

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 17 June 1996	3. REPORT TYPE AND DATES COVERED Final Technical 1 Oct 92 - 30 Sep 95	
4. TITLE AND SUBTITLE CHEMISTRY INVOLVING THE PREPARATION, ISOLATION, AND IMMOBILIZATION OF III-V COMPOUND SEMICONDUCTOR NANOCRYSTALS AND QUANTUM DOTS			5. FUNDING NUMBERS F49620-93-1-0004 2303/BS 61102F	
6. AUTHOR(S) RICHARD L. WELLS AND LOUIS A. COURY				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Duke University Durham, NC 27708-0346			8. PERFORMING ORGANIZATION REPORT NUMBER Final Technical Report DU/DC/FTR	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 DUNCAN AVENUE, SUITE B115 BOLLING AIR FORCE BASE, DC 20332-0001 CAPT Hugh DeLong			10. SPONSORING / MONITORING AGENCY REPORT NUMBER AFOSR-TR-96 0387	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution Unlimited  <b>19960726 082</b>				
13. ABSTRACT (Maximum 200 words) Dehalosilylation reactions have afforded the unique III-V (13-15) dimers $[X_2GaP(SiMe_3)_2]_2$ ( $X = Cl, Br, I$ ) and a stable substance having the empirical formula $Cl_3Ga_2P$ is isolable, all of which have been thermally decomposed to yield nanocrystalline GaP; thus, they are new single-source precursors to GaP. Also, $[Cl_3Ga_2(As,P)]_n$ has been synthesized and shown to be a single-source precursor to the ternary semiconductor GaAsP. In addition, a new, low temperature solution phase metathetical synthesis of the nanocrystalline III-V semiconductors GaP, GaAs, GaSb, InP, InAs and InSb has been developed. Optical characterization techniques revealed strong evidence for quantum confinement effects, and XRD, HRTEM, BET, STM and AFM data have shown the materials to be nanometer size particles. A comparison of the electrical properties of nanocrystalline InAs and a <i>p</i> -type InAs wafer using STS showed clear evidence of a larger bandgap for the nanoparticles. Also, poly(pyrrole) films were grown which contained either GaAs or InAs particles and were imaged by HRTEM and STM. Methanol extraction of the as-synthesized nanocrystals from the metathetical reaction of $GaCl_3$ with $(Na/K)_3As$ resulted in surface derivatization of the nanoparticles in which methanol capped GaAs quantum dots were obtained. Also, the heterogeneous reaction between $GaBr_3$ and $Li_3N$ afforded a precursor which, on pyrolysis under vacuum or $NH_3$ , yielded nanosized GaN and elemental Ga. The gallium nitride was characterized by XRD, XPS, and UV/vis spectroscopies, TEM microscopy, and elemental analysis.				
14. SUBJECT TERMS nanocrystals, quantum dots, III-V compound semiconductors, synthesis, structure			15. NUMBER OF PAGES 8	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFMC)

FINAL TECHNICAL REPORT

01 October 1992 through 30 April 1996

Grant F49620-93-1-0004

**Chemistry Involving the Preparation, Isolation, and Immobilization  
of III-V Compound Semiconductor Nanocrystals and Quantum Dots**

Professor Richard L. Wells, Principal Investigator  
voice: 919-660-1541  
fax: 919-660-1605  
e-mail: wells@chem.duke.edu

Louis A. Coury, Co-Principal Investigator  
voice: 919-660-1547  
fax: 919-660-1605  
e-mail: coury@chem.duke.edu

Department of Chemistry  
Paul M. Gross Chemical Laboratory  
Box 90346  
Duke University  
Durham, NC 27708-0346

17 June 1996

**Title: *Chemistry Involving the Preparation, Isolation, and Immobilization of III-V Compound Semiconductor Nanocrystals and Quantum Dots***

**PI:** Professor Richard L. Wells  
Department of Chemistry  
Gross Chem. Lab., Box 90346  
Durham, NC 27708  
voice: (919) 660-1541  
fax: (919) 660-1605  
e-mail: wells@chem.duke.edu

