1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE 3. REPORT TYPE AND DATES COVERED
31 August 1996 Final 1 Jan 91 - 31 May 91

5. FUNDING NUMBERS
DAAL03-91-G-0153

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U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 28612.6-MS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. ABSTRACT (Maximum 200 words)
During the course of this ARO-funded project, we were able to make significant advances in the fundamental understanding and growth of phosphorous (P) containing compounds including indium phosphide (InP), gallium phosphide (GaP), and gallium indium phosphide (GalnP) using four new P precursors: TBP, BPE, TDMAP, and TBBDMAP. This work has resulted in: (1) further development of safe and improved sources specifically for chemical beam epitaxy (CBE); (2) determination of growth mechanisms involving the new source materials; and 3) significant improvements of the quality of phosphorous (P)-based compound materials grown by CBE while reducing human and environmental risks associated with the growth of these materials.

The main objective of this research was to improve the quality of P-containing III/V semiconductors grown by CBE using organometallic sources and to grow InP, GaP, and GalnP without thermally precracking the P source. Fundamental pyrolysis studies and the growth of InP, GaP, and GalnP using four alternative precursors TBP, BPE, TDMAP, and TBBDMAP was performed. The first reported growth of GalnP without precracking the phosphorous source, TDMAP, and the first reported growth of InP, GaP, and GalnP without precracking the phosphorous source, TBBDMAP were performed under this ARO-sponsored research.

14. SUBJECT TERMS
Chemical Beam Epitaxy, New Precursors, Phosphorus, GaP, InP, GalnP

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED

Enclosure 1

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102
NEW SOURCES FOR CHEMICAL BEAM EPITAXY

Final Report

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31 August 1996

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER 28612MS

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TABLE OF CONTENTS

ABSTRACT (FORM SF 298) ................................................................. I
TITLE PAGE .................................................................................. II
TABLE OF CONTENTS ................................................................. III
STATEMENT OF THE PROBLEM STUDIED .................................. 1
SUMMARY OF THE MOST IMPORTANT RESULTS ...................... 4
LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS .......... 6
LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL .......... 8
BIBLIOGRAPHY ........................................................................ 9
NEW SOURCES FOR CHEMICAL BEAM EPITAXY

STATEMENT OF THE PROBLEM STUDIED

Serious problems still exist with the CBE technique. A heavy concentration of effort needs to be given to the further development and testing of alternative (i.e., non-hydride), safer liquid organometallic group V sources designed specifically for the CBE growth technique. Although CBE has developed and matured somewhat over the last decade, an understanding of the chemical reactions occurring at the surface of the epitaxial layer is still lacking. There have recently been published reports of devices grown by CBE using TBP [1] however, no direct effort was devoted to understanding the cracker cell temperature, material and construction dependence on the phosphorous species used for growth. Typically, tertiarybutylphosphine (TBP) is cracked at very high temperatures such that P2 is the dominant phosphorous species. No convincing explanation of how P2 is formed has been reported in the literature. While this approach might be acceptable for applications involving TBP today, clearly there will come a point at which the CBE technique will be limited by a lack of understanding regarding precursor cracking and radical formation. An understanding of the growth process is also necessary in order to guide the selection of source molecules and to fully exploit the potential of CBE. This understanding is not trivial to obtain and we have made major inroads into developing a comprehensive picture of the P-precursor role in the CBE growth process.

The objective of the work funded by ARO was to make significant and substantial improvements in the CBE process for the growth of phosphorous-based III/V compound materials uncluding the possibility of growing InP without thermally precracking the phosphorous source. During the last few years, the limitations imposed on the CBE technique by a restricted choice of source molecules has begun to be realized. This has led to the development of new precursors and to the important realization that the design of the precursor molecules is an essential part of the design of the overall epitaxial process.

