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6. AUTHOR(S)
Thomas F. Kuech
Kevin L. Bray

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dept. of Chemical Engineering
University of Wisconsin
1415 ENGINEERING DR.
MADISON, WI 53706

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13. ABSTRACT *(Maximum 200 words)*

The controlled introduction of oxygen into GaAs and $In_xGa_{1-x}As$ during metal organic vapor phase epitaxy was studied through the development of unique oxygen doping sources. The electrical, optical and other deep level properties of the GaAs:O defect were studied over an oxygen concentration range of 10^{16} to 10^{20} cm^{-3}. Oxygen introduces several levels into the band gap of GaAs leading to the compensation of the electrically active shallow dopants and a reduction in the band edge photoluminescence. High resistivity GaAs films can be produced using oxygen doping with resistivities in excess of 10^9 Ω•cm indicating that this material can be one of the most effective device isolation materials yet developed. Since this process is easily integrated into the existing MOVPE growth technology, high resistivity layers can be made part of the device structure. The immediate application of these materials could be in microwave devices where the high resistivity of the materials can be used to eliminate the device crosstalk which can diminish the performance of these circuits. High power electronic devices and higher performance optical detectors may also be possible.

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METAL-ORGANIC VAPOR PHASE EPITAXY OF CONTROLLED DEEP LEVEL STRUCTURES

Final Report

Thomas F. Kuech
Kevin L. Bray

Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin

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U.S. Army Research Office

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Foreword

Chemical impurities, such as oxygen, have a major impact on the performance and lifetime of modern heterostructure devices. These devices have widespread use in areas such as microwave and optical communications, optical recording and light detection. Many of these impurities originate as contaminants in the growth system used to form these materials. Oxygen is perhaps the most common and the most important of these impurities. In particular, oxygen is thought to be responsible for the degradation of solid state lasers. Metal-organic vapor phase epitaxy (MOVPE) is one of the major growth techniques used in both research and manufacturing of these devices. A problem encountered in the study of these important impurities, and the electronic defects they produce, is the lack of a systematic means of incorporation. Through the development of new chemical sources, we have been able to controllably incorporate oxygen in order to fully understand its behavior and subsequent impact on device performance. The incorporation of oxygen into GaAs introduces several electronic defect states. The electronic and optical properties of these states yields information on the local structure and chemistry of the defect. An intriguing outcome of these studies is the development of a means to introduce levels of oxygen into semiconductors at concentrations which far exceed their equilibrium solid solubility. These highly doped structures have interesting properties in their own right. The incorporated oxygen, as a deep level, acts as a sink for electronic carriers. Controlled oxygen doping is a means by which the extremely high resistivity materials can be produced in thin layer form. We have recently determined the resistivity of these high oxygen concentration films. Resistivities in excess of 10^9 Ω•cm can be produced indicating that this material can be one of the most effective device isolation materials yet developed. Since this process is easily integrated into the existing MOVPE growth technology, high resistivity layers can be made part of the device structure. The immediate application of these materials could be in microwave devices where the high resistivity of the materials can be used to eliminate the device crosstalk which can diminish the performance of these circuits. High power electronic devices and higher performance optical detectors may also be possible.

Summary of Important Results

1. Development of $(C_2H_5)_2AlOC_2H_5$ as a Controlled Oxygen Source

A new oxygen source was developed during the grant period. The diethyl aluminum ethoxide, (Et_2AlOEt, or $(C_2H_5)_2AlOC_2H_5$), was used in the successful oxygen doping of GaAs. This source may have advantages over the previously employed dimethyl aluminum alkoxide, (Me_2AlOMe or $(CH_3)_2AlOCH_3$). This new source has a lower vapor pressure than Me_2AlOMe which is useful in introducing the small dopant concentration of the compound into the gas phase during growth. Additionally, the Et_2AlOEt is a liquid at room temperature in contrast to the solid source Me_2AlOMe. The liquid source should leads to the enhanced reproducibility of the oxygen introduction into the epitaxial layer.

