Therefore, recovery and recycling of arsenic and gallium from the current filter cake would be extremely difficult. This, combined with the problems sometimes encountered with meeting arsenic discharge limits for the filtrate, led the authors to develop a process that not only will treat for arsenic, but will do so in a way to allow for recovery of both arsenic and gallium.

4.2 APPROACH FOR METALS RECOVERY

UDRI has found that for the development of many pollution prevention and treatment systems, especially in areas (such as this) where there is no proven solution to the problem, it is best to begin with almost an "Edisonian" approach wherein the widest possible selection of realistic concepts are evaluated. The advantage to this approach is that it precludes inherent prejudices for or against options which may have problems associated with implementation. The disadvantage to this approach is that the researcher is confronted with the need to "start from the ground up" in the development of a treatment solution. This disadvantage can be overcome through the use of a simple, straightforward phased test approach (as described in this section). This testing approach will quickly weed out those potential candidates (or variables) which appear to have shortcomings associated with their continued use in the program.

A literature search revealed only one previous paper detailing "recovery" of gallium and arsenic from polishing wastewaters.[42] The described process, involving two evaporation steps (and thus having high energy demands), did not result in a separation of gallium and arsenic from one another. Therefore, it truly was necessary to start from the "ground up" for the development of a recovery approach.

Phase I testing involved the preparation of "surrogate" solutions containing 250 ppm gallium (as $GaCl_3$) or arsenic (as Na_3AsO_4), half of the solutions contained oxidizer (H_2O_2) and the other half did not. (No polishing agent was added to these Phase I solutions - as the intent was merely to identify technically feasible chemical treatment/recovery options.) Candidate treatment options (listed in Table 4-2 and 4-3) were then evaluated using the prepared "surrogate" solutions. The residual metal concentrations (after settling) were measured using a Perkin Elmer AA spectrophotometer. Table 4-2 details those options which were tested in Phase I for arsenic separation and recovery, while Table 4-3 details those options which were tested for gallium separation and recovery. Observations and comments about each of the candidate treatment/ recovery options tested are also included in Tables 4-2 and 4-3.

Phase I testing indicated that the most likely candidate for successful arsenic removal/recovery is a procedure that results in an arsenate species precipitate. Operational difficulties were encountered with sulfide precipitation and stannous reduction procedures in the presence of 5% oxidizer. The shortcomings described in Table 4-2 for other approaches indicated that arsenate precipitation is the only reasonable

treatment/recovery option that could be used if arsenic recovery after removal is a goal. With this in mind, an attempt was made to coprecipitate both gallium and arsenic as "gallium arsenate" from simulated polishing wastes using a number of techniques (e.g., pH and temperature control, "salting out" of solution, etc.). If successful, "gallium arsenate" species could then be reduced back to gallium arsenide. All attempts to prepare this species were unsuccessful - gallium arsenate exhibits too high a solubility.[43]

Table 4-2
Treatment/Recovery Procedures for As Considered and Tested in Phase I

Procedure	Cited References by Number (See Reference Section)	Comments/Observations
1) Pyrogallol chelation	44,45,46	Successful for +3 valence state of As; unsuccessful for As+5 and in presence of oxidizer.
2) Gallic acid chelation	44,455,46	Unsuccessful under all application conditions.
3) Sulfide precipitation a) NaHS b) Thioacetamide	44,47,48,49,50	Precipitation without oxidizer resulted in formation of very fine particle size which was difficult to settle or filter; attempted precipitation in presence of oxidizer was unsuccessful.
4) Arsenate precipitation	51,52,53	Successful (using calcium and magnesium) with and without oxidizer.
5) Chemical reduction a) Stannous ion b) Sulfite ion c) Hypophosphite ion d) Aluminum metal e) Magnesium metal	54	Stannous ion successful both with and without oxidizer; although required concentration was much higher for oxidizer. Sulfite and hypo-phosphite unsuccessful for all conditions. Aluminum and magnesium resulted in highly toxic arsine formation.
6) Ion exchange	55	Successful with no oxidizer; unsuccessful in presence of oxidizer.
7) Ferric hydroxide (baseline)		Successful with and without oxidizer.

A number of potential candidates were found which appeared suitable for gallium recovery; the most favorable being hydroxide or phosphate precipitation. Although fluoride precipitation also appeared favorable for gallium recovery, there was some concern on the part of the researchers about adding large concentrations of a fluoride

Table 4-3
Treatment/Recovery Procedures for Ga
Considered and Tested in Phase I*

Procedure	Cited References by Number	Comments/Observations
1) Chelation a) Hydroxyquinoline b) Tannic acid c) Trioctylamine d) Pyrogallol/gallic acid	 44,56,57,58,59 44, 60 60,61,62,63,64,65 66	Hydroxyquinoline and dibromohydroxyquinoline precipitation was effective in absence of oxidizer; consistent results were difficult to obtain in presence of oxidizer. Other chelating agents were ineffective.
2) Hydroxide precip. a) NaOH b) NH4OH c) Urea	67,68,69	Gelatinous precipitates produced under all conditions with NaOH and NH4OH. Urea failed to precipitate Ga in presence of oxidizer, possibly due to oxidation of urea.
3) Phosphate precipitation a) sodium phosphate b) triethyl phosphate	70	Precipitation using sodium phosphate successful under all conditions. Triethyl phosphate failed to precipitate Ga.
4) Oxalate precipitation a) sodium oxalate b) diethyl oxalate	71,72	Precipitation unsuccessful under all conditions.
5) Malonate precipitation	73	Precipitation unsuccessful under all conditions.
6) Sulfide precipitation	74	Fine particle size of precipitates made physical separation difficult; no precipitation occurred in presence of oxidizer.
7) Fluoride precipitation	75	Precipitation successful under all conditions for Ga.
8) Chemical reduction a) stannous ion b) hypophosphite ion c) metallic zinc	54,76,77,78	Removal using stannous ion successful under all conditions; higher concentrations necessary in presence of oxidizer. Zinc and hypophosphite removal unsuccessful.
9) Ion exchange	55	Removal unsuccessful in presence of oxidizer.
10) Ferric hydroxide (Baseline)		Successful with and without oxidizer.

