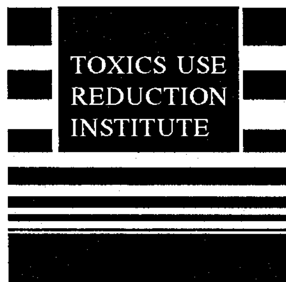

THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE

ARSINE SOURCE REPLACEMENT

For the Growth of Gallium Arsenide Via MOCVD

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University of Massachusetts Lowell

Arsine Source Replacement for the Growth of Gallium Arsenide via MOCVD

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The Toxics Use Reduction Institute Matching Grants Program

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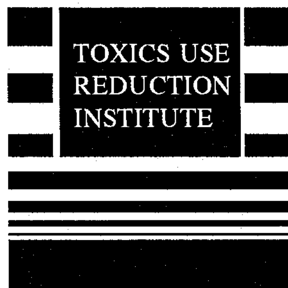

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to governments to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

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Toxics Use Reduction Institute
Matching Grants Program

The Institute annually provides direct funding to Massachusetts industries on a matching basis for toxics use reduction (TUR) feasibility and technology studies. The Matching Grants Program was initiated in FY93 to facilitate the development and use of innovative techniques that reduce the use of toxic chemicals or the generation of toxic byproducts in Massachusetts businesses. Grants are awarded on a competitive basis for companies to conduct TUR studies at their facilities. Recipients prepare project reports which assist in transferring toxics use reduction technologies and methods to other companies. The opinions and conclusions expressed in this report are those of the authors and not necessarily those of the Toxics Use Reduction Institute.

The following feasibilty study involves the systematic evaluation of arsenic containing reagents that could potentially replace arsine gas from the process and manufacturing of microwave semiconductor diodes. The reagent would act as an input substitution in the Semiconductor Materials Laboratory at the Burlington Facility of M/A-COM. The study is divided as follows:

I. INTRODUCTION

II. GROUP V SOURCE EVALUATION

III. RELATIVE COSTS ANALYSIS

IV. SUMMARY

I. INTRODUCTION

M/A-COM's Semiconductor Materials Laboratory at the Burlington Facility utilizes arsine gas as a precursor to the growth of gallium arsenide films grown in its metalorganic chemical vapor deposition (MOCVD) process. There are several problems associated with the use of this material. First, and, foremost is the toxicity of arsine gas. The median lethal concentration (LC50) of arsine in air is 20 ppm at exposure times of 4 hours. The OSHA Hazard Communication Standard (29CFR1910.1200, Appendix A) defines a chemical with a LC50 of 20 ppm as highly toxic. It may be possible to achieve this concentration in air when using pure arsine gas in the event of a line puncture or valve failure. Second, the Materials Lab consumes up to 40 pounds of pure arsine per year in three MOCVD reactors. Shipping and storage of arsine cylinders poses potential risk to both the community and the work environment in the event of a transportation accident. Third, studies indicate that as little as 25% of the arsine used in the MOCVD process is decomposed at typical growth temperatures of 650 degrees C. The remaining material is pyrolyzed in a combustion chamber and converted into arsenic (tri)oxide. The efficiency of the pyrolysis in the combustion chamber is assumed to be 100%. It is expected that non-hydride arsenic subsitutes will reduce arsenic losses and waste because of there inherent thermal instability.

As a result of increasing concerns over the impact of an accidental release, a pro-active approach has been taken by M/A-COM. The goal of this program is to analyze the possible alternatives for the group V element. An objective review of all arsenic precursors ensues. The compounds evaluated have all been used in the growth of gallium arsenide layers. Finally, recommendations will be made regarding which substitute best fits M/A-COM's needs.

II. GROUP V SOURCE EVALUATION

The technical requirements for a Group V source substitution are: lower toxicity than arsine, high vapor pressure (greater than 50 torr at room temperature is preferred), low temperature stability, pyrolysis at temperatures of 400 degrees C and greater, and no inherent purity limitations such as excess carbon contamination. There should be no parasitic or pre-reactions occuring with the Group III source upstream of the seed.