2. Incorporation of Oxygen into Epitaxial GaAs

The oxygen introduction into the growing GaAs has been shown to be a strong function of growth temperature and gas phase ratio of AsH_3 /$(CH_3)_3Ga$, the As and Ga growth precursors. The oxygen incorporation decreases exponentially with increasing growth temperature and exhibits a power law type decrease with increasing V/III ratio. Under all conditions, the incorporated oxygen was found to compensate any intentionally introduced shallow donors, such as Si, through the formation of Al_x-O or isolated O deep level complexes. Comparison of carrier concentration profiles in the epitaxial layers with secondary ion mass spectroscopic profiles indicates that the drop in carrier concentration is on the order of the oxygen incorporation.

3. Deep Level Transient Spectroscopy Measurements of the Oxygen Level in Epitaxial GaAs

Deep level transient spectroscopy (DLTS) measurements of the compensated materials have found that the concentration of deep levels in the upper half of the band gap, which is accessible through the use of Schottky barrier structures, is far less than the indicated loss of carriers. This interesting observation indicates that the oxygen deep level responsible for the compensation is most probably in the lower half of the GaAs band gap. Oxygen doping in GaAs using DEALO was found to compensate both shallow donors and acceptors. Multiple deep level peaks were observed, and the relative peak heights were found to vary with the dopant concentrations. This observation implies that there are multiple 'M-O', where M=Ga or Al, configurations in the GaAs:O based films. We have identified for the first time a Si-O based defect in GaAs which we have tentatively assigned to the deepest DLTS peak. These studies indicate that the oxygen based defect in GaAs and related materials can form a family of defect structures in comparable concentrations, dominated by emission peaks at ~0.75 and ~0.9 eV.

4. Luminescence Properties of GaAs:O

Photoluminescence (PL) studies of GaAs:O have been completed. The PL from samples, containing oxygen concentrations ranging from 10^{16} cm^{-3} to 10^{20} cm^{-3}, has been measured as a function of temperature. The near-IR PL spectra exhibited broad discernible bands located at approximately 0.8 eV and 1.07 eV. The lower energy band position was approximately independent of oxygen concentration. Pronounced intensity effects were noticed as the oxygen concentration was varied at a given temperature. In samples with [O] $\sim 10^{16}$ cm^{-3}, the 12 K PL spectrum consisted of a dominant band at 1.10 eV and only a very weak band at the lower energy. As the oxygen concentration was increased, the 12K PL intensity of the higher energy band continuously decreased relative to the lower energy band until, in samples with [O] $\sim 10^{20}$ cm^{-3}, the lower energy band was the dominant feature in the PL spectrum. Pronounced intensity effects were noticed as the temperature was varied at a given oxygen concentration. Complete quenching of all photoluminescence was observed at temperatures above ~150 K for all samples.

5. Semi-insulating GaAs:O Resistivity Determination

The resistivity of the DEALO-doped GaAs is extremely high. We have determined the temperature dependent resistivity in these materials through n-i-n vertical transport test structures. Resistivities of more than 2×10^9 Ω-cm at 294 K have been determined from the ohmic region of current-voltage (I-V) curves. An activation energy of ~0.81 eV was deduced from temperature-dependent resistivity measurement. This activation energy is closely related to the dominant deep level emission peaks as determined by DLTS. These resistivities are suitable for potential use the incorporation of these materials into GaAs-based structures, such as MESFETs and thyristors.