* Note: One reagent cited as a gravimetric reagent for gallium, cupferron, was not tested due to its high toxicity.

compound (e.g., NaF) to a wastewater system, as this water would then require treatment for fluoride removal prior to discharge.

Following review of the phase I results, a sequential precipitation process was proposed for GaAs polishing wastes, wherein the arsenic species was first removed as an

insoluble arsenate with the gallium then being removed either as a hydroxide or phosphate. These proposed processes were evaluated more thoroughly in Phase II testing.

4.3 PHASE II TESTING OF METHODS FOR ARSENIC RECOVERY

Arsenic removal efficiency using metal arsenate precipitation is dependent upon the following process variables:

- Specific metal employed;
- System pH;
- System temperature; and
- Reactant concentrations.

In order to minimize the costs associated with arsenic removal, inexpensive metal-arsenate systems were chosen for the treatment/recovery process. An additional restriction required that the metal additive not be toxic, so as to preclude subsequent treatment requirements for the wastestream. Phase I testing indicated the feasibility of using calcium- or magnesium as the metal additives in arsenate precipitation systems. Additional metal additive systems considered included iron-arsenate and manganese-arsenate precipitation. These were not tested because the calcium and magnesium systems appeared to be both technically successful and cost effective

The literature indicates that the ferric hydroxide coprecipitation process currently used in industry for waste treatment is in actuality a combination ferric arsenate-ferric hydroxide precipitation process; that is, the arsenic is primarily precipitated in the form of ferric arsenate. Optimum pH conditions for the calcium, magnesium, and iron systems were derived from the literature (Figure 4.2). Optimum pH conditions for ferric-arsenate removal is in the acidic regime (pH 2-3). Optimum pH conditions for calcium-arsenate (pH 11-12) and magnesium-arsenate (pH 9-11) are basic. Figure 4.2 also indicates that the magnesium- and calcium-arsenate systems are at least as effective as the ferric-arsenate system for arsenic removal. Additional process-related concerns can be found in the existing literature.[51-53, 79-81]

Samples of GaAs polishing wastewaters were obtained from American X-tal Technology (AXT) in Fremont, California in August, 1996. Measured arsenic concentrations in these wastewaters at the time of their sampling were 210 to 215 ppm. (Slightly lower initial gallium concentrations of 145 to 150 ppm were measured in these same wastewaters, as will be discussed.) The pH of the solutions varied from 8.3 to 8.8, depending upon the concentration of alumina polish present in the samples.

An initial evaluation of the effectiveness of the four metal systems was conducted by adjusting the pH of 25 ml samples of this wastewater to the desired pH with NaOH or HNO_3, adding the metal salt (as chlorides) for a 10:1 metal to As ratio on a mole basis, centrifuging for 10 minutes, and then extracting the top portion for As analysis using a

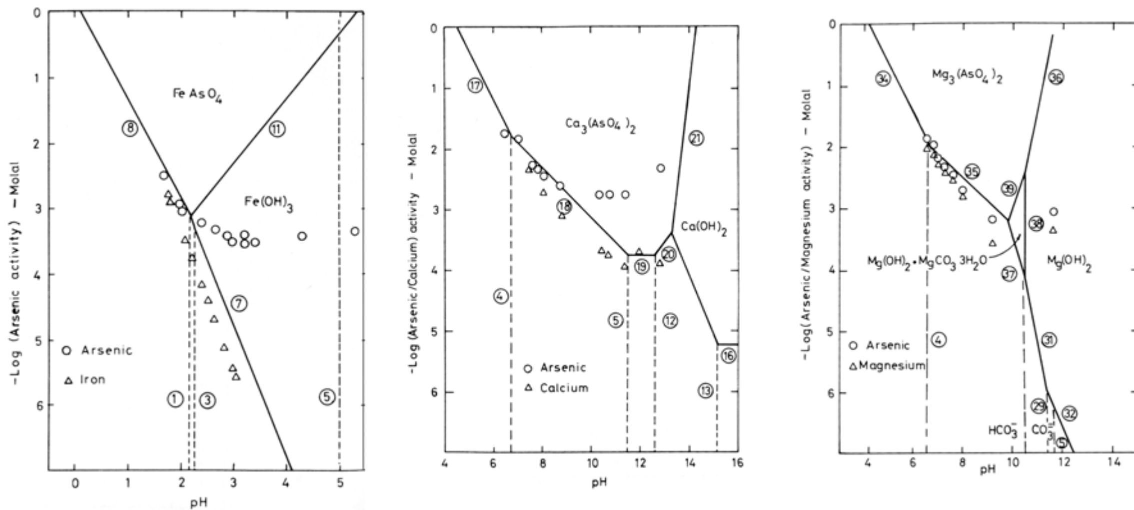


Figure 4.2 - Comparison of Metal Arsenate Systems[47]

Perkin-Elmer Model 3030B AA spectrophotometer following procedures outlined in EPA Methods for Water and Wastewater, part 200.[43] The pH meter used was calibrated with 4.00, 7.00, and 10.00 standards, and the AA spectrophotometer was calibrated using 10, 100, and 250 ppm standards. System temperature during these tests was maintained at 25°C ± 1°C.