**co-PI:** Professor Louis A. Coury, Jr.  
Department of Chemistry  
Gross Chem. Lab., Box 90346  
Durham, NC 27708  
voice: (919) 660-1547  
fax: (919) 660-1605  
e-mail: coury@chem.duke.edu

**Grant Number: F49620-93-1-0004**

**Award Period: 1 October 1992 through 30 September 1995  
(no-cost extension granted through 30 April 1996)**

**Award Amount: \$587,227**

---

## 1.1 SUMMARY OF ACCOMPLISHMENTS DURING FUNDING PERIOD

Studies of dehalosilylation and LiCl elimination reactions have afforded interesting new III-V (13-15) compounds (see section 1.2, publications 1-5). It is of particular interest that the dimers  $[X_2GaP(SiMe_3)_2]_2$  have been isolated as stable crystalline compounds from reactions of  $GaX_3$  ( $X = Cl, Br, I$ ) with  $(Me_3Si)_3P$  in a 1:1 mole ratio (see section 1.2, publications 1 and 5). The structures of the compounds where  $X = Cl$  or  $Br$  were elucidated by single-crystal X-ray analyses, and they are the first examples of gallium-phosphorus dimers containing all exocyclic halogen ligands on the metal center. In addition, it has been demonstrated that  $GaCl_3$  and  $(Me_3Si)_3P$  mixed in a 2:1 mole ratio react to yield a stable substance having the empirical formula  $Cl_3Ga_2P$  (see section 1.2, publication 5). The latter and the three dimers have been thermally decomposed at the relatively low temperature of 300 °C to yield nanocrystalline GaP; thus, they are new single-source precursors to GaP. Application of the methodology which afforded the single-source precursor  $(Cl_3Ga_2P)_n$  has been used to synthesize  $[Cl_3Ga_2(As,P)]_n$ , a single-source precursor to a ternary III-V semiconductor, namely, gallium arsenide phosphide (see section 1.2, publication 9). The ternary material exhibits hybrid characteristics of the two binaries, with d-spacing values directly between those of GaAs and GaP. This is conclusive evidence for a semiconductor solid-solution, according to Vegard's Law (see section 1.2, publication 11).

The development of a new, low temperature solution phase synthesis of nanocrystalline III-V semiconductors GaP, GaAs, GaSb, InP, InAs and InSb has also been reported by us (section 1.2, publications 6 and 7). The methodology involves *in situ* formation of the sodium/potassium pnictide, followed by reaction with the metal halide to form semiconductor quantum dots. Our novel approach employing chelating solvents in the synthesis to limit the growth of III-V semiconductor particles to nanoscale dimensions has been demonstrated in various III-V cases. The materials produced by this method have been extensively characterized by a variety of techniques such as scanning electron microscopy (SEM), scanning tunneling microscopy (STM) and spectroscopy (STS), atomic force microscopy (AFM), multi-point Brunauer Emmett Teller (BET) surface area analysis, X-ray diffraction (XRD), electron dispersive X-ray analysis (EDXA), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), photoacoustic spectroscopy (PAS), UV/vis absorption spectroscopy of both solid-state samples and colloidal dispersions, photoluminescence measurements, and elemental analysis (EA). The optical characterization techniques revealed strong evidence for quantum confinement effects;

and the XRD, HRTEM, BET, STM and AFM data have shown the materials to be nanometer size particles.

In particular, nanocrystalline GaAs and InAs samples have been examined in detail. Six different techniques were used to determine the mean GaAs particle size, both before and after irradiation with high-intensity ultrasound. Comparable size parameters were obtained from XRD, HRTEM, BET and STM data; and the absorption edges in UV spectra were severely blue-shifted, consistent with quantum confinement effects (section 1.2, publication 8). A comparison of the electrical properties of nanocrystalline InAs and a *p*-type InAs wafer using STS showed clear evidence of a larger bandgap for the nanoparticles. The extent of the increase in bandgap was roughly consistent with predictions of the effective mass model (EMM) when the mean particle size obtained from STM data was used in the calculations (section 1.2, publications 10 and 11). Finally, poly(pyrrole) films were grown which contained either GaAs or InAs particles and were imaged by HRTEM and STM. The latter technique indicated that the InAs particles were conductive and distinguishable from the polymer matrix.