The following is a list of compounds that have been used in the growth of arsenic-containing semiconductor layers. (These compounds are not limited to binary semiconductors, i.e. gallium arsenide. In many cases their usefulness have been demonstrated in the high purity growth of ternary and quarternary devices. This paper attempts to identify the material-type grown when discussing the merits of each compound).

A concise description follows each alternative compound. In all but one case, the arsenic containing substitute is less toxic than arsine gas. With this in mind, direct substitution into existing metalorganic chemical vapor depor deposition reactors was considered. For example, electrochemical generation of arsine (point-of-use) may be feasible. However, system modifications may eliminate its contention.

In addition to the technical requirements listed above, the ideal substitute should also be commercially and readily available, economically competitive, and easily adapted into existing equipment, i.e. defined "bubbler" geometry.

elemental arsenic:

From a safety standpoint, elemental arsenic is a favorable substitute for arsine in the growth of gallium arsenide films. With a vapor pressure of 1 torr at 370 degrees C., it is the least hazardous replacement to work with. As a cosequence of the low vapor pressure, it is necessary to heat the gas handling network, which can be cumbersome and costly.

Thin film gallium arsenide layers have been grown using elemental arsenic by heating a boat containing the arsenic to approximately 450 degrees C. and combining it with trimethylgallium vapor [1]. Layers were grown between 625 and 750 degrees C. However, the layers were characterized as p-type at growth temperatures less than 700 degrees C. due to carbon incorporation. It is postulated that the addition of atomic hydrogen would lower the background p-type concentration, but not to an acceptable level [2]. Also, "oval" defects were observed [3] similar to those obtained via molecular beam epitaxy, MBE. Finally, it is unlikely that high purity aluminum gallium arsenide would be grown from arsenic and group III alkyls. The reason for this is the lack of atomic hydrogen present to react with the excess carbon.

A recent laser-enhanced method of epitaxial growth has been reported using elemental arsenic and triethylgallium [4]. N-type backgrounds in the low E15cm^{-3} range are capable. Seven nine's purity arsenic is available today. It is believed that this technique is just beginning to be explored and that it holds some promise (although production equipment may be a long way off).

monoethylarsine:

This group V candidate meets the criterion for a suitable replacement for arsine. It is relatively unstable and has a very workable vapor pressure of 197 torr at zero degrees C. Furthermore, the decomposition of monoethylarsine generates an active arsenic hydride species (dihydro arsenic radical) that contributes to high purity growth. The mechanism involves the reaction of methyl radicals (from trimethylgallium decomposition) with this activated dihydro arsenic radical, thus, preventing carbon acting as an acceptor atom [5]. High purity gallium arsenide epitaxial layers have been grown in an atmospheric metalorganic chemical vapor deposition reactor (vertical configuration). The background net carrier concentrations were in the high E14/cc range, and n-type. This was also accomplished at V/III ratios of about 4/1. Technically, monoethylarsine has demonstrated the capability of replacing arsine gas in the MOCVD process.

trimethylarsenic

This compound has an acceptable vapor pressure of 238 torr at 20 degrees C. In addition, it has a low toxicity (see table 1). It can be troublesome, however, for two reasons. It is very stable (a pyrolysis temperature greater than arsine) and its decomposition produces active methyl radicals that contribute to p-type doping. Some of the lowest background levels have been reported in the1-5E16 cm^{-3}, p-type [6]. This concentration is particularly high for gallium arsenide power devices. Finally, it is typical to obtain poor surface quality when substituting with trimethylarsenic and trimethylgallium, although this can be overcome with an arsine passivation step prior to growth [7].

triethylarsenic

The vapor pressure of this compound makes it only slightly attractive to replace arsine in the metalorganic chemical vapor deposition systems. This relatively low vapor pressure, 238 torr at 20 gegrees C., would require excessive flow rates and/or elaborate heating set-ups, as is the case for elemental arsenic. Nevertheless, gallium arsenide layers have been grown using this group V alkyl. Background doping levels in the E14 cm^{-3} range had low 77K mobilities (13,000 $cm^2/v\text{-}s$) indicating compensated material have been reported [8]. The compensation was due to the presence of carbon in the layers .