The plots of residual As concentrations versus pH for each of these metal systems is shown in Figure 4.3. Several important issues were determined from this study:

1) Given the proper pH conditions, the removal effectiveness of Fe, Ca, and Mg arsenates are comparable. The fluctuations in residual metal concentrations at identical pH values for identical metals indicates that further optimization is a function of physical separation, not of chemistry. For example, 7 calcium arsenate samples were filtered through a 0.1 micron filter, while 7 others were centrifuged for 10 minutes. The resultant residual concentration profiles confirm the hypothesis that the physical separation method is as important as the chemical process used.
2) Manganese offers no advantage over the use of iron, calcium or magnesium.
3) At higher pH values, gallium (e.g. gallium hydroxide) resolubilizes. Therefore, for those systems which utilize high pH values for As removal (especially calcium-arsenate), gallium will remain in solution, allowing for subsequent removal of gallium containing very low concentrations of arsenic.
4) The sludge volumes produced are very high, but this is due in large part to the large amount of polish present. In fact, once precipitation occurs (i.e., after the addition of the soluble metal chlorides), the solution is so "thick" that air bubbles can become "trapped" in the resultant slurry mix. Although this effect was not as noticeable at lower pH values (e.g., < 9), a definite "thickening" of the solution still occurs. This probably contributes to the separation difficulties encountered in industry with the ferric hydroxide precipitation.

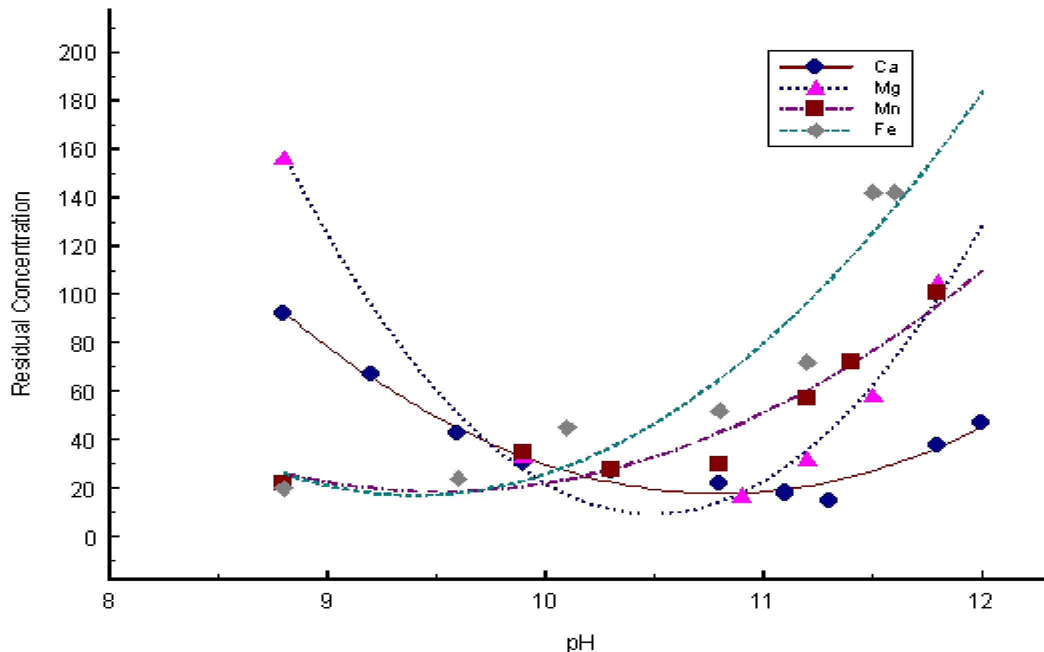


Figure 4.3 - Experimental Residual Concentrations of As as a Function of pH and Metal-Arsenate System at 25°C.

The first issue is especially important for this wastestream. As mentioned previously, even prior to treatment, the solution has a milky appearance due to the high concentrations of very fine alumina polish suspended within. A number of techniques (e.g., centrifugation, filtration through 0.1 micron filters, use of settling aids) were attempted to remove this polish prior to treatment for arsenic removal, but all were unsuccessful. This suggests that the polish itself imparts colloidal properties to this solution, and this ***strongly*** affects any subsequent physical separation process. In fact, variability in residual arsenic concentrations, as was seen from sample to sample in our experiments, is to be expected from day to day in an industrial setting due to the nature of the colloidal suspension of polish. None of the treatment approaches tested resulted in arsenic concentrations acceptable for discharge, primarily because flocculating agents and coagulants typically used in actual industrial practice were not included in the tests.

The literature indicates that for the arsenate systems of interest, higher temperatures reduce the solubility of the resultant precipitates. Therefore, a subsequent test program similar to that described above was performed wherein calcium precipitations were performed at two higher temperature values (40 and 60°C). Experimental results for these tests are plotted versus the 25°C data in Figure 4.4. This information suggests that the increase in arsenic removal achieved at elevated temperatures for this wastestream may not be worth the energy cost of raising the temperature. In addition, no significant decrease in the sludge volume due to elevated temperatures was observed.

