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FINAL REPORT

USE OF D_2 TO ELUCIDATE OMVPE GROWTH MECHANISMS

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SUMMARY

The research during this project concentrated on two important areas of organometallic vapor phase epitaxial growth: 1) A study of the pyrolysis reactions and rates for five new antimony precursors trivinylantimony (TVSb), triisopropylantimony (TIPSb), triallylantimony (TASb), tertiarybutyldimethylantimony (TBDMSb), and diisopropylantimonyhydride (DIPSbH). They have been compared with the standard precursor, trimethylantimony (TMSb). The pyrolysis temperatures for both TIPSb, TASb, TBDMSb, and DIPSbH are all much lower than for TVSb, which is similar to TMSb. The pyrolysis mechanisms are surprisingly dissimilar. TVSb decomposes mainly via a reductive elimination mechanism. TASb decomposes by homolysis, while TIPSb pyrolyzes via homolysis and a β-elimination reaction. For TBDMSb, the pyrolysis mechanism is believed to be homolysis, followed by disproportionation reactions. For DIPSbH, the pyrolysis process is more complex, involving a reductive elimination reaction where one of the isopropyl radicals leaves, taking with it the H attached directly to the Sb. At high temperature, a beta-elimination reaction apparently occurs where the leaving group is isopropene. 2) The effect of adding tertiarybutyl radicals (from azo-t-butane pyrolysis) on the low temperature growth of GaAs using trimethylgallium (TMGa) and arsine. The pyrolysis of both precursors is stimulated by t-butyl radicals. The growth rate at 450°C is found to be enhanced by a factor of 6, giving good morphology layers. The properties of the layers were studied using X-ray diffraction, photoluminescence, and Raman spectroscopy.

The technique used for the pyrolysis studies is mass spectrometry with the pryolysis occurring in various ambients including H_2, He, and D_2. The latter allows labelling of reaction products involving interactions with the ambient.

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I. INTRODUCTION

This three year research project has produced the first systematic study of the pyrolysis and growth reactions for the wide range of antimony precursors used in atmospheric pressure OMVPE. In addition, the basic insights obtained from earlier studies on As precursors have been used to improve the low temperature growth of GaAs by adding tertiarybutyl radicals to the system. It shows considerable promise for wide-spread use, since low-temperature growth is desirable for a number of applications, including the currently popular growth of As-rich, semiinsulating GaAs. Two major features of the results stand out: 1) the reaction mechanisms are more complex than originally anticipated, and 2) a true picture of the complex reactions occurring can only be obtained by examining the entire range of precursors in the same apparatus using similar conditions and techniques.

The complexity of the reaction mechanisms has necessitated the development and use of a number of techniques, including: 1) isotopic labelling of the parent molecules, 2) use of a D_2 ambient to allow labelling of the reaction products, and 3) addition of radicals to the system using the azo compounds R_2N_2, which pyrolyze at low temperatures giving R radicals (either methyl, ethyl, or t-butyl) and inert N_2. By combining these tools, a reliable determination of the reaction mechanism can be made.

The results of this project have formed the basis of 13 talks at National and International conferences and 21completed papers. It is worth noting that 9 of the talks were invited, indicating the recognition by the scientific community of the significance of this research.