The carbon is reportedly reduced when one switches from trimethylgallium (TMG) to triethylgallium (TEG) as their group III source. Less reactive C=C byproducts from the decomposition of TEG (beta-elimination) inhibit the incorporation af carbon impurity atoms more than the methyl radicals produced from the thermal decomposition of TMG (homolysis) [9].

diethylarsine

This group V substitute has been used effectively in the growth of gallium arsenide despite its very low vapor pressure (1 torr @ 18 degrees C.). Background concentrations at growth temperatures less than 580 degrees C. have been reported to be in the low E14

cm^{-3} range and shown to be n-type. Also, extremely low V/III ratios (as low as unity) have been reported. This is possibly due to the low pyrolysis temperature of diethylarsine (less than 500 degrees C.) [10]. Unfortunately, low deposition temperatures prevent growth of high purity, aluminum gallium arsenide. Uniform, high carrier gas flows over (multi) 3-4" wafers may be difficult to control due to the undesirably low vapor pressure. Finally, morphological problems have been reported at growth temperatures greater than 700 degrees C. [11]. The toxicity of diethylarsine is not known.

dimethylarsine

This compound has a convenient vapor pressure of 176 torr at 0 degrees C. Gallium arsenide epitaxial layers grown in an atmospheric MOCVD reactor yielded p-type results in the mid E15 cm^{-3} range. Carbon is the acceptor impurity from the methyl radical byproduct of trimethylgallium and/or dimethylarsine pyrolysis. N-type conversion occurs at high V/III ratios (greater than 60) making it less efficient than other replacement compounds. Carbon concentration is reported to decrease at lower growth rates and increase substrate misorientation [11].

At growth temperatures less than 630 degrees C., surface morphology deteriorates indicating either a high decomposition temperature or a non-optimal arsenic species for epitaxial growth [11].

phenylarsine

The vapor pressure of phenylarsine is less than adequate at 2 torr at room temperature. Experiments have shown that the thermal decomposition structure of this compound would assist in minimizing carbon contamination. This has been demonstrated using triethylgallium and phenylarsine. This combination has produced high purity gallium arsenide films 1E15 cm^{-3}, n-type, with mobilities of 38,000 cm^2/v-s at 77K. The V/III ratio was between 2 and 4 [12]. The toxicity of this material is not well known. It is expected to be less than that of arsine.

tertiarybutylarsine

Tertiarybutylarsine has been researched more extensively than any other group V substitute. This is, in part, due to vigorous marketing techniques by the sole manufacturer and distributor, American Cyanamid (currently purchased by Air Products). An objective view was, nevertheless, maintained when weighing its effectiveness against the other, less examined, replacement compounds.

The vapor pressure of tertiarybutylarsine (96 torr vapor pressure at 10 degrees C.) makes it a viable candidate for replacement of the group V hydride in the metalorganic chemical vapor deposition growth of gallium arsenide.

Due to the size of its carbon radical, tertiarybutylarsine is more thermally unstable than the trimethyl and triethyl group V compounds. Almost 25% of tertiarybutyl-arsine decomposes at temperatures less than 500 degrees C. Full decomposition occurs at 610 degrees C [13]. MESFETs have been grown using tertiarybutylarsine in a metalorganic

chemical vapor deposition reactor at 60 torr. The Ft and Fmax are comparable to arsine-grown material, as well as, material grown by molecular beam epitaxy [14].

In general, n-type background concentrations can be achieved in the mid E14 cm^{-3} range using tertiarybutylarsine and trimethylgallium grown under atmospheric conditions [15-17]. Although reports have indicated a need to use triethylgallium with tertiarybutylarsine in order to reduce carbon acceptor incorporation [15], atmospheric conditions with trimethylgallium can produce high purity gallium arsenide and aluminum gallium arsenide layers [16,17].

In addition to carrier concentrations and electron mobilities, luminescence properties of quantum well structures grown comparing arsine with tertiarybutylarsine. Trimethylgallium was used as the group III source and in both cases the electronic and optical properties were comparable. There is some concern that gas phase reactions between the trimethylgallium and tertiarybutylarsine results in a poor growth rate uniformity. However, this seems to be controlled by increasing the carrier gas flow through the reaction chamber [16].

(Prior to1990, publications indicated high unintentionally doped backgrounds in the E15/cc range. For microwave power devices, this was unacceptable. Both silicon and carbon were identified as the impurity. Better synthesis techniques allowed for lower impurity concentrations over time).