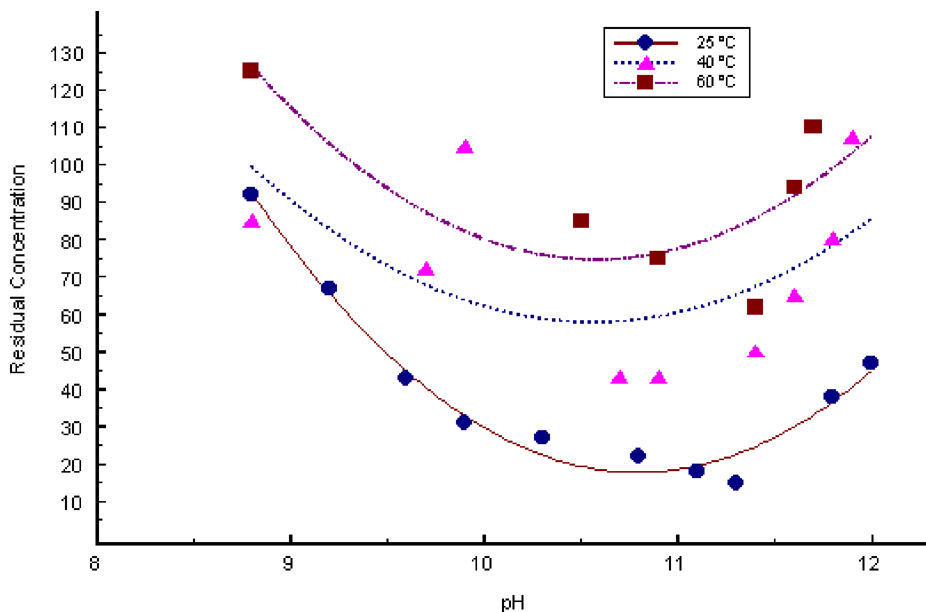


Figure 4.4 - Experimental Residual Concentrations of As in Calcium Arsenate Precipitates as a Function of pH and Temperature.

Finally, the effect of additive metal concentration upon residual arsenic (and gallium) concentrations was studied using the procedure described above, with a fixed pH value for each metal (11.8 for Ca, 10.5 for Mg, 9.6 for Fe). The experimental results are shown in Table 4-4.

The lowest metal-to-arsenate ratio utilized for calcium or magnesium is 1.5:1, whereas a 1:1 ratio is used for iron. These ratios were selected based on the precipitation reactions:

$$3Ca^{+2} + 2AsO_4^{-3} \Rightarrow Ca_3(AsO_4)_2 \quad \text{(Eq. 2)}$$

$$Fe^{+3} + AsO_4^{-3} \Rightarrow FeAsO_4 \quad \text{(Eq. 3)}$$

The data in Table 4-4 suggest that a metal-to-arsenic ratio of 2:1 is sufficient for both calcium and magnesium to remove arsenic, whereas much higher amounts of iron are necessary to achieve comparable removal efficiencies. In addition, it was found that for magnesium, and especially calcium, increased metal-to-arsenic ratios noticeably increase the volume of sludge produced (hence, the majority of the sludge for greater-than-stoichiometric concentrations is likely the metal hydroxide of the additive metal).

Table 4-4
Comparison of Metal-Arsenate Systems for As and Ga Removal/Recovery from GaAs Polishing Wastewaters at Different Metal-As Ratios.

Metal Sample	Metal:As Ratio (mole)	Final pH (±0.2)	Sludge Vol. (%)*	Residual As conc. (ppm ±1)	Residual Ga conc. (ppm ±1)
Ca - 32	1.5:1	10.3	24.3	25	154
Ca - 33	2:1	10.3	25.8	25	176
Ca - 34	5:1	10.5	36.9	21	158
Mg - 8	1.5:1	8.4	22.8	16	36
Mg - 9	2:1	8.5	24.5	18	34
Mg - 10	5:1	8.8	31.7	17	35
Fe - 14	1:1	7.1	-	78	16
Fe - 15	2:1	7.4	-	57	10
Fe - 16	5:1	7.6	-	39	31

* Sludge removed was transferred to graduated cylinders to measure volume remaining. This number compared to the original volume of wastewater tested is the reported sludge volume percent. Sludge volumes for the ferric hydroxide process were not measured.

4.4 PHASE II TESTING OF METHODS FOR GALLIUM RECOVERY

The efficiency of gallium removal from the polishing wastewater is dependent upon the following process variables:

- The particular anionic species chosen in which to precipitate gallium;
- System pH;
- System temperature; and
- Reactant concentrations.

Phase I studies indicated that two anionic species were suitable for gallium precipitation; hydroxide and phosphate. Because the intended final fate of these precipitates is conversion (through a reduction process) to elemental gallium, it was decided that use of gallium hydroxide as a precipitate would be less problematic. That is, reduction of gallium phosphate would likely yield gallium phosphide which would then in turn have to be converted to gallium metal, or even elemental phosphorus. Neither of these outcomes is desirable. Therefore, it was decided that phosphates would not be added to the wastewaters, since they would potentially interfere with conversion of the precipitates to a recoverable material.

The concentrations of gallium in the as-received wastewater samples from AXT were slightly lower (e.g., 50 ppm less) than the arsenic concentrations in the same samples. This is attributable to the fact that at the observed pH of these samples (8.3 to 8.8), gallium hydroxide is relatively insoluble in water. The samples received from AXT were taken from the top of the collection tank for the polishing waste; therefore, any

precipitated gallium hydroxide had a chance to partially settle in the collection tank prior to sample collection.

