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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 (GaInP) 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 GaInP without thermally precracking the P source. Fundamental pyrolysis studies and the growth of InP, GaP, and GaInP using four alternative precursors TBP, BPE, TDMAP, and TBBDMAP was performed. The first reported growth of GaInP without precracking the phosphorous source, TDMAP, and the first reported growth of InP, GaP, and GaInP without precracking the phosphorous source, TBBDMAP were performed under this ARO-sponsored research.				
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NEW SOURCES FOR CHEMICAL BEAM EPITAXY

Final Report

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U.S. ARMY RESEARCH OFFICE

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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 P_2 is the dominant phosphorous species. No convincing explanation of how P_2 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 including 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 (PH_3) 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 PH_3 is the extreme hazard associated with its use [2]. Additional problems are the high pyrolysis temperature for PH_3 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 PH_3 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 PH_3 are at the upper end of the acceptable range of stability. This leads to incomplete pyrolysis at normal growth temperatures, especially for PH_3 . 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-*t*butyl 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 PH_3 . The product of TBP pyrolysis should therefore be PH_2 .

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 CH_3 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), trisdimethylaminophosphine (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 PH_3 .

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). Obtained 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

1. H.H. Ryu, L.P. Sadwick, G.B. Stringfellow, T. Groshens, and R.W. Gedridge, Jr., "Chemical beam epitaxy of InP, GaP and GaInP using tertiarybutylbis(dimethylamino)phosphine without pre-cracking," accepted to *J. Electron. Mat.*
2. C. W. Hill, G. B. Stringfellow and L. P. Sadwick, "A Comparison of the Reactions of Phosphorus Precursors on Deposited GaP and InP Films," Accepted to *J. Cryst. Growth.*
3. H.H. Ryu, L.P. Sadwick, G.B. Stringfellow, T. Groshens, and R.W. Gedridge, Jr., "Chemical beam epitaxy of InP without precracking using tertiarybutylbis-(dimethylamino)phosphine," accepted to *J. Cryst. Growth.*
4. C.W. Hill, T.J Groshens, R.W. Gedridge, Jr., G.B. Stringfellow, and L.P. Sadwick, "Low-Pressure Pyrolysis Studies of a New Phosphorus Precursor: Tertiarybutylbisdimethylaminophosphine," Accepted to *J. Electron. Mater.*
5. C.W. Hill, G.B. Stringfellow and L.P. Sadwick, "Trisdimethylaminophosphorus, Reactions at Low Pressure on GaP, InP and Quartz Surfaces," Accepted to *J. Cryst. Growth.*
6. C.W. Kim, G.B. Stringfellow and L.P. Sadwick, "CBE Growth of InP using BPE and TBP: A Comparative Study," Accepted to *J. Cryst. Growth.*

7. C. Hill, L.P. Sadwick, and G.B. Stringfellow, "Pyrolysis of Tertiarybutylphosphine at Low Pressure," *J. Electron Mater.* vol. 24, p 731 (1995).
8. H.H. Ryu, G.B. Stringfellow, L.P. Sadwick, R.W. Gedridge, Jr., and A.C. Jones, "Chemical Beam Epitaxial Growth of GaInP using a Novel Group V source," Accepted to *Journal of Applied Physics*.

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*.
2. C.W. Kim, L.P. Sadwick, and G.B. Stringfellow, "Effects of the V/III Ratio and Cracker Cell Temperature on InP Grown by Chemical Beam Epitaxy using EDMIn and BPE," submitted to *J. Vac. Sci. Tech B*.
3. C.W. Kim, L.P. Sadwick, and G.B. Stringfellow, "Effects of V/III Ratio on the Quality of InP Grown by CBE using EDMIn and TBP," submitted to *J. Electron. Mat.*.
4. H.H. Ryu, L.P. Sadwick and G.B. Stringfellow, " Chemical beam epitaxial growth of GaInP using TBP, TIPGa and EDMIn," submitted to *J.Cryst. Growth*..
5. H.H. Ryu, G.B. Stringfellow, and L.P. Sadwick," Effects of cracker cell temperature and V/III ratio on GaInP grown by chemical beam epitaxy using TIPGa, EDMIn and TBP," submitted to *J.Vac. Sci Tech*.
6. C.W. Kim, L.P. Sadwick, and G.B. Stringfellow, "Chemical Beam Epitaxial Growth of InP using EDMIn and BPE," submitted to *J.Electron. Mat.*
7. C.W. Kim, L.P. Sadwick, and G.B. Stringfellow, "Influence of the Cracker Cell Temperature on the Quality of InP Grown by CBE using EDMIn and TBP," submitted to *J.Cryst. Growth*..