The design of precursor molecules rests partially on an understanding of the characteristics of organometallic molecules discovered over the last few decades. An
example of a useful rule is that the M-R bond strength decreases with an increase in the number of carbons bonded to the central carbon, i.e., the one forming a bond to the M atom. Thus, the temperature at which homolytic fission of the M-R bond occurs decreases in the order M-methyl, M-ethyl, M-t-butyl [2]. However, an additional important consideration is the nature of the pyrolysis and growth reactions occurring during the epitaxial growth process. In CBE, the group V precursors are normally cracked separately before entering the growth chamber. In order to understand the incorporation of carbon from the radicals into the solid, it is necessary to completely understand the pyrolysis pathways for both the cation and anion precursor molecules. It may not be sufficient to study the pyrolysis processes for the isolated precursors, since the pyrolysis processes are frequently coupled. In CBE, it is expected that the precursors travel from the inlet to substrate without collisions. However, our data acquired to date may indicate otherwise.

At present, phosphine (PH₃) is an attractive precursor since it provides H radicals on the surface leading to the removal of C-containing radicals that come from pyrolysis of the group III precursors. The atomic H causes a reduction of carbon incorporation into the solid. The main disadvantage of PH₃ is the extreme hazard associated with its use [2]. Additional problems are the high pyrolysis temperature for PH₃ and water contamination from the walls of the large steel cylinders in which it is frequently stored [3].

The hazard associated with the use of arsine and PH₃ provided the initial motivation for the development of liquid, organometallic group V precursors. However, development of less hazardous organometallic precursors has led to other advantages for CBE. For example, several of the newly developed sources pyrolyze at lower temperatures, as such they are suitable for lower temperature growth. The idea of designing special precursors to solve specific problems associated with the use of the group V hydrides for CBE is appealing and, eventually, will be mandatory.
The molecules must pyrolyze at the relatively low temperatures used for CBE growth. Artificially structured materials with features on the order of Angstroms in size are important for many device applications. These features may be blurred by diffusion at high growth temperatures. For CBE, we have developed P-precursors that do not require thermal precracking [4-6, 8-11]. This required developing molecules stable enough for purification and storage without decomposition which would pyrolyze during a single adsorption lifetime on the surface at the growth temperature.

Arsine and PH₃ are at the upper end of the acceptable range of stability. This leads to incomplete pyrolysis at normal growth temperatures, especially for PH₃. The M-R bond strength is decreased as the number of carbons bonded to the central carbon atom increases [2]. Thus, precursors with M-ethyl, M-isopropyl, and M-isobutyl bonds pyrolyze at similar temperatures, which are somewhat lower than for M-H and M-methyl bonds. Even weaker are the M-tbutyl bonds. Of course, the weakest bonds in a molecule are the first to break; thus, the pyrolysis temperature for TBP, with one P-t-butyl bond and 2 P-H bonds, is determined by the P-t butyl bond strength, which is several hundred degrees lower than for PH₃. The product of TBP pyrolysis should therefore be PH₂.

The requirement for high purity semiconductor layers imposes what is perhaps the least understood and most complex constraint on the group V sources. Since the very early CBE growth studies, carbon contamination has been a concern. As an example, for CBE growth of GaAs using TMGa, the simplest model for carbon incorporation is that CH₃ radicals adsorbed on the GaAs surface decompose, leading to carbon incorporation, unless H radicals from the group V precursor are also present on the surface. This leads to a simple consideration for the design of the group V precursor, namely that the molecule contain at least one M-H bond. Presumably, two M-H bonds would be better and three would be best. However, as we examine specific precursor molecules, it is found that this
rule is overly simple: The pyrolysis reactions occurring in the cracker cell determine which species arrive at the solid/vapor interface during growth.

We have studied the pyrolysis of tertiarybutylphosphine (TBP), trisdimeethylaminophosphine (TDMAP), and tertiarybutylbis(dimethylamino)phosphine (TBBDMAP) in an ersatz CBE reactor in detail [4-7]; the pyrolysis of these three precursors occurs at much lower temperatures than for PH₃.

SUMMARY OF THE MOST IMPORTANT RESULTS

During the course of this ARO-funded project, we were able to make significant advances in the fundamental understanding and growth of phosphorous (P) containing compounds including indium phosphide (InP), gallium phosphide (GaP), and gallium indium phosphide (GaInP) for the chemical beam epitaxy (CBE) technique using four new P precursors listed below. This work has resulted in: (1) substantial further development of safe and improved sources specifically for CBE; 2) determination of growth mechanisms involving the new source materials; and 3) significant improvements of the quality of phosphorous (P)-based compound materials grown by CBE while reducing human and environmental risks associated with the growth of these materials.