The literature contains sufficient information about the solubility of gallium hydroxide to allow an understanding of what is happening to the gallium during the arsenic recovery processes, and thus to optimize the subsequent gallium recovery process.[67,82,83] When sodium (or potassium) hydroxide is applied to a solution containing gallium, various hydrated oxides and hydroxides of gallium begin to precipitate as the pH rises. At a certain pH, however, a new species, sodium gallate [$NaGa(OH)_4$] is favorable, which is soluble in water. The pH at which this species is formed depends greatly upon the type and concentration of other ions, but it is generally in the pH range of 9.7 to 11.[82] In other basic environments, such as in NH_4OH, the gallate species does not occur. The literature suggests that the minimum solubility of gallium hydroxide species is at a pH of 5 to 7, depending again upon ionic conditions. Finally, the literature also suggests that the solubility of gallium hydroxide decreases with decreasing temperature. Based on this information, a metal gallate/ gallium hydroxide based recovery concept was chosen for testing.

Figure 4.5 illustrates the measured amount of residual gallium remaining in solution as a function of metal-arsenate system and pH, while figure 4.6 shows the effect of temperature during metal-arsenate precipitation upon residual gallium concentrations in this waste stream. The effect of calcium. magnesium, and iron concentrations upon residual gallium concentrations were shown above in Table 3-4.

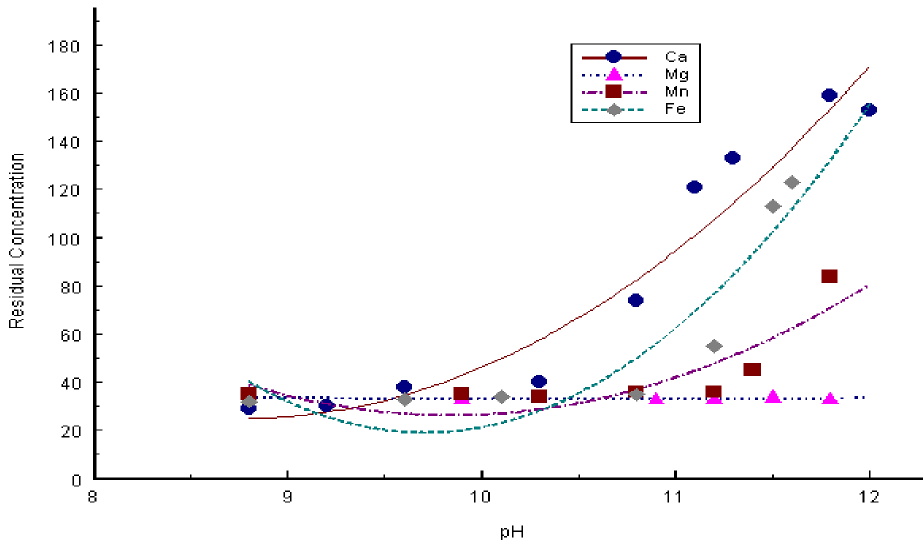


Figure 4.5 – Measured Residual Ga Concentrations as a Function of Metal-Arsenate System and pH at 25°C

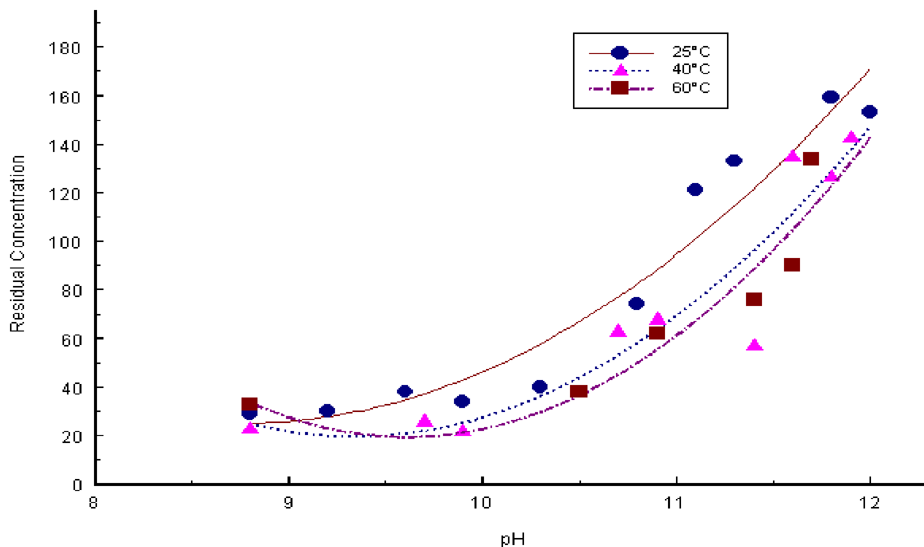


Figure 4.6 – Measured Residual Ga Concentrations Following Calcium Arsenate Precipitation as a Function of Temperature and pH

This information suggests that the optimum conditions to solubilize gallium during arsenic precipitation for this wastestream is to utilize a calcium-arsenate precipitation at room temperature, at pH conditions of 11 or higher. It was surprising that in this concentration regime, gallium concentrations were not higher for the magnesium-arsenate removal. (Perhaps because magnesium gallate precipitates.)