Modulation doped InAlAs/InAsP heterostructures grown in an atmospheric metalorganic chemical vapor deposition reactor demonstrated no difference between the arsine grown and the tertiarybutylarsine grown material. Variable temperature Hall-effect data, low temperature photoluminescence, and high magnetic field measurements were used to characterize the samples [18-21].

The toxicity of tertiarybutylarsine indicates an LC50 of approximately 70 ppm making it less hazardous than arsine (see table 1).

dimethylaminoarsenic

This compound has a workable vapor pressure of 10 torr at 55 degrees C. Preliminary data using trimethylgallium in a metalorganic chemical vapor deposition reactor indicate high carbon content. High purity films grown via metalorganic molecular beam epitaxy [22]. Dimethyl-aminoarsenic can yield gallium arsenide films with low carbon backgrounds [23], but at this time the levels are unacceptably high for microwave power devices.

dimethyl gallium di-tertiary butyl arsenide

This compound has been used in chemical beam epitaxy and metalorganic molecular beam epitaxy systems. Low carbon content is possible [24]. Insufficient data (in metalorganic chemical vapor deposition systems) at this time.

trifluoromethyl arsenic

Very acceptable vapor pressure of 115 torr at -10 degrees C. It has also been shown to be 100 times less toxic than arsine and 10 times less toxic than tertiarybutylarsine [24]. This low toxicity has created interest further exploration as a substitute chemistry. It is believed that the fluorine ions could present a problem with existing stainless steel plumbing, as well as, quartzware. Only speculated as a suitable replacement for arsine at this time.

electrochemical arsine generator

In this technique, an arsenic cathode, immersed in a potassium hydroxide electrolyte, is reduced supplying arsine to the growth chamber [25,26]. One drawback with this technique is moisture, a byproduct of the reaction. Molecular sieves and purifiers are necessary to achieve acceptable results. Low n-type background can be achieved, although aluminum gallium arsenide purity is more difficult. More problematic, however, is sustaining a consistent concentration of arsine over extended growth periods [27]. (This hydride generator "system" is offered commercially by Electron Transfer Technologies, Princeton, NJ and Advance Technologies Materials, Danbury, CT).

zeolite based storage system

This system is based on gas adsorption phenomenon into the microcavities of synthetic calcium zeolite beads [28]. This technique is designed to eliminate high pressure arsine gas cylinders (dilute concentrations), thus making it a safer alternative. Surface morphologies are acceptable, but compensated layers were reported. At this time, this appears to be an unlikely replacement for arsine.

potassium arsenide

By controlling the addition of water to the potassium arsenide, low pressure, high purity arsine can be generated. Gallium arsenide/aluminum gallium arsenide graded index separate confinement heterostructure (GRINSCH) single quantum well lasers were grown with this hydride generation technique [29]. The results are reported to be comparable to arsine grown metalorganic chemical vapor deposition material. Because arsine is generated, one has the toxicity problems associated with the hydride. An unlikely candidate for replacement at this time.

arsenic trichloride

Although this has been considered as a possible alternative, the chlorine produced in the reduction process etches the substrates (orentation dependant at temperatures less than 900 degrees C.) causing faceting and fish-scaling of the surface [30]. Also, the chloride creates contamination problems that effect purity. Finally, availablity is scarce. Because of these two reasons, arsenic trichloride was not further evaluated. (The halide-based gallium arsenide growth systems used arsenic trichloride extensively in the past).

III. RELATIVE COST ANALYSIS

Due to the low cost, arsine remains the choice source of arsenic for gallium arsenide growth. In this cost analysis, prices of three potential replacements are examined. The prices have been verbally quoted and are based on orders in the1 kilogram per year range. As a result of tertiarybutylarsine, monoethylarsine, and diethylarsine being more thermally unstable than arsine, higher cracking efficiencies can be expected.

Flow diagram 1 represents a typical scenario of arsine useage during a gallium arsenide epitaxial growth sequence.

