Group III Materials: New Phases and Nano-particles with Applications in Electronics and Optoelectronics

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Date Submitted: 31 December, 1999
Final Report

Long-term Research Goal

Development of a molecular understanding of (a) the control exerted by a molecular precursor over the structure of a solid state material and (b) the complexation and surface modification of semiconductor surfaces.

S&T Objectives

1. Demonstrate molecular control for the MOCVD growth of gallium and indium chalcogenides.
2. Demonstrate a molecular model approach to the prediction of suitable binding groups to semiconductor surfaces.
3. Demonstrate the application of surface coordination chemistry to the control over the electronic properties of semiconductor nano-particles.

Approach

We have chosen to perform our research using a combination of traditional organometallic chemistry and materials science. We are attempting to exploit the chemical control allowed by synthetic chemistry towards the control of electronic properties. For example, we have investigated the MOCVD growth of gallium and indium chalcogenides using pre-chosen molecular templates.

S&T Completed

Volatile trends are established for a series of organometallic molecular solids with a cubane geometry and the general form [(R)Ga(μ₃-E)]₄, where R = Me₃C(Bu), EtMe₂C, Et₂MeC, or Et₃C and E = S, Se, or Te. While the temperature of volatilization, T₂₀ defined as 20% mass loss from thermogravimetric analysis, was found to generally increase in a linear fashion with respect to increasing molecular mass, perturbations were observed that can be attributed to intermolecular ligand interactions. Sublimation enthalpies (ΔHₘₚ) for each cubane were calculated from thermogravimetric data, which show that the dependence of ΔHₘₚ on the degree of branching of the alkyl ligand appears to be more substantial than molecular mass effects alone. The C-H…H-C van der Waals interactions between alkyl substituents are estimated to account for more than 60% of the ΔHₘₚ in the organometallic cubane system, [(R)Ga(μ₃-E)]₄. Calculations based on the number of hydrogen atoms present in each alkyl yields an approximate value of ca. 4 kJ·mol⁻¹ for each C-H…H-C interactions. Using the TGA sublimation data vapor pressures may be calculated for each of the cubane compounds over a wide range of temperatures. All new cubanes have been characterized by MS, NMR, IR, and TG/DTA. The molecular structures of [(Et₃C₂)Ga(μ₁-CI)]₂, [(Et₃C)Ga(μ₃-S)]₄, and [(Et₃C)Ga(μ₃-Se)]₄ have been determined by X-ray crystallography.

The gallium-chalcogen-heterocubanes [Cₚ⁺Ga(μ₃-E)]₄, E = S (1), Se (2), and [Cₚ⁺Ga(μ₁-Se)]₄ (3), have been synthesized by dehalosilylation reactions between E(SiMe₃)₂ (E = S, Se) and RGaCl₂, R = Cₚ⁺ (C₅Me₅) and Cₚ⁺ (C₅Me₂Et), and are characterized by elemental analyses, NMR spectroscopy, and mass spectrometry. The structure of compound 2 was determined by X-ray diffraction. The use of compounds 1 and 2 as single source MOCVD precursors for the low temperature growth of Ga₅E₃ films at 290 - 310 °C is described. The as-deposited films were amorphous, however, upon thermal annealing (500 °C) the films crystallized to the thermodynamic cubic phases. The corresponding tellurium analog decomposed in the solid state at 220 °C forming a gallium rich product.

Gallium selenide (GaSe) thin films have been grown at 325 - 370 °C by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) using the single source precursors [(R)Ga(μ₁-Se)]₄ (R = CM₅, C₅Et₂Me, and C₅Et₂Me). In contrast, the growth of gallium telluride from [(R)Ga(μ₁-Te)]₄ is accomplished at 285 - 310 °C by low pressure metal-organic chemical vapor deposition (LP-MOCVD). Characterization of the films by Auger electron spectroscopy (AES), Rutherford backscattering (RBS), and wavelength dispersive...
spectroscopy (WDS) microprobe analysis shows all the films to have Ga:Se (E = Se, Te) compositions of 1:1 with a low degree of impurities (C < 2%; O < 0.1%). From X-ray diffraction (XRD) and transmission electron microscopy (TEM) the GaSe and GaTe films were found to be polycrystalline hexagonal layered GaE structures, with a preferred c-axis orientation independent of substrate. For GaSe this represents the thermodynamically stable phase, while hexagonal-GaTe is a metastable phase that converts to the thermodynamic monoclinic form on annealing at 500 °C. Diffraction results yield appropriate lattice parameters of \(a = 4.1\) Å (TEM) and \(c = 16.38\) Å (XRD) for hexagonal GaTe. Crystallite and particle size measurements reveal that the as-deposited films consist of oriented \(ca. 10\) nm crystalline particles. The formation of these hexagonal layered structures is proposed to occur as a consequence of the fragmentation of the cubic's Ga4E4 core during deposition, and the formation of trimeric "Ga3E3" building blocks.