As a final "proof-of-concept" for the arsenic and gallium recovery process from these wastewaters, five 25 ml replicate samples of polishing wastewaters were first subjected to a simulated treatment/recovery system from this process. The first unit operation in the tested concept was a calcium arsenate precipitation process at 25°C, with a calcium-to-arsenic ratio of 5:1, and in pH ranges from 11-12. The resultant precipitate was allowed to settle, the sludge volume and pH measured, and a 5 ml sample of the filtrate drawn off for Ga and As analysis using AA spectrophotometry. The filtrate was then treated with sulfuric acid (to simulate etching acids, another wastestream available at these facilities) in the second unit operation to adjust the pH to conditions at which gallium hydroxide will precipitate. The volume of the gelatinous precipitate of gallium hydroxide sludge was then measured as well as the solution pH. The resultant precipitate was filtered, and a 10 ml sample of the filtrate was drawn off for Ga and As analysis. Finally, the third unit operation featured further treatment with ferric iron, to simulate the existing coprecipitation process that can be used for a final polishing step in the treatment prior to discharge. Sludge volumes, final pH, and residual As and Ga concentrations were measured for these samples. All five trials resulted in residual arsenic concentrations less than 5 ppm, with recovery of the majority of the original dissolved arsenic (as calcium arsenate) and gallium (as gallium hydroxide).

4.5 PROCESS FOR RECOVERY OF MATERIALS FROM AQUEOUS WASTES

As a result of the above studies, a process has been developed and tested on actual GaAs polishing wastes which not only allows for the treatment of a toxic species (arsenic), but does so in a way that allows for its recovery and reuse. The process also recovers the "strategic" metal gallium from these waste streams. The developed process is shown in Figure 4.7. In the first step, the pH of the wastewaters is adjusted to between 11.5 and 12 with sodium hydroxide. A soluble calcium salt is added in metal-to-arsenic ratios of no more than 5:1, but preferably 2:1 (to minimize sludge volume). The resultant precipitate is passed into a centrifuge which removes precipitated calcium arsenate and polish. Centrifuged sludge possessed an average solids concentration of 8.4% without further filtration. The centrate liquid is added to precipitation supernatant liquid and then passed into a second reaction tank wherein the pH is adjusted to between 6 and 8 through the use of waste etching acids. The resultant fine, gelatinous precipitate of gallium hydroxide is allowed to settle, and is filtered through a 0.1 to 0.5 micron filter. The final supernatant and filtrate liquids are then sent to the (existing) ferric hydroxide coprecipitation system for final treatment of residual arsenic. Removal of the colloidal polish particles in the first (calcium arsenate) precipitation results in greater ease for physical separation of precipitates in the two subsequent treatment processes. Centrifugation is the preferred separation technique for the first unit operation in the process due to the nature of the suspended solid material; filtration is acceptable for the two subsequent processes.

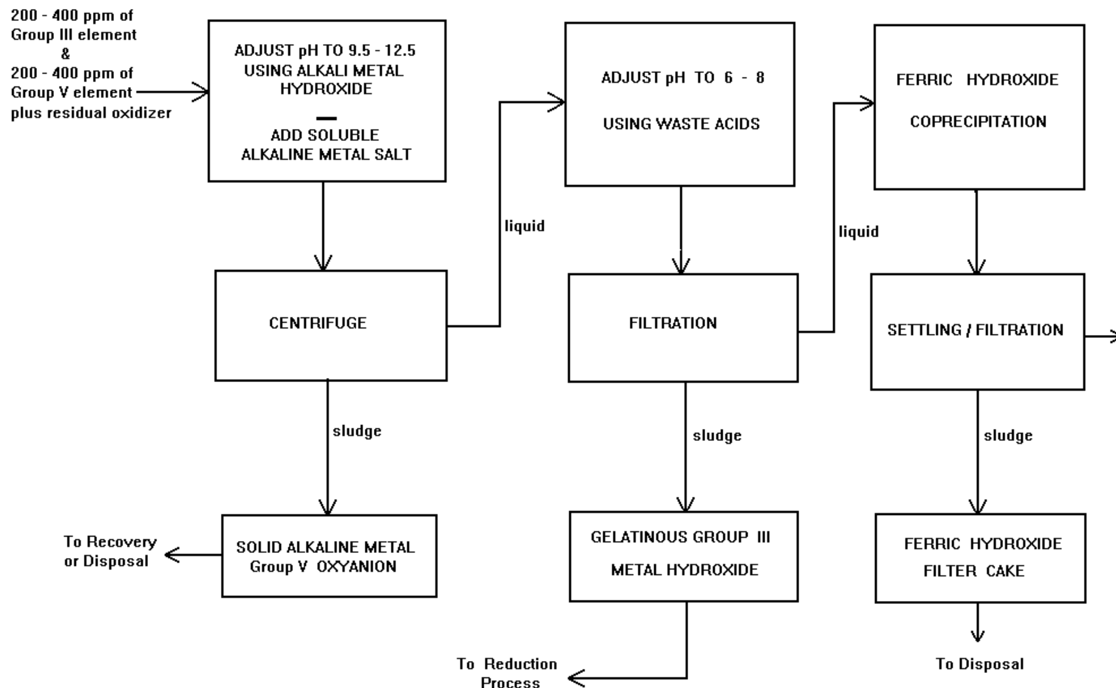


Figure 4.7 - Developed Process for the Sequential Recovery of Gallium and Arsenic from GaAs Polishing Wastes.