Methanol extraction of the as-synthesized nanocrystals from the metathetical reaction of GaCl<sub>3</sub> with (Na/K)<sub>3</sub>As, *vide supra*, resulted in surface derivatization of the nanoparticles in which methanol capped GaAs quantum dots were obtained (publication 12). The surface bound methanol facilitates the formation of colloidal suspensions of GaAs. The average particle size of the colloidal GaAs obtained by evaporating the methanol solvent was approximately 5 nm. The capped GaAs nanocrystals have been characterized by XRD, XPS, NMR, FT-IR PAS, HRTEM, elemental analysis, and UV-vis spectroscopy.

In addition, heterogeneous reactions between MBr<sub>3</sub> (M = Ga, In) and Li<sub>3</sub>N in refluxing aromatic or aromatic/ diglyme solvents were investigated as a potential route to nanocrystalline GaN and In N powders. For M = Ga, the pyrolysis of the as-prepared precursors at 450-500 °C under vacuum or NH<sub>3</sub> yielded nanosized GaN and elemental Ga. Gallium nitride was characterized by XRD, XPS, and UV/vis spectroscopies, TEM microscopy, and elemental analysis. For M = In, the reactions were highly solvent dependent and resulted exclusively in redox products such as indium(I) bromide, InBr, and elemental In (publication 13).

## 1.2 PUBLICATIONS OF AFOSR-FUNDED WORK (1993-1996)

1. Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Woudenberg, R. C.; Jasinski, J. P. "Synthesis, Characterization, and Thermal Decomposition of [Cl<sub>2</sub>GaP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, a Potential Precursor to Gallium Phosphide," *Organometallics* **1993**, *12*, 2832.
2. Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. L. "Aluminum-Phosphorous Chemistry: Preparation and Structural Characterization of [Et<sub>2</sub>AlP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, Et(Cl)<sub>2</sub>Al•P(SiMe<sub>3</sub>)<sub>3</sub>, and *i*-Bu<sub>2</sub>(Cl)Al•P(SiMe<sub>3</sub>)<sub>3</sub>," *Organometallics* **1993**, *12*, 3333.
3. Wells, R. L.; McPhail, A. T.; Self, M. F. "Synthesis and Characterization of Trimethylsilyl Phosphide Derivatives of Dineopentylindium Chloride. X-ray Crystal Structures of [Me<sub>3</sub>(Me<sub>3</sub>CCH<sub>2</sub>)InP(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>InP(SiMe<sub>3</sub>)<sub>2</sub>In(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl, and (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>InP(SiMe<sub>3</sub>)<sub>2</sub>In(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>PH(SiMe<sub>3</sub>)," *Organometallics* **1993**, *12*, 3363.
4. Self, M. F.; McPhail, A. T.; Jones III, L. J.; Wells, R. L. "Synthesis and Molecular Structures of R(Me<sub>3</sub>CCH<sub>2</sub>)In•E(SiMe<sub>3</sub>)<sub>3</sub> (R = Me<sub>3</sub>CCH<sub>2</sub>, E = P or As; R = Me, E = P)," *Polyhedron* **1994**, *13*, 625.