ANNUAL USEAGE RATE:

ARSINE:(15 LBS./YEAR/REACTOR)(454 GRAMS/LBS.)=***6,810 GRAMS/YEAR***

6,810 GRAMS/78 GRAMS/MOL ARSINE = 87 MOLS ARSINE

on a 1:1 basis,

tertiarybutylarsine, (TBA):
(87 MOLS ARSINE)(134 GRAMS/MOL TBA) = ***11,650 GRAMS TBA***

diethylarsine, (DEA):
(87 MOLS ARSINE)(134 GRAMS/MOL DEA) = ***11,650 GRAMS DEA***

monoethylarsine, (MEA):
(87 MOLS ARSINE)(106 GRAMS/MOL MEA) = ***9,222 GRAMS MEA***

Gallium Arsenide GROWTH EFFICIENCY: GROUP V / GROUP III RATIO

ARSINE:	**25:1**
TBA:	***5:1***
MEA	***4:1***
DEA:	***2:1***

(11,650 GRAMS TBA)(5/25) = 2,330 GRAMS TBA/YEAR/REACTOR

(9,222 GRAMS MEA)(4/25) = 1,475 GRAMS MEA/ YEAR/REACTOR

(11,650 GRAMS DEA)(2/25) = 930 GRAMS DEA/YEAR/REACTOR

ANNUAL COST:

	unit cost	grams consumed	total cost
arsine	$0.95	6,810	$ 6,470
TBA	$15.00	2,330	$34,950
DEA	$ 25.00	930	$23,250
MEA	$25.00	1,475	$36,875

(Unit prices are expected to drop significantly once batch production is utilized and patent applications are arranged).

NOTE: When one examines the safety monitoring systems, maintenance, employee safety training, gas storage cabinets and associated safety manifolds, disposal costs, permits, and facility evacuations (lost production) that may occur when using arsine, the costs have been estimated to be as high as $300K [31].

(Other cost/benefit concepts that are being more and more utilized today are attempts to quantify the risks associated with continued use of arsine gas. Probability exposure analysis and "value on human life" surveys are recent methods that are being examined that may affect the user costs).

IV. SUMMARY

A direct input substitution methodology was the vehicle used in this toxics use reduction feasibility study. The objective was to research all reagents that have been used in gallium arsenide thin film growth (via metalorganic chemical vapor deposition, MOCVD) and suggest a suitable replacement chemistry for the highly toxic arsine gas. End-of-the-pipe solutions, such as exhaust gas detoxification by wet or dry chemical

scrubbing processes, were not considered. Such processes, however, are widely chosen as a way of handling toxic gases. An appropriate input substitution may not negate the use of effluent cleansing in a semiconductor facility. However, the associated costs such as: maintaining a scrubbing system, toxic hydride monitoring equipment, permits and insurance liability, and facility evacuations can be reduced.