II. RESULTS

1. Pyrolysis of Antimony Precursors

A number of novel antimony sources, thought to be useful for low temperature OMVPE growth, have become available recently. The pyrolysis temperatures and mechanisms of a number of these precursors have been studied in an effort to evaluate their usefulness for OMVPE, particularly in terms of the vapor pressures, the pyrolysis temperatures, and the likelyhood of avoiding severe carbon contamination problems. The novel precursors, trivinylantimony (TVSb), triisopropylantimony (TIPSb), triallylantimony (TASb), tertiarybutyldimethylantimony (TBDMSb), and diisopropylantimonyhydride (DIPSbH) have been compared with the standard trimethylantimony (TMSb). The experimental results show that the pyrolysis temperatures for TIPSb is much lower than for TMSb. TBDMSb pyrolyzes at even lower temperatures, but the lowest pyrolysis temperatures were obtained for TASb and DIPSbH. In fact, these materials are so unstable that they may not be suitable for OMVPE because of the potential for pyrolysis in the bubbler during storage. The pyrolysis mechanisms for these five precursors are surprisingly dissimilar. TVSb decomposes mainly via a reductive elimination mechanism. TASb decomposes by homolysis, while TIPSb pyrolyzes via homolysis and a β-elimination reaction. For TBDMSb, the pyrolysis mechanism is believed to be homolysis, to form DMSb and tertiarybutyl radicals. This is followed by DMSb disproportionation reactions producing Sb and TMSb, which does not pyrolyze at low temperatures. For DIPSbH, the pyrolysis process is more complex, involving a reductive elimination reaction where one of the isopropyl radicals leaves, taking with it the H attached directly to the Sb. At high temperature, a beta-elimination reaction apparently occurs where the leaving group is isopropene.

These results appear to suggest that TIPSb, TBDMSb, and DIPSbH will all be suitable for OMVPE growth both in terms of the low pyrolysis temperature and the probability that layers with low carbon contamination levels will result. However, unexpectedly high carbon contamination levels were obtained for DIPSbH, possibly as a result of reactions with the In source, trimethylindium (TMIn). Thus, the most promising precursor is TBDMSb, followed by TIPSb.

2. Effects of Radicals on OMVPE Growth

The dramatic effects of radicals in the pyrolysis of common In, Ga, As, and P precursors suggests a novel technique for low temperature growth. In the past, the low temperature growth process has been stimulated using laser irradiation or plasma excitation. However, the ability to generate radicals at low temperature using azo compounds might also be useful. This hypothesis was tested by adding azo-t-butane (ATB) during the OMVPE growth of GaAs using trimethylgallium (TMGa) and arsine. The pyrolysis of both precursors is stimulated by t-butyl radicals. The low temperature growth rate is found to be enhanced. For example, at 450°C, the GaAs growth rate is increased by a factor of 6 by the addition of ATB to the system. The morphology of the resulting epitaxial layers of GaAs is also improved. X-ray diffraction, photoluminescence, and Raman spectroscopy have been used to demonstrate the quality of the resulting GaAs layers.

III. SUMMARY OF RESULTING TALKS AND PAPERS

TALKS (presented by G.B. Stringfellow unless noted)

1) G.B. Stringfellow, "New Sources for OMVPE", 10th Symposium on Alloy Semiconductor Physics and Electronics, July 18-19, 1991, Nagoya, Japan (Plenary Talk).

2) G.B. Stringfellow, "Fundamental Aspects of Vapor Growth and Epitaxy", 7th International Conference on Vapor Growth and Epitaxy, July 15-17, 1991, Nagoya, Japan (Plenary Talk).

3) **S.H. Li**, C.H. Chen, and G.B. Stringfellow, "Radical Assisted Organometallic Vapor Phase Epitaxy", 18th International Symposium on Gallium Arsenide and Related Compounds, Seattle, September, 1991.

4) **D.S. Cao**, Z.M. Fang, and G.B. Stringfellow, OMVPE Growth of AlGaSb and AlGaAsSb, Electronic Materials Conference, Boulder, June 1991.

5) S.H. Li, C.A. Larsen, and G.B. Stringfellow, Pyrolysis Studies of Novel Sb Precursors, Fifth Workshop on Organometallic Vapor Phase Epitaxy, Panama City, Florida, April, 1991.

6) **S.H. Li** and G.B. Stringfellow, Monoethylarsine Pyrolysis Mechanisms - Alone and with Trimethylgallium, Electronic Materials Conference, Boulder, CO, June 1991.

7) G.B. Stringfellow, Novel Precursors for Organometallic Vapor Phase Epitaxy, 10th International Conference on Crystal Growth, San Diego, CA, August 16-22, 1992. (Invited Talk).

8) G.B. Stringfellow, Organometallic Vapor Phase Epitaxy, International Crystal Growth Summer School, Palm Springs, CA, August 9-14, 1992. (Invited Talk).