5. Aubuchon, S. R.; McPhail, A. T.; Wells, R. L.; Giambra, J. A.; Bowser, J. "Preparation, Characterization and Facile Thermolysis of  $[X_2GaP(SiMe_3)_2]_2$  (X = Br, I) and  $(Cl_3Ga_2P)_n$ ; New Precursors to Nanocrystalline Gallium Phosphide," *Chem. Mater.* **1994**, *6*, 82.
6. Kher, S. S.; Wells, R. L. "A Low Temperature, Solution Phase Synthesis of III-V Semiconductor Nanocrystals," *Mat. Res. Soc. Symp. Proc.* **1994**, *351*, 293.
7. Kher, S. S.; Wells, R. L. "A Straightforward, New Method for the Synthesis of Nanocrystalline Gallium Arsenide and Gallium Phosphide," *Chem. Mater.* **1994**, *6*, 2056.
8. Hagan, C. R. S.; Kher, S. S.; Halaoui, L. I.; Wells, R. L.; Coury Jr., L. A. "Determination of Relevant Size Parameters for Sonicated and Unsonicated Nanocrystalline GaAs Particles," *Anal. Chem.* **1995**, *67*, 528.
9. Aubuchon, S. R.; Lube, M. S.; Wells, R. L. "Preparation and Thermolysis of a Single-Source Precursor to Gallium Arsenide Phosphide," *Chem. Vap. Deposition* **1995**, *1*, 28.
10. Wells, R. L.; Kher, S. S.; Aubuchon, S. R.; Lube, M. S.; Hagan, C. R. S.; Halaoui, L. I.; Coury Jr., L. A. "Macroscopic Quantities of Nanoscopic Materials: Synthesis, Characterization and Immobilization of Nanocrystalline Binary and Ternary III-V (13-15) Compound Semiconductors," *Polym. Mater. Sci. Eng.* **1995**, *73*, 206.
11. Halaoui, L. I.; Kher, S. S.; Lube, M. S.; Aubuchon, S. R.; Wells, R. L.; Coury Jr., L. A. "Synthesis, Characterization and Immobilization of Nanocrystalline Binary and Ternary III-V (13-15) Compound Semiconductors," *ACS Books Series* **1996**, *622*, 178.
12. Kher, S. S.; Wells, R. L. "Synthesis and Characterization of Colloidal Nanocrystals of Capped Gallium Arsenide," *Nanostruct. Mater.*, **1996**, *7(6)*, in press.
13. Wells, R. L.; Janik J. F. "Heterogeneous Solution Reactions Between  $MBr_3$  (M = Ga, In) and  $Li_3N$ . Formation and Characterization of nanocrystalline GaN powders," *European J. Solid State and Inorg. Chem.* **1996**, submitted.

### 1.3 PRESENTATIONS ON AFOSR-FUNDED WORK AT MEETINGS (1993-1996)

1. Laske, J. L.; Wells, R. L.; Self, M. F.; McPhail, A. T. "Chemistry of Aluminum-Phosphorus Compounds: X-ray Crystal Structures of  $[Et_2AlP(SiMe_3)_2]_2$ ,  $Et(Cl)_2Al\cdot P(SiMe_3)_3$  and  $i-Bu_2(Cl)Al\cdot P(SiMe_3)_3$ ," 205th National Meeting of the American Chemical Society, **1993**, Denver, CO. *Oral Presentation*.
2. Self, M. F.; Wells, R. L.; Jones III, L. J.; McPhail, A. T. "Synthesis, X-ray Structures and Reactivity of Neopentylindium Chlorides and Trimethylsilyl Pnictide Derivatives; Unusual Products from Straightforward Reactions," 205th National Meeting of the American Chemical Society, **1993**, Denver, CO. *Oral Presentation*.
3. Aubuchon, S. R.; Self, M. F.; Wells, R. L.; Jasinski, J. P.; Woudenberg, R. C.; Butcher, R. J. "Preparation and Thermal Decomposition of Compounds of the General Formula  $[X_2GaP(SiMe_3)_2]_2$  (X = Cl, Br, I); New Precursors to GaP," 205th National Meeting of the American Chemical Society, **1993**, Denver, CO. *Oral Presentation*.