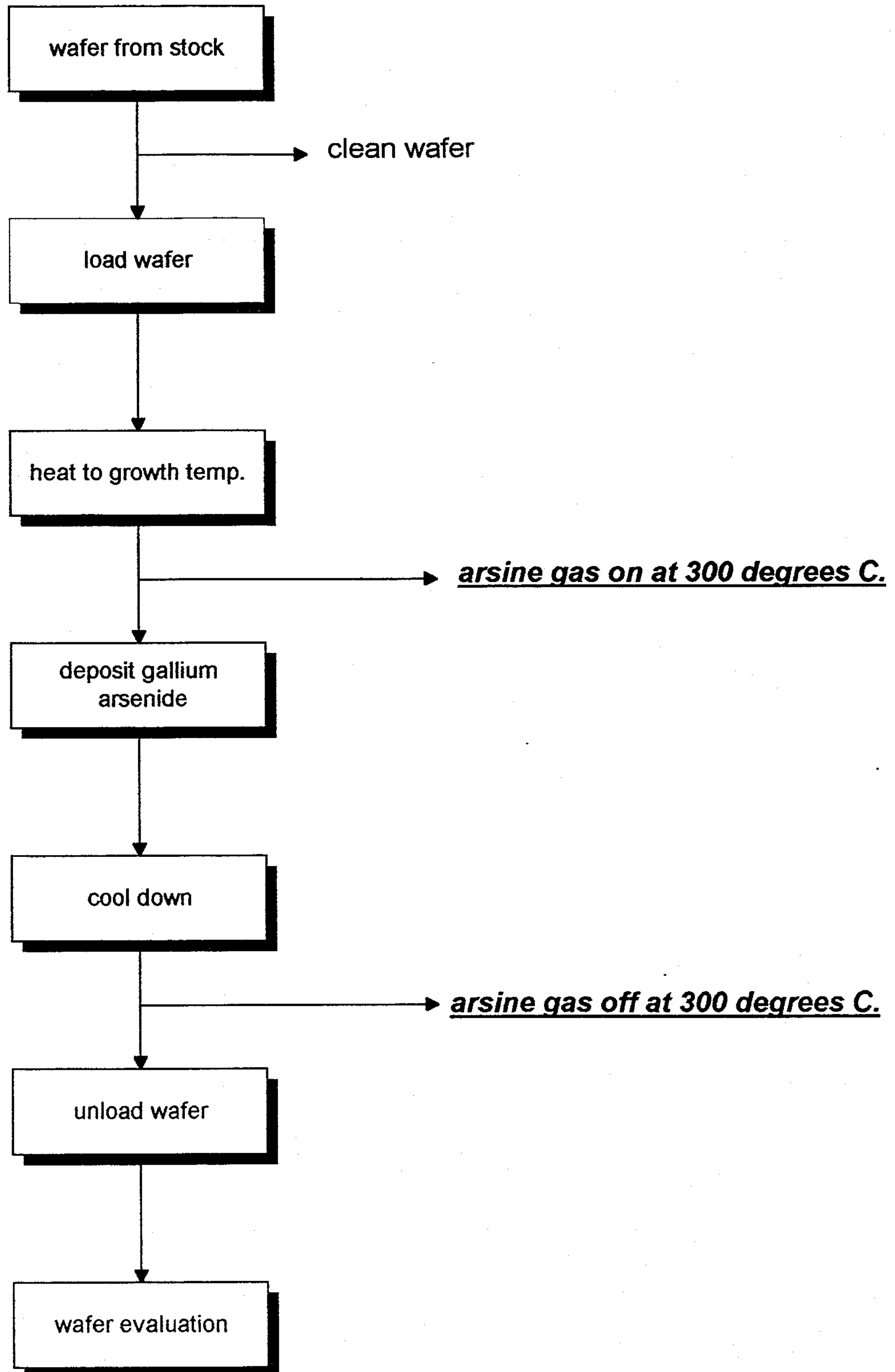
Their is no dispute that arsine is a highly toxic gas that requires skilled, technical people in its manufacturing, packaging, distribution, and use. In addition, arsine's thermal stability creates less efficient ratios of arsenic to gallium when growing gallium arsenide layers than with, for example, metal alkyl hydride replacement compounds. As a result, increased flow rates, excess oxide formation, and increased dependance on the combustion exhaust chamber and scrubbing system is realized.

At M/A-COM's Burlington Semiconductor facility, three substitute replacements can act as direct substitutes for arsine gas. They have been identified as tertiarybutylarsine (TBA), monoethylarsine (MEA), and diethylarsine (DEA). They all meet the acceptance criteria of low toxicity and thermal stability, workable vapor pressure, and packaged for direct replacement in existing MOCVD equipment. DEA has the least acceptable vapor pressure which makes it the least likely candidate. MEA is very attractive because it meets all the criteria in addition to being evaluated in an MOCVD reactor very similar to the production units at M/A-COM. This is offset by its present high cost.

The plethora of data demonstrating the use of TBA as a viable alternative to arsine makes it the most attractive alternative. The unit cost for TBA is the lowest of the three. This price has been quoted and full scale production is underway. Its final acceptabilty criterion was its reported ability to grow high purity gallium arsenide films for microwave power generation in reactors presently being utilized in production at M/A-COM.