5.0 ECONOMIC ASSESSMENT

5.1 FACTORS AFFECTING THE ECONOMICS OF GaAs AND OTHER III-V MATERIAL RECOVERY SYSTEMS

Discussions with semiconductor manufacturers indicated that similar levels of wastage were to be seen for all types of semiconductors. Because of similarities in the chemistry and physics of III-V semiconductors (including InP, GaP and InAs) it soon became obvious that with only slight changes, all of the processes developed for GaAs could be applied to other III-V manufacturing. Thus, as part of the evaluation of the pollution prevention concepts developed under this research effort, the researchers performed an estimate of the economic benefits associated with the recovery and recycling technologies for the III-V semiconductor manufacturing industry. The economic calculations that are made here are confined to the U.S., and only to the III-V semiconductor manufacturing industry.

Three cost contributors make up the majority of the cost benefits associated with recovery of toxic and/or strategic materials. These are:

1) elimination of short-term environmental costs associated with waste disposal,
2) elimination or minimization of long-term liabilities that could be incurred in the event of a release of hazardous wastes, and
3) elimination of some raw materials costs due to the reduction in usage because they are replaced with recycled materials.

It was quickly found that item #3 offers significant economic benefits due to the high costs of gallium and indium. Raw material costs for III-V elements at present can be estimated as shown in Table 5-1.

Table 5-1 Estimated III-V Raw Material Costs

Material	Estimated Present Cost
Gallium	$1/gram = $900,000/ton
Indium	$0.25/gram = $225,000/ton
Aluminum	Negligible
Arsenic	$0.05/gram = $45,000/ton
Phosphorus	Negligible
Antimony	$0.06/gram = $54,000/ton

The above costs do not take into account the additional processing that is necessary for purification of raw materials to level of purity that is required for semiconductor growth. Nor do they take into account the additional processing to convert these metals into organometallic species for epitaxial growth processes. In other words, benefits accruing from recovery of materials that do not require these additional processing steps are not considered here, making this analysis very conservative.

In order to estimate an annual benefit from materials recovery, it was first necessary to ascertain the volumes of III-V materials currently being produced in this country. No definitive volume numbers by year could be found in the literature for the year 1995. It is known that in 1985, 20 tons of bulk gallium arsenide were produced in the U.S. However, not only was 1985 more than 10 years ago, it was rather early in the "lifetime" of this semiconductor material. Since 1985, a multitude of additional uses for gallium arsenide have been developed. No U.S. Bureau of Mines information could be found for annual usage of gallium (or arsenic, for that matter), but a 1992 value is available for germanium usage, which is used almost exclusively in some special semiconductor devices. The 1992 usage of germanium (7 tons), along with the 1985 value of gallium arsenide produced, provides a basis for estimating the bulk tonnage of GaAs crystals produced in this country in 1995. These estimated values are shown in Table 5-2 below. The 1995 usage of GaAs was estimated to be 20 to 30 times greater than the usage of germanium. However, to be conservative, a multiplier of only 15 is used. Discussions with industry sources provided the basis for estimating other III-V usage.

Table 5-2 Estimated Annual Tonnage of Bulk III-V Crystals Produced in 1995 in the U.S.

Compound		Tonnage
Gallium Arsenide	-	100 tons
Indium Phosphide	-	10 tons
All other III-V compounds	-	0.5 to 1 tons (total)

Although these III-V compounds are formulated with 1:1 atomic ratios of Group III and Group V elements, one must recall that the weights of these elements differ. Therefore, although 10 tons of gallium arsenide contain roughly 5 tons each of gallium and arsenic, 10 tons of indium phosphide contain approximately 8 tons of indium and 2 tons of phosphorus.

In 1995, 2.5 tons of arsine and 6.5 tons of phosphine were produced and used in the U.S. in 1995 for epitaxial growth and doping operations. It is estimated that approximately 0.5 tons each of organoarsines and organophosphines as well as some organoantimony compounds were used in these processes, thereby contributing a total of 10 tons of gaseous Group V source materials used in 1995. Because the ratio of Group V to Group III elements is typically 2:1, it is further estimated that 5 total tons of Group III elements (gallium, indium, aluminum) were used in epitaxial growth processes in 1995. Because gallium and indium are heavier than aluminum, it is estimated that 2 tons each of

gallium and indium were used in organometallic form in 1995. In addition, molecular beam epitaxy processes typically utilize the elemental species of these Group III and V elements. Therefore, it is estimated that 3.5 tons of arsenic, 7.5 tons of phosphorus, 0.5 tons of antimony, 2.5 tons of gallium, 2.5 tons of indium, and 1.5 tons of aluminum were used in all aspects of epitaxial growth and doping operations in 1995.

5.2 IMPORTANT ECONOMIC FACTORS FOR SOLID AND AQUEOUS GALLIUM ARSENIDE RECOVERY

It is estimated that 100 tons/year of bulk gallium arsenide crystals are produced in this country, and it is known that from crystal growth to final chip production approximately 75% of these materials are wasted (sawing wastes, wafer breakage, out-of spec pieces and chips. Then an estimated 75 tons of gallium arsenide are wasted annually, or approximately 37.5 tons each of gallium and arsenic. Therefore, the total cost of raw materials that become wastes are as shown in Table 5-3.