4. Laske, J. L.; Wells, R. L.; Self, M. F.; McPhail, A. T. "Chemistry of Aluminum-Phosphorus Compounds: X-ray Crystal Structures of  $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ ,  $\text{Et}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  and  $i\text{-Bu}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ ," 107th Sectional Conference of the North Carolina Section of the American Chemical Society, 1993, Raleigh, NC. *Oral Presentation.*
5. Self, M. F.; Wells, R. L.; Jones III, L. J.; McPhail, A. T. "Synthesis, X-ray Structures and Reactivity of Neopentylindium Chlorides and Trimethylsilyl Pnictide Derivatives; Unusual Products from Straightforward Reactions," 107th Sectional Conference of the North Carolina Section of the American Chemical Society, 1993, Raleigh, NC. *Oral Presentation.*
6. Aubuchon, S. R.; Self, M. F.; Wells, R. L.; Jasinski, J. P.; Woudenberg, R. C.; Butcher, R. "Preparation and Thermal Decomposition of Compounds of the General Formula  $[\text{X}_2\text{GaP}(\text{SiMe}_3)_2]_2$  (X = Cl, Br, I); New Precursors to GaP," 107th Sectional Conference of the North Carolina American Chemical Society, 1993, Raleigh, NC. *Oral Presentation.*
7. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Workshop - The Modern Problems of Heteroorganic Chemistry, 1993, Moscow, Russia. *Invited Presentation.*
8. Wells, R. L. "Chemistry Involving the Preparation, Isolation, and Immobilization of III-V Compound Semiconductor Nanocrystals and Quantum Dots," Air Force Office of Scientific Research, Surface Chemistry and Molecular Dynamics Contractors' Conference, 1993, Irvine, CA. *Invited Presentation.*
9. Coury Jr., L. A.; Hagan, C. R. S.; Wells, R. L.; Kher, S. S. "Electrochemistry and Microscopy of Nanocrystalline III-V Materials," AFOSR-Rome Laboratory Workshop on NLO/Quantum Dot Materials, 1994, Hanscom AFB, Bedford, MA. *Invited Presentation.*
10. Wells, R. L.; Kher, S. S.; Aubuchon, S. R. "Chemistry Involving the Preparation, Isolation, and Immobilization of III-V Compound Semiconductor Nanocrystals and Quantum Dots," AFOSR-Rome Laboratory Workshop on NLO/Quantum Dot Materials, 1994, Hanscom AFB, Bedford, MA. *Invited Presentation.*
11. Hagan, C. R. S.; Coury Jr., L. A.; Wells, R. L.; Aubuchon, S. R.; Kher, S. S. "Electrochemical, Spectroscopic and Microscopic Characterization of Sonicated Nanocrystalline Gallium Arsenide," Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, 1994, Chicago, IL. *Poster Presentation.*
12. Aubuchon, S. R.; Wells, R. L. "Preparation and Thermal Analysis of Single-Source Precursors to 13-15 Compound Semiconductors," 207th National Meeting of the American Chemical Society, 1994, San Diego, CA. *Oral Presentation.*
13. Kher, S. S.; Wells, R. L. "A Low Temperature, Solution Phase Synthesis of III-V Semiconductor Nanocrystals," Symposium V: Molecularly Designed Ultrafine/Nanostructured Materials; Materials Research Society Meeting, 1994, San Francisco, CA. *Poster Presentation.*
14. Hagan, C. R. S.; Coury Jr., L. A.; Wells, R. L.; Aubuchon, S. R.; Kher, S. S. "Characterization of Nanocrystalline GaAs," 108th Sectional Conference of the North Carolina Section of the American Chemical Society, 1994, Durham, NC. *Poster Presentation.*