The main objective of this research was to improve the quality of P-containing III/V semiconductors grown by CBE using organometallic sources and to grow InP, GaP, and GaInP without thermally precracking the P source. The approach taken was to develop and test novel, much less hazardous group V precursors which also lead to improved material quality, in particular to lower background carbon contamination levels and lower cracker cell temperatures. This, by necessity, involved detailed and controlled experiments to elucidate the best growth conditions and techniques to produce material most suited to final device fabrication using the new precursors. Over the past four years we have put forth substantial effort to develop a clear physical understanding of the reactions occurring within
the CBE chamber during growth (such as the pyrolysis process and the role of hydrogen in hydrocarbon desorption from the substrate surface) so as to develop CBE into a technique that will provide a higher level of performance than is presently available.

This research project was designed to link fundamental advances in materials growth techniques utilizing safer sources to reduce environmental and personal safety concerns to improvements in material growth and flexibility. We were able to realize our ultimate goal for this project by growing InP, GaP, and GaInP without thermally cracking the P-precursor (TBBDMAP). This result is of major importance and provides significant direction and insight into making CBE a mature, cost-effective and environmentally safe materials growth technique.

In the last four years we have accomplished the following major tasks:
1) Design and construction of a custom CBE chamber and associated apparatus.
2)* Design and implementation of a completely novel cracker cell.
3) Design and construction of two ultrahigh vacuum (UHV) ersatz pyrolysis chambers.
4) Fundamental studies of the pyrolysis of four alternative precursors tertiarybutylphosphine (TBP), bisphosphinoethane (BPE), trisdimethylaminophosphine (TDMAP), and tertiarybutylbis(dimethylamino)phosphine (TBBDMAP)
5) Growth of InP, GaP, and GaInP using TBP, BPE, TDMAP and TBBDMAP.
6) The first reported growth of GaInP without precracking the phosphorous source, TDMAP.
7) The first reported growth of InP, GaP, and GaInP without precracking the phosphorous source, TBBDMAP.
8) The most detailed studies of TBP-grown InP and GaInP to date.
9) The most detailed study of BPE-grown InP to date.
10) Correlation of pyrolysis results of 4) with growth studies in 5) through 9). Obtain a one-to-one correspondence between our growth and cracker cell pyrolysis studies.
11) Growth optimization of InP and GaInP including the following parameters: substrate T, group-V cracker cell T, V/III source flow ratio, and group III flow rate.

12) Studied in detail the effect of cracker cell temperature on the residual impurity incorporation.

*This custom-designed cracker cell has been highly successful in growing InP, GaP, and GaInP by CBE and will cost less than $1K to commercially manufacture (compared to over $25K for present commercially available cracker cells). This work is important as there are still significant problems with commercially available cracker cell gas injectors. Degradation of the cell materials with use drastically reduces the functional lifetime of conventional, commercial CBE gas injectors. We have found that our fourth (Mark IV) generation cells do not suffer any measurable degradation in their functional integrity after a period of over six months of heavy use. We have also designed the cells so that they are extremely easy and inexpensive to repair.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

Accepted Publications


**Submitted Publications**

1. C.W. Kim, L.P. Sadwick, and G.B. Stringfellow, "Chemical Beam Epitaxial Growth of InP using EDMIn and TBP," submitted to *CHEMICAL VAPOR DEPOSITION*.


**Refereed Proceedings**


**Conference Presentations**


### LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

Dr. L.P. Sadwick, Associate Professor

Dr. G.B. Stringfellow, Professor

Three Graduate Students (Ph.D. degrees awarded as a result of work performed on this ARO project):

- Dr. ChungWoo Kim, Ph.D. MS&E Autumn 1995.
  Ph.D. Title: "Growth of InP by safe-source CBE," Ph.D. Advisor: L.P. Sadwick

- Dr. Hyukhyun Ryu, Ph.D. MS&E Spring 1996.

Dr. Christopher W. Hill, Ph.D. MS&E Spring 1996.
Ph.D. Title: "Low Pressure Pyrolysis Studies of Phosphorus Precursors for Chemical Beam Epitaxy," Ph.D. Advisor: G.B. Stringfellow.

BIBLIOGRAPHY