9) G.B. Stringfellow, Thermodynamic & Kinetic Aspects of III-V Epitaxy, Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, Valais, Switzerland, March 15-21, 1992. (Invited Talk).

10) G.B. Stringfellow, Comparison of Epitaxial Techniques for III-V Layer Structures, Croissance de cristaux et de couches epitaxiales a applications electroniques et optiques, Valais, Switzerland, March 15-21, 1992. (Invited Talk).

11) G.B. Stringfellow, CVD Growth With Novel Precursors, 1992 Gordon Research Conference, The Chemistry of Electronic Materials, Ventura, CA, 2-6 March 1992. (Invited Talk).

12) G.B. Stringfellow, Fundamentals of Thin Film Growth, American Conference on Crystal Growth, Baltimore, 1-6 August, 1993.(Plenary Talk).

13) G.B. Stringfellow, OMVPE Growth of III/V Alloys Using Novel Antimony Precursors, Workshop on Antimonide Materials Chemistry and Growth, February 28-March 1, 1994, Austin Texas. (Invited Talk).

PAPERS (Publications in Peer-reviewed Professional Journals and Refereed Book Chapters during the period 30 November 1990 through 30 April 1994 supported (and acknowledged) by AFOSR funds.

1) S.H. Li, C.H. Chen, and G.B. Stringfellow, Radical Assisted Organometallic Vapor Phase Epitaxy, in *Gallium Arsenide and Related Compounds, 1991* ed. G.B. Stringfellow (The Institute of Physics, Bristol)(1991) pp. 553-558.

2) G.B. Stringfellow, New Sources for OMVPE, Record of the Semiconductor Physics and Electronics Symposium, Nagoya, Japan, (1991).

3) G.B. Stringfellow, Fundamental Aspects of Vapor Growth and Epitaxy, J. Crystal Growth **115** 1 (1991).

4) S.H. Li, C.H. Chen, D.H. Jaw, D.H. , and G.B. Stringfellow, Radical-Assisted OMVPE Growth of GaAs, Appl. Phys. Lett. **59** 2124 (1991).

5) D.S. Cao,Z.M. Fang, and G.B. Stringfellow, OMVPE Growth of AlGaSb and AlGaAsSb, J. Crystal Growth **113** 441 (1991).

6) S.H. Li, R.W. Gedridge, and G.B. Stringfellow, Decomposition Studies of Triisopropylantimony and Triallylantimony, J. Electron. Mater. **20** 457 (1991).

7) C.A. Larsen, R.W. Gedridge, S.H. Li, and G.B. Stringfellow, Decomposition Mechanisms of Antimony Source Compounds for OMVPE , *Chemical Perspectives of Microelectronic Materials - II* (Materials Research Society, Pittsburg, Penn, 1991), pp. 129-134.

8) S.H. Li, C.A. Larsen, and G.B. Stringfellow, Monoethylarsine Pyrolysis Alone and with Trimethylarsine, J. Electron. Mater. **20**, 187 (1991). (won JEM outstanding student paper award for 1991).

9) S.H. Li,C.A. Larsen, and G.B. Stringfellow, Radical Reactions in Pyrolysis of Triethylarsine and Diethylarsine, J. Crystal Growth **112**, 515 (1991).

10) C.A. Larsen, R.W. Gedridge, and G.B. Stringfellow, Decomposition Mechanisms of TVSb and Reactions with TMGa, Chemistry of Materials **3**, 96 (1991).

11) G.B. Stringfellow, Mechanistic Study of Organometallic Vapor Phase Epitaxy, in *Epitaxial Crystal Growth* , ed. E. Lendvay (Trans Tech Publications, Zurich, 1991).

12) S.H. Li, C.A. Larsen, and G.B. Stringfellow, Comparative Pyrolysis Study of Ethylarsines, J. Crystal Growth **107**, 32 (1991).

13) C.A. Larsen, S.H. Li, and G.B. Stringfellow, Decomposition Mechanisms of Trimethylantimony and Reactions with Trimethylindium, Chemistry of Materials **3**, 39 (1991).