6. Oxygen Doping of $In_xGa_{1-x}As$

The defect engineering in MOVPE $In_xGa_{1-x}As$ and InP by controlled oxygen doping using DEALO was studied. DEALO doping has led to the incorporation of Al and O, and the compensation of shallow Si donors in $In_xGa_{1-x}As$:Si with $0 \leq x \leq 0.25$. With the same DEALO mole fraction during growth, the incorporation of Al and O was found to be independent of x, but the degree of carrier compensation was smaller at larger x. DLTS investigation on a series of $In_xGa_{1-x}As$:Si:O samples with $0 \leq x \leq 0.18$ showed that oxygen incorporation led to a set of deep levels, similar to those found in DEALO doped GaAs. The characteristic deep levels appeared to remain at a relatively constant energy with respect to the valence band of the $In_xGa_{1-x}As$. As the In mole fraction was increased, one or more of these deep levels became resonant with the conduction band, and led to a high electron concentration in oxygen doped $In_{0.53}Ga_{0.47}As$. Low temperature PL at 12 K on the same set of samples revealed the quenching of the near-band edge peak, and the appearance of new oxygen-induced emission features. DEALO doping in InP has also led to the incorporation of Al and O, and the compensation of Si donors as well as the reduction of PL intensity due to oxygen-induced multiple deep levels. It was also found that the use of DEALO during the growth of high In content materials (such as InP or $In_{0.53}Ga_{0.47}As$) tends to degrade surface morphology, resulting in a hazy surface finish.

7. High Pressure Characterization of GaAs:O

High pressure-low temperature photoluminescence experiments were carried out on GaAs:O. The goal of these experiments will be to elucidate the relationship of the oxygen-related deep levels in epitaxial GaAs:O to the band structure. The ambient pressure spectrum shows the two near-IR PL bands (~0.8 eV and ~1.1 eV) characteristic of oxygen in epitaxial GaAs. Upon application of pressure, both bands shift to higher energy. The larger shift of the higher energy band (~8.9 meV/kbar) compared to the lower energy band (~2.3 meV/kbar) leads to better resolution of the initially overlapped peaks (e.g. 11 kbar spectrum). At pressures above ~25 kbar, both PL bands begin to quench and a new band appears at ~0.6 eV. The new band continues to grow and the original bands continue to quench as the pressure is raised further. Above ~30 kbar, the original bands are completely quenched and the new band persists and shifts at a rate of 2.5 meV/kbar to higher energy. The new band gains intensity up ~40-45 kbar, levels off and then begins to quench at ~55 kbar. Complete quenching of the new band occurs by ~80-85 kbar. The pressure shift results suggest that the ~1.1 eV PL transition is associated with the conduction band while the ~0.8 eV transition is associated with the valence band or an internal transition of the oxygen-related defect. The results also indicate the presence of a resonant oxygen-related state located ~200 meV above the conduction band edge at ambient pressure. The state is present in the band gap between ~25 and ~80 kbar and is responsible for a 0.6 eV luminescence band.

8. Device Applications of GaAs:O

The short radiative lifetime of GaAs:O allows it to serve as a useful high speed detector material. We have been interacting with the Naval Research Laboratory (NRL) in the area of materials characterization and applications. NRL (M. Frankel) has measured very short lifetimes (<1 ps) for highly oxygen doped GaAs. These measurements indicate that GaAs:O could be used as an integrable material for high speed detection at wavelengths shorter than ~850-nm. The high resistivity of GaAs:O was investigated through collaboration with K. Jones at the Army laboratory at Fort Monmouth. There is a device need for very high resistivity layers which can be integrated into an optical thyristor structure. The current technology requires very thick layers in order to stand off the required voltage. We are collaborating with Dr. Kenneth Jones on a project which will determine if these materials are suitable for these Army applications.