Table 5-3 Estimated Annual Costs of Raw Material Wasted in the Form of Solids from Gallium Arsenide Crystals

Gallium Costs:	37.5 tons X $900,000/ton =	$33,750,000
Arsenic Costs:	37.5 tons X $45,000/ton =	1,687,500
TOTAL		**$35,437,500**

In communications with industry sources, it was indicated that the metals lost during aqueous etching and polishing operations equal approximately 2% of bulk crystal raw material inputs. Therefore, 2 tons per year of gallium arsenide can be assumed to be lost during aqueous etching and polishing operations. Estimates based on these numbers are shown in Table 5-4.

Table 5-4 Estimated Annual Costs of Raw Material Wasted in the Form of Aqueous Streams from Gallium Arsenide

Gallium Costs	1 ton X $900,000/ton =	$900,000
Arsenic Costs	1 ton X $45,000/ton =	$45,000
TOTAL		**$945,000**

5.3 IMPORTANT ECONOMIC FACTORS FOR SOLID AND AQUEOUS INDIUM PHOSPHIDE WASTE RECOVERY

Similar calculations were performed for raw material costs for indium phosphide semiconductor manufacturing, since that is another important III-V semiconductor whose production volume is expected to grow in the near future. The estimated annual cost of raw material wasted in the form of solids from indium phosphide crystal production is based on an estimate of 6 tons wasted at a cost of $225,000 per ton for a total of

$1,350,000. The estimated annual cost of wasted raw materials as aqueous wastes from indium phosphide production is based on an annual estimate of 0.16 tons wasted. Using the same cost per ton of raw materials, this gives $36,000 per year worth of raw materials wasted in the aqueous waste streams of indium phosphide producers.

5.4 IMPORTANT ECONOMIC FACTORS FOR RECOVERY OF OTHER III-V COMPOUNDS

Similar calculations were also performed for the other III-V compounds that are currently being produced in the U.S. The calculated values for the raw material losses and potential savings are shown in the final summary table.

5.5 ECONOMIC FACTORS FOR RECOVERY OF WASTES FROM III-V EPITAXIAL PROCESSES

The reactor systems currently used for III-V epitaxial growth processes currently operate at about 25% efficiency - that is, 75% of the input material ends up as wastes in the form of solid wastes on reactor walls (which is then land disposed), or in the form of scrubber waters or oxidized species from treatment operations to the reactor exhausts. Cost calculations for these waste streams are shown in Table 5-5.

Table 5-5 Estimated Annual Costs of Raw Material Losses in Epitaxial Growth Processes

Gallium losses	2.5 tons X 0.75 X $900,000/ton =	$1,687,500
Indium losses:	2.5 tons X 0.75 X $225,000/ton =	$ 421,900
Aluminum losses:	negligible cost	
Phosphorus losses:	negligible cost	
Arsenic losses:	3.5 tons X 0.75 X $45,000/ton =	$ 118,100
Antimony losses:	0.5 tons X 0.75 X $54,000/ton =	$ 20,000
TOTAL		**$2,247,500**

5.6 SUMMARY

The numbers presented in this section are disturbing in that they represent very appreciable dollar costs in an industry that is still in its first couple decades of existence. There are three means to accomplish reductions of these costs. The first involves the work that UDRI has performed under the subject grant involving capture and recovery of the toxic and valuable metals from the processing steps. The second involves the development and construction of more efficient processing steps that do not result in 75 to 85% wastage. The third alternative may be the development and substitution of lower cost alternatives for some III-V semiconductor materials.

The potential dollar savings presented here are probably low. A great deal of simplicity was used in order to estimate these values. For example, the costs associated with the extensive purification and synthesis processes to produce semiconductor-grade material sources were not considered. One must also consider that this industry is expected to double in size before the end of the century due to the tremendous increase in demand from the private sector for III-V devices. Some of the materials that are currently being produced in the one ton per year range are expected to undergo dramatic increases in demand. Other III-V materials which now only appear in research laboratories will begin to be commercially produced before the end of the century. For example, gallium nitride has been proven as a blue LED material, and commercial production of this material should soon begin. Finally, one needs to consider the large quantities of wastes from prior years that have either already been land disposed or are being stored in warehouses because the parent companies do not wish to dispose of them. All of these factors will raise the total dollar value of the materials that can be recovered using the technologies developed under this grant. A summary of the estimated value of these is presented in Table 5-6.

Table 5-6 Total Estimated Annual Dollar Value of Wasted Raw Materials from III-V Semiconductor Growth Operations

Source	Dollar Value – 1995
Gallium Arsenide - all solid wastes	$35,437,500
Gallium Arsenide - aqueous wastes	$945,000
Gallium Antimonide - all solid wastes	$178,900
Gallium Phosphide - all solid wastes	$168,700
Indium Phosphide - all solid wastes	$1,350,000
Indium Phosphide - aqueous wastes	$36,000
Indium Antimonide - all solid wastes	$52,300
Indium Arsenide - all solid wastes	$50,600
Aqueous wastes exclusive of GaAs and InP	$10,000
Epitaxial Growth and Doping - all III-V elements	$2,247,500

Evaluating the worth of the recoverable materials requires further estimations. If it is assumed that in the early stages of implementation, only 10% of the available material would be processed, then, based on gallium arsenide alone, $3.5 million worth of materials could be recovered annually. This quantity would be appropriate for a typical foundry. Capital and operating costs should be minimal for the processes sized for a typical GaAs foundry, with capital equipment estimated at less than $500,000 per plant and annual operating costs of less than $150,000 per plant. In such a case, extremely favorable cost recovery rates could be achieved for implementation of the developed processes.

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