15. Kher, S. S.; Wells, R. L. "A New Method for Solution Phase Synthesis of III-V Nanocrystals," 108th Sectional Conference of the North Carolina Section of the American Chemical Society, **1994**, Durham, NC. *Oral Presentation*.
16. Aubuchon, S. R.; Wells, R. L. "Preparation and Thermal Analysis of Single-Source Precursors to 13-15 Compound Semiconductors," 108th Sectional Conference of the North Carolina Section of the American Chemical Society, **1994**, Durham, NC. *Oral Presentation*.
17. Kher, S. S.; Wells, R. L. "New Method for Solution-Phase Synthesis of III-V Semiconductor Quantum Particles and Their Characterization," 208th National Meeting of the American Chemical Society, **1994**, Washington, DC. *Oral Presentation*.
18. Baldwin, R. A.; Aubuchon, S. R.; Lube, M. S.; Laske, J. L.; Wells, R. L.; White, P. S. "On the Preparation and Characterization of Binary and Ternary 13-15 Materials," 208th National Meeting of the American Chemical Society, **1994**, Washington, DC. *Poster Presentation*.
19. Wells, R. L.; Coury Jr., L. A. "Chemistry Involving the Preparation, Isolation and Immobilization of III-V Compound Semiconductor Nanocrystals and Quantum Dots," AFOSR Molecular Dynamics and Inorganic Materials Contractors' Conference, **1994**, Washington, DC. *Invited Poster Presentation*.
20. Halaoui, L. I.; Hagan, C. R. S.; Kher, S. S.; Wells, R. L.; Coury Jr., L. A. "Determination of Particle Size for Nanocrystalline GaAs Before and After Irradiation with High-Intensity Ultrasound," Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, **1995**, New Orleans, LA. *Poster Presentation*.
21. Kher, S. S.; Wells, R. L. "Synthesis and Characterization of As-Prepared Capped Gallium Arsenide Quantum Dots," 209th National Meeting of the American Chemical Society, **1995**, Anaheim, CA. *Oral Presentation*.
22. Halaoui, L. I.; Kher, S. S.; Wells, R. L.; Coury Jr., L. A. "STM Studies of Quantum Dot Semiconductors," 109th Sectional Conference of the North Carolina Section of the American Chemical Society, **1995**, Chapel Hill, NC. *Oral Presentation*.
23. Wells, R. L.; Kher, S. S.; Aubuchon, S. R.; Lube, M. S.; Hagan, C. R. S.; Halaoui, L. I.; Coury Jr., L. A. "Macroscopic Quantities of Nanoscopic Materials: Synthesis, Characterization and Immobilization of Nanocrystalline Binary and Ternary III-V (13-15) Compound Semiconductors," Symposium on Nanostructured Materials; 210th National Meeting of the American Chemical Society, **1995**, Chicago, IL. *Invited Presentation*.
24. Coury Jr., L. A.; Halaoui, L. I.; Kher, S. S.; Lube, M. S.; Wells, R. L. "Scanning Tunneling Microscopy and Spectroscopy of Nanocrystalline III-V Semiconductors," Annual Meeting of Southeastern Association of Analytical Chemists, **1995**, Greensboro, NC. *Oral Presentation*.
25. Halaoui, L. I.; Lube, M. S.; Wells, R. L.; Coury Jr., L. A. "Immobilization of Q-InAs on Electrode Surfaces and in Polymer Films: an STM and STS Investigation," *New Challenges & Opportunities in Materials Science*, Annual Symposium of the NC Section of the Materials Research Society, **1995**, Microelectronics Center of NC; RTP, NC. *Poster Presentation*.

26. Janik, J. F; and Wells, R. L. "Formation and Characterization of Nanocrystalline Gallium Nitride, GaN," 211th National Meeting of the American Chemical Society, 1996, New Orleans, LA. *Poster Presentation.*
27. Janik, J. F; and Wells, R. L. "Formation and Characterization of Nanocrystalline Gallium Nitride, GaN," 110th Sectional Conference of the North Carolina Section of the American Chemical Society, 1996, Raleigh, NC. *Oral Presentation.*
28. Wells, R. L. "Synthesis, Characterization and Immobilization of Nanocrystalline Binary and Ternary III-V (13-15) Compound Semiconductors", 110th Sectional Conference of the North Carolina Section of the American Chemical Society, 1996, Raleigh, NC. *Invited Presentation.*
29. Wells, R. L. "Synthesis, Characterization and Immobilization of Nanocrystalline Binary and Ternary III-V(13-15) Compound Semiconductors", The Fargo Conference on Main Group Chemistry, 1996, Fargo, ND. *Invited Presentation.*

#### 1.4. INVITED SEMINARS ON AFOSR-FUNDED WORK

1. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Texas Christian University, Department of Chemistry, Departmental Seminar, 1993.
2. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Southern Methodist University, Department of Chemistry, Departmental Seminar, 1993.
3. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," The University of Texas at Austin, Science and Technology Center, Seminar, 1993.
4. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," North Dakota State University, Department of Chemistry, Departmental Seminar, 1994.
5. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Elon College, Chemistry Department Seminar, 1994.
6. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Clemson University, Department of Chemistry, Departmental Seminar, 1994.
7. Coury Jr., L. A.; Madigan, N. A.; Hagan, C. R. S.; Murphy, T. J.; Cooper, E. L.; Halaoui, L. I.; Kher, S. S.; Wells, R. L. "Electrochemistry and Ultrasound," The University of Georgia, Department of Chemistry, Analytical Division Seminar, 1995.
8. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," University of Colorado, Department of Chemistry, Inorganic Division Lecture, 1995.

9. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," University of New Mexico, Department of Chemistry Seminar, **1995**.
10. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," Wake Forest University, Department of Chemistry Seminar, **1995**.
11. Wells, R. L. "Pathways to Nanocrystals of Gallium Arsenide and Related III-V (13-15) Compound Semiconductors," University of South Carolina, Department of Chemistry Seminar, **1996**.

#### **1.5 PATENT ARISING FROM AFOSR-FUNDED WORK**

Wells, R. L and Kher, S. S.. "Method of Synthesizing III-V Semiconductor Nanocrystals", *U.S. Patent No. 5,474,591*, December **1995**.

#### **1.6 PERSONNEL SUPPORTED WITH AFOSR FUNDING**

1. Hagan, Carolynne R. S.; graduate student, 1992-1994; Ph.D. **1994**.
2. Aubuchon, Steven R.; graduate student, 1992-1994; Ph.D. **1994**.
3. Halaoui, Lara I.; graduate student, 1993-1996.
4. Kher, Shreyas S.; post-doctoral research associate, 1993-1996.
5. Janik, Jerzy F.; post-doctoral research associate, 1995-1996.

#### **1.7 DISSERTATIONS OF STUDENTS SUPPORTED WITH AFOSR FUNDING**

1. Dr. Carolynne R. S. Hagan, "Characterization of the Effects of Ultrasound on Mass Transport in Electrolytic Solutions, at Extended Electrode Surfaces, and on Nanocrystalline Gallium Arsenide," ©1994, published by: UMI, Pub. # 9510833, 300 North Zeeb Road, Ann Arbor, MI 48106.

##### *Executive Summary of Portion of Work Supported by AFOSR:*

Sonication of nanocrystalline GaAs was shown to decrease the size of aggregates without damaging the crystallites responsible for quantum confinement effects. Samples of nanocrystalline GaAs which were sonicated, as well as unsonicated control samples were characterized using powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), multipoint Brunauer Emmett Teller surface area measurement (BET), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), and UV/vis optical absorption spectroscopy. The above techniques were compared in terms of the average particle size determined by each for the same GaAs sample. Comparable results were obtained from XRD, HRTEM, BET, and STM. UV/vis absorption thresholds were consistent with quantum confinement effects (*i.e.*, severely blue-shifted optical absorption edges), but the particle sizes calculated from such data using the effective mass model of Brus were complicated by scattering effects over some wavelength ranges.

2. Dr. Steven R. Aubuchon, "Organometallic Routes to Nanocrystalline 13-15 Semiconductor Materials," published by: UMI, Pub. # 9521471, 300 North Zeeb Road, Ann Arbor, MI 48106.

*Executive Summary of Portion of Work Supported by AFOSR:*

Through the use of dehalosilylation, new compounds were prepared which contain the Ga-P bond. These include two Lewis acid/base adducts containing phenyl groups on the gallium centers, and a novel compound which exhibits mixed-bridging of two gallium centers by a chlorine atom and a phosphorus atom. In addition, a new class of dimeric species was isolated and characterized by X-ray crystallography. These dimers contain all exocyclic halogen ligands on the metal centers, and are the first of this type reported in the Ga-P system. Several of the isolated novel compounds were thermally decomposed to yield powders containing nanocrystalline GaP. This thermolysis was studied by thermogravimetric analysis (TGA). The powders were characterized by elemental analysis and X-ray powder diffraction (XRD). Analysis of the XRD powder patterns of the GaP resulting from each of the precursor indicated a mean particle size of *ca.* 3 nm. In addition, a new precursor to GaP of the formula  $(\text{Ga}_2\text{P}\text{Cl}_3)_n$  was prepared and thermolyzed. A similar precursor of the formula  $[\text{Ga}_2(\text{P}/\text{As})\text{Cl}_3]_n$  was also studied. The thermolysis product of this material was characterized by elemental analysis, XRD, and X-ray photoelectron spectroscopy (XPS). Through the analysis, it was concluded that the material consists of a solid solution of GaP and GaAs of the empirical formula  $\text{GaAs}_x\text{P}_y$  ( $0.6 < x, y < 0.9$ ). This represents one of the first reported solid state syntheses of a ternary 13-15 material.