The low cost of using arsine gas is still a major factor when exploring a direct substitute. Present costs are expected to drop significantly as demand increases. The associated costs of running arsine are already in place. However, California has already passed an ordinance restricting aspects of toxic gas use. Massachusetts has identified arsine as a toxic chemical of the use of which is to be reduced over the next several years. No legislation has been passed yet, but it appears to be coming soon. In conclusion, from an economic viewpoint, M/A-COM's use of arsine gas is the most cost effective. Close attention should be paid to the manufacturer's of all arsenic precursors as prices are expected to drop for the alternatives as quantities increase. In addition, new chemistries may become available that will rival the ones currently being evaluated. The ultimate arsine substitute may not have been identified yet. If a decision was to be made today, the reccommended alternative to arsine gas in the MOCVD of gallium arsenide would be tertiarybutylarsine.

PROCESS FLOW DIAGRAM FOR GROWTH OF GALLIUM ARSENIDE EPITAXIAL LAYERS



flow diagram 1.

table 1.

COMPOUND	carbon contamination	stability	vapor pressure	LC50
arsenic	2	2	1	solid
arsine	5	2	5	5 to 40 ppm
monoethylarsine	5	4	5	3000 ppm
trimethylarsenic	1	1	5	20,000 ppm
triethylarsine	1	2	3	1060 ppm
diethylarsine	3	5	?	???
dimethylarsine	1	2	5	130ppm
phenylarsine	4	4	1	???
tertiarybutylarsine	4	5	5	70 to 90 ppm
dimethylaminoarsenic	1	3	3	>500 ppm
dimethyl gallium di-tertiary butyl arsenide	3	?	?	???
trifluoromethyl arsenic	?	?	5	>500ppm
arsine generator	5	2	5	5 to 40
zeolite base	5	2	5	5 to 40
potassium arsenide	5	2	?	
arsenic trichloride	4	3	4	

1-unacceptable, 5-acceptable

adapted from Stringfellow, J. Electr. Mat., 17, Nov., 88

1. R Bhat, et al, J. Electron Materials *14*, 438, 1985
2. Tzeng, et al, J. Electrochem. Soc., *135*, 452, 1988
3. Tokumitsu, et al, J. Appl. Phys., *55*, 3163, 1984
4. Chu, et al, J. Electron Mat., *20*, 6, 1991
5. Speckman et al, Appl. Phys. Lett., Vol. 56, No. 12, 19, March, 1990
6. Lum, et al, J. Electron Mat., *17*, 101, 1988
7. Brauers, et al, J. Crys. Growth, *93*, 7-14, 1988
8. Lum, et al, Appl. Physics Letters, *52*, 1475, 1988
9. Speckman, et al, Appl. Physics Letters, *50*, 11, 1987
10. Bhat, et al, Appl. Physics Letters, *50*, 1194, 1987
11. Chen et al, J. of Crys. Growth, 96 (1989), 497-504
12. Brauers, et al, J Crys. Growth, *93*, 7-14, 1988
13. Kaul, et al, J. of Crys. Growth, *123*, 411-422, 1992
14. Mao, et al, IEEE Electron Device Letters, vol.11, No. 9, Sept., 1990
15. Material data from American Cyanamid publication, 1990
16. Hummel, et al, Appl. Physics Letters, *57*, 695, 1990
17. Kikkawa, et al, J. Appl Physics, *67*, 7576, 1990
18. Pan et al, Inst. Phys. Conf., Ser. No. 129: Chap. 3, paper presented at the Int. Symp. GaAs and Related Compounds, Karuizawa, 1992
19. Pan et al, Appl. Phys. Lett., 61, (21), Nov., 23, 1992
20. discussions with Noran Pan, Raytheon Research, Lexington, MA
21. Sundarum, et al, Appl. Physics Letters, *54*, 671, 1989
22. Material data from Air Products, 1991
23. Hovel, et al, J. Crys. Growth, *124*, 129-135, 1992
24. Muhr, et al, Chemtronics, 1989, Vol. 4, Marcmh
25. Valdes, et al, J. Electrochem. Soc., *138*, 1654, 1991
26. Buckley, et al, Appl. Phy. Letters, *57*, 1684, 1990
27. Burke, J. Crys. Growth, *124*, 292-299, 1992
28. Sillman, et al, Appl. Physics Letters, *56*, 174, 1990
29. Hummel, et al, Appl. Phys. Letters, *60*, 1483, 1992
30. Ghandhi, VLSI Fabrication Principles, John Wiley & Sons, copyright 1983
31. Material data and discussions with American Cyanamid