14) G.B. Stringfellow, Novel Precursors for Organometallic Vapor Phase Epitaxy, J. Crystal Growth **128**, 503 (1993).

15) D.S. Cao, C.H. Chen, C.W. Hill, S.H. Li, G.B. Stringfellow, D.C. Gordon, D.W. Brown, and B.A. Vaartstra, Decomposition Studies of Tertiarybutyldimethylantimony, J. Electron. Mater. **21** 583 (1992).

16) G.B. Stringfellow, Basic Principles of Organometallic Vapor Phase Epitaxy, Proceedings of International Summer School on Crystal Growth (to be published).

17) G.B. Stringfellow, Comparison of Epitaxial Growth Techniques for III/V Layer Structures, Crystal Growth and Epitaxy, ed. H.J. Scheel, pp. 241-254, 1993.

18) G.B. Stringfellow, Thermodynamic and Kinetic Aspects of III/V Epitaxy, Crystal Growth and Epitaxy, ed. H.J. Scheel, pp. 225-239, 1993.

19) G.B. Stringfellow, Novel Precursors for Organometallic Vapor Phase Epitaxial Growth, J. Crystal Growth, Vol 128, pp. 503-510, 1993.

20) G.B. Stringfellow, Fundamentals of Thin Film Growth, J. Crystal Growth **137**, 212 (1994).

21) G.B. Stringfellow, OMVPE Reaction Kinetics, Chapter in Handbook of Crystal Growth, ed. D. Hurle (Elsevier, Amsterdam) (Invited Chapter, to be published).

IV. STUDENTS SUPPORTED AND GRADUATED

1. S.H. Li -- PhD, MSE, June 1991.
2. D.S. Cao -- PhD, MSE, March 1991.
3. Chris Hill -- PhD, MSE, Not yet complete.
4. Y.S. Chun -- PhD,MSE, Not yet complete.

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Stringfellow, G.B., Selected to appear in *Who's Who in America,* 47th edition, 1992.
Stringfellow, G.B., Selected to appear in *Who's Who in the World,* 11th edition, 1992.
Stringfellow, G.B., Paper Selected for Inclusion in "A Perspective on Crystal Growth", An Historical Collection of 25 Papers in Celebration of 25 Years of the Journal of Crystal Growth, 1992.
Stringfellow, G.B., Editor, Proceedings of 6th International Conference on Metal Organic Vapor Phase Epitaxy, 1992.
Stringfellow, G.B., Editor, Proceedings of 18th International Symposium on GaAs and Related Compounds, 1992.
Stringfellow, G.B., Editor, Phase Equilibrium Diagrams: Semiconductors and Chalcogenides (American Ceramic Society, Westerville, Ohio, 1992).
Li, S.H., Selected for Annual Outstanding Paper Award for the Journal of Electronic Materials, 1991 -- for his paper entitled "Monoethylarsine Pyrolysis Mechanisms - Alone and with Trimethylgallium" (paper #8, above).

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The research concentrated on two important areas of organometallic vapor phase epitaxial growth: 1) A study of the pyrolysis reactions and rates for five new antimony precursors: trivinylantimony (TVSb), triisopropylantimony (TIPSb), triallylantimony (TASb), tertiary-butyldimethyl-antimony (TBDMSb), and diisopropylantimonyhydride (DIPSbH). They have been compared with the standard precursor, trimethylantimony (TMSb). The pyrolysis temperatures for TIPSb, TASb, TBDMSb, and DIPSbH are all much lower than for TVSb, which is similar to TMSb. The pyrolysis mechanisms are surprisingly dissimilar. 2) The effect of adding tertiarybutyl radicals (from azo-t-butane pyrolysis) on the low temperature growth of GaAs using trimethylgallium (TMGa) and arsine. The pyrolysis of both precursors is stimulated by t-butyl radicals. The growth rate at 450°C is found to be enhanced by a factor of 6, giving good morphology layers. The properties of the layers were studied using X-ray diffraction, photoluminescence, and Raman spectroscopy.

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