Refereed Proceedings

1. H.H. Ryu, C.W. Kim, L.P. Sadwick, G.B. Stringfellow, R. W. Gedridge, Jr., and A.C. Jones, "Growth of InP, GaP, and GaInP by Chemical Beam Epitaxy using Alternative Sources, Institute of Physics Conference Proceedings Series Number 141, Compound Semiconductors, p. 383, 1994.
2. L.P. Sadwick, C.W. Kim, H.H. Ryu, C.W. Hill, G.B. Stringfellow, R. W. Gedridge, Jr., and A.C. Jones, "Chemical Beam Epitaxial Growth of GaP and InP using Alternative, Safer Precursors," Compound Semiconductor Epitaxy, Materials Research Society Symposium Proceedings on Compound Semiconductor Epitaxy, Vol. 340, 1994, p.167.

Conference Presentations

1. H.H. Ryu, C.W. Hill, L.P. Sadwick, and G.B. Stringfellow, T. Groshens, R.W. Gedridge, Jr., and R. T. Lareau, "InP Grown By CBE Using Uncracked Tertiarybutylbisdimethylaminophosphine," *Electronic Materials Conference*, June 26-28, 1996, Santa Barbara, CA.

2. L.P.Sadwick, and G.B. Stringfellow, and H.H. Ryu, T. Groshens and R.W. Gedridge, Jr., and R. T. Lareau, "CBE Growth of InP, GaP, and GaInP using Uncracked Tertiarybutylbisdimethylaminophosphine - Implications for Conventional MBE," *Ninth International Conference On Molecular Beam Epitaxy*, August 5-9, 1996, Malibu, CA.
3. CBE R.W. Gedridge, Jr., L.P. Sadwick. G.B. Stringfellow, C.W. Hill, and C.R. Abernathy, " Invited Talk "Novel Organometallic Precursors for the CBE growth of InP-Based Semicondutor Materails," *Fifth International Chemical Beam Epitaxy Conference*, La Jolla, CA, August 13-16, 1995.
4. C.W. Kim, G.B. Stringfellow and L.P. Sadwick, "CBE Growth of InP using BPE and TBP: A Comparative Study," *Fifth International Chemical Beam Epitaxy Conference*, La Jolla, CA, August 13-16, 1995.
5. H.H. Ryu, C.W. Hill, G.B. Stringfellow, and L.P. Sadwick, and R.W. Gedridge, Jr., "GaInP Grown By CBE Using Uncracked Trisdimethylaminophosphine," *Electronic Materials Conference*, June 1995, Charlottesville, VA
6. H.H. Ryu, C.W. Kim, L.P. Sadwick, G.B. Stringfellow, R.W. Gedridge, Jr., and A.C. Jones, "Growth of InP, GaP, and GaInP by Chemical Beam Epitaxy using Alternative Sources, *21st International Symposium on Compound Semiconductors*, San Diego, CA, Sept. 19-23, 1994.
7. L.P. Sadwick, C.W. Kim, H.H. Ryu, C.W. Hill, G.B. Stringfellow, R. W. Gedridge, Jr., and , A.C. Jones, "Chemical Beam Epitaxial Growth of GaP and InP using Alternative, Safer Precursors," *MRS 1994 Spring Meeting Symposium E*, San Francisco CA, Apr. 4-8, 1994.
8. L.P. Sadwick, C. Hill, C.W. Kim, H.H. Ryu, and G.B. Stringfellow, "InP Growth by Chemical Beam Epitaxy using Safe Phosphorus Sources, *6th International Conference on Indium Phosphide and Related Materials Indium Phosphide and Related Materials*, Santa Barbara, CA, March 28-31, 1994.
9. L.P. Sadwick, C. Hill, C.W. Kim, H.H. Ryu, and G.B. Stringfellow, "Fundamental Pyrolysis Studies of Safe Phosphorus Precursors," *SPIE OE/LASE '94*, Los Angeles, CA, Jan. 22-25, 1994.

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.

Ph.D. Title: "Growth of InGaP by CBE using novel precursors," Ph.D. Advisor: L.P. Sadwick.

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.

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10. H.H. Ryu, L.P. Sadwick, G.B. Stringfellow, T. Groshens, and R.W. Gedridge, Jr., "Chemical beam epitaxy of InP without precracking using tertiarybutylbis-(dimethylamino)phosphine," accepted to *J.Cryst. Growth*.
11. H.H. Ryu, G.B. Stringfellow, L.P. Sadwick, R.W. Gedridge, Jr., and A.C. Jones, "Chemical Beam Epitaxial Growth of GaInP using a Novel Group V source," Accepted to *Journal of Applied Physics*.