List of Publications, Technical Reports and Technical Presentations

Publications

1. "Chemical and physical effects in oxygen incorporation during the metalorganic vapor phase epitaxial growth of GaAs", by T. F. Kuech, S. Nayak, J. W. Huang, and J. Li, to be published in J. Cryst. Growth.
2. "Influence of oxygen on surface morphology of metalorganic vapor phase epitaxy grown GaAs (001)", by S, Nayak, J. W. Huang, J. M. Redwing, D. E. Savage, M. G. Lagally, and T. F. Kuech, to be published in Appl. Phys. Lett.
3. "Controlled oxygen incorporation in indium gallium arsenide and indium phosphide grown by metalorganic vapor phase epitaxy", by J. W. Huang, J. M. Ryan, K. L. Bray, and T. F. Kuech, to be published in J. Electron. Mater.
4. "Oxygen-based deep levels in metalorganic vapor phase epitaxy indium gallium arsenide", by J. W. Huang, T. F. Kuech, and T. J. Anderson, to be published in Appl. Phys. Lett.
5. "Intentional defect incorporation in metalorganic vapor phase epitaxy indium gallium arsenide by oxygen doping", by J. W Huang and T. F. Kuech, to be published in Mat. Res. Soc. Symp. Proc. **378** (1995).
6. "Ultrafast photodetector materials based on oxygen-doped metalorganic vapor phase epitaxy GaAs ", by M. Y. Frankel, J. W Huang, and T. F. Kuech, Appl. Phys. Lett. **66** (1995) 634.
7. "Electrical characterization of semi-insulating metalorganic vapor phase epitaxy GaAs Grown by Controlled Oxygen Incorporation ", by J. W Huang and T. F. Kuech, J. Cryst. Growth **145** (1994) 462.
8. "Multiple deep levels in metalorganic vapor phase epitaxy GaAs grown by controlled oxygen incorporation", by J. W Huang and T. F. Kuech, Appl. Phys. Lett. **65** (1994) 604.
9. "The effect of temperature and oxygen concentration on the photoluminescence of epitaxial metalorganic vapor phase epitaxy GaAs:O", by J. M. Ryan, J. W Huang, T. F. Kuech, and K. L. Bray, J. Appl. Phys. **76** (1994) 1175.
10. "Controlled impurity introduction in CVD : chemical, electrical, and morphological influences", by T. F. Kuech, J. M. Redwing, J. W. Huang, and S. Nayak, Mat. Res. Soc. Symp. Proc. **334** (1994) 189.

11. "Deep level structure of semi-insulating MOVPE GaAs grown by controlled oxygen incorporation", by J. W Huang and T. F. Kuech, Mat. Res. Soc. Symp. Proc. **325** (1994) 305.

12. "Alkoxide precursors for controlled oxygen incorporation during metalorganic vapor phase epitaxy GaAs and $Al_xGa_{1-x}As$ growth", by J. W Huang, D. F. Gaines, T. F. Kuech, R. M. Potemski, and F. Cardone, J. Electron. Mater. **23** (1994) 659.

Technical Reports

Technical Reports associated with this grant submitted Jan. of 1993, 1994, and 1995.

Technical Presentations

1. **Invited,** “Chemical and Physical Effects in Impurity Incorporation in GaAs Growth”, T.F. Kuech, Japan-US Joint Workshop on Atomic Scale Mechanisms of Epitaxial Growth, Honolulu, HA, May 10-12, 1995.

2. "Similarities in the Photoluminescence Properties of Oxygen-doped GaAs and Nominally Undoped AlGaAs", Ryan, M.J.; Huang, J.W.; Kuech, T.F.; Bray, K.L.; 1995 Electronic Materials Conference, June 21-23, 1995, Charlottesville, VA.

3. "High Pressure Study of the Photoluminescence of Oxygen-doped MOVPE GaAs", Ryan, J.M., Huang, J.W., Kuech, T.F., Bray, K.L., American Physical Society National Meeting, March 20-24, 1995; San Jose, CA.

4. "Oxygen-based deep levels incorporation in metalorganic vapor phase epitaxy InP", by J. W Huang, J. Li, and T. F. Kuech, presented at the 1995 EMC, Charlottesville, VA, 1995.

5. “Growth and characterization of metalorganic vapor phase epitaxy $In_xGa_{1-x}As$ with controlled oxygen incorporation”, by J. W Huang and T. F. Kuech, presented at ICCG-XI, Hague, the Netherlands, 1995.

6. “Intentional defect incorporation in metalorganic vapor phase epitaxy $In_xGa_{1-x}As$ by oxygen doping”, by J. W Huang and T. F. Kuech, presented at the 1995 MRS Spring Meeting, San Francisco, CA, 1995.

7. “Controlled oxygen incorporation in $In_xGa_{1-x}As$ and InP grown by metalorganic vapor phase epitaxy”, by J. W Huang, J. M. Ryan, K. L. Bray, and T. F. Kuech, presented at the 7th biennial workshop on OMVPE, Fort Meyers, FL, 1995.

8. "Deep level characteristics of MOVPE GaAs grown by controlled oxygen incorporation", by J. W Huang, T. F. Kuech, and M. Y. Frankel, presented at the 1994 EMC, Boulder, CO, 1994.

9. "Electrical characterization of semi-insulating MOVPE GaAs grown by controlled oxygen incorporation", by J. W Huang and T. F. Kuech, presented at ICMOVPE VII, Yokohama, Japan, 1994.

10. **Invited,** "Epitaxial Growth and Impurity Behavior", T.F.Kuech, Emory University, Physics Department Seminar, Jan. 21, 1994.

11. **Invited,** "Oxygen in GaAs: Growth, Impurity Behavior, and Applications", T.F.Kuech, State University of New York at Buffalo, April 18, 1994.

12. "The effect of temperature and oxygen concentration on the photoluminescence of epitaxial metalorganic vapor phase epitaxy GaAs:O", by J. M. Ryan, J. W Huang, T. F. Kuech, and K. L. Bray, presented at 1994 APS March Meeting, Pittsburgh, PA, 1994.

13. **Invited,** "Chemical and Physical Effects in Impurity Incorporation in GaAs", T.F. Kuech, American Chemical Society Meeting, Aug. 23-24, 1994, Washington, DC.

14. **Invited,** Kinetic and Growth Studies of Doping and Growth Precursors", T. F. Kuech, , *Twelfth International Conference on Chemical Vapor Deposition*, 183rd Meeting of the Electrochemical Society, Hawaii, May 16-21, 1993.

15. **Invited,** "Controlled Impurity Introduction in CVD: Chemical, Electrical and Morphological Influences", T.F.Kuech, , Materials Research Society Meeting, Boston, MA, December 1-5, 1993.

16. "Deep level structure of semi-insulating MOVPE GaAs grown by controlled oxygen incorporation", by J. W Huang and T. F. Kuech, presented at 1993 MRS Fall Meeting, Boston, MA, 1993.

17. "Alternative aluminum alkoxide precursors for controlled oxygen incorporation in MOVPE GaAs: growth and chemistry", by J. W Huang, D. F. Gaines, T. F. Kuech, R. M. Potemski, and F. Cardone, presented at ACCG-10, Baltimore, MD, 1993, and Amoco/University Poster Session, Naperville, IL, 1993.

18. "Alkoxide precursors for controlled oxygen incorporation during MOVPE GaAs and $Al_xGa_{1-x}As$ growth", by J. W Huang, D. F. Gaines, T. F. Kuech, R. M. Potemski, and F. Cardone, presented at the 1993 EMC, Santa Barbara, CA, 1993.

19. **Invited,** "Chemical Vapor Deposition: Kinetics and Growth Morphology", T.F. Kuech, Materials Research Society, Boston, MA, Dec.1, 1992.

All Participating Personnel

Faculty:

Professor Kevin L. Bray
Professor Thomas F. Kuech

Graduate Students (Ph.D Student, Dept. of Chemical Engineering)

All listed have been partial support. Their research activities are indicated.

James Michael Ryan - High Pressure Measurements on GaAs:O
Jen-Wu Huang - Growth and Electrical Characterization
Jeff Cederberg - Growth of Oxygen Doped Alloys
Jiangli Li - heterostructure Characterization
John Geisz - Photoreflectance Measurements