The reaction of Ga(\(\text{Bu})_3\) with 1 molar equivalent of a carboxylic acid yields the carboxylate bridged dimeric compounds, \([(\text{Bu})_2\text{Ga}(\mu-\text{O}_2\text{CR})_2]\), where \(R = \text{Ph} (3), \text{C}_6\text{H}_4-3-\text{CN} (4), \text{C}_6\text{H}_4-3-\text{Br} (5)\), respectively. Similarly, reaction of Ga(\(\text{Bu})_3\) with HSPh yields the thiolate bridged compound, \([(\text{Bu})_2\text{Ga}(\mu-\text{SPh})_2]\) (6). The molecular structures of compounds 3, 4, and 6 have been determined by X-ray crystallography. The Ga...Ga and Ga-ligand inter-atomic distances for these compounds, as well as group 15 and 16 donor bridging ligands, are compared to the values for the surface of GaAs and cubic-GaS in order to determine their suitability as linkage groups for self-assembled monolayers.

Gallium and indium selenide nanoparticles have been grown during metal organic chemical vapor deposition (MOCVD) of films from the single source precursors \([(\text{Bu})\text{GaSe}]_4\) and \([(\text{EtMe}_2\text{C})\text{InSe}]_4\), respectively. Vapor phase decomposition of the precursors leads to thermodynamic phase formation as well as particle formation.

A range of In-Se bond forming reactions have been investigated, including: insertion of selenium into either an In-C or In-S bond, reaction of an indium halide with a magnesium selenolate, and via chlorosilane elimination. The reaction of In(\(\text{Bu})_3\) with Se yields \([(\text{Bu})_2\text{In}(\mu-\text{Se})\text{Bu}]_2\) (9) and \([(\text{Bu})\text{In}(\mu_3\text{-Se})]_4\) (10). In contrast, the reaction of In(\(\text{Me}_2\text{Et})_3\)) (7) and In(\(\text{Bu})_3\) with Se preferentially forms \([(\text{Me}_2\text{Et})\text{In}(\mu_3\text{-Se})]_4\) (11) and \([(\text{Bu})\text{In}(\mu_3\text{-Se})]_4\) (12), respectively. The reaction of compound 7 with Te yields \([(\text{Me}_2\text{Et})\text{In}(\mu_3\text{-Te})]_4\) (13). Compound 10 is also formed from the reaction of \([(\text{Bu})_2\text{In}(\mu-\text{S}\text{Bu})_2]\) with either Se or Se=PH3, while both compounds 9 and 10 may be prepared from the reaction of \([(\text{Bu})_2\text{In}(\mu-\text{Cl})]_n\) with \((\text{BuSe})\text{MgCl}\). Similarly, \([(\text{Bu})_2\text{In}(\mu-\text{Se})\text{Bu}]_2\) (14) may be prepared from \([(\text{Bu})_2\text{In}(\mu-\text{Cl})]_2\). However, reaction of \([(\text{Me}_2\text{Et})\text{In}(\mu-\text{Cl})]\) (12) with \((\text{Bu})\text{E})\text{MgCl} (E = S, Se, Te) yields \([(\text{Me}_2\text{Et})\text{In}(\mu_3\text{-S})]_4\) (15), compound 11, and compound 13, respectively. Reaction of \([(\text{Bu})_2\text{M}(\mu-\text{Cl})]_n\) (M = In, Ga) with Se(SiMe3)2 yields the silyl selenolate compounds, \([(\text{Bu})_2\text{M}(\mu-\text{SeSiMe}_3)]_2\), M = In (16) and Ga (17). The various In-Se bond forming reactions are compared. The molecular structures of compound 9 and \([(\text{Bu})_2\text{In}(\mu-\text{S}\text{Bu})_2]\) have been determined by X-ray crystallography.

The solid state structure of di-tert-butyl indium chloride, \([(\text{Bu})_2\text{In}(\mu-\text{Cl})]\), has been determined by X-ray diffraction, and consists of polymeric \([\mu-\text{Cl}]_{\infty}\) chains arranged in an unusual saw-tooth pattern motif. The indium atom is in a severely distorted coordination environment approximated as a capped trigonal planar geometry. The structure of \([(\text{Bu})_2\text{In}(\mu-\text{Cl})]_{\infty}\) is compared to \([(\text{Me})_2\text{In}(\mu-\text{Cl})]_{\infty}\).

Indium selenide (InSe) thin films have been grown at 230 - 420 °C by low pressure metal-organic chemical vapor deposition (MOCVD) using the single source precursors \([(\text{Bu})_2\text{In}(\mu-\text{Se})\text{Bu}]_2\) and \([(\text{Me}_2\text{Et})\text{In}(\mu_3\text{-Se})]_4\). Characterization of the films by energy dispersive X-ray analysis (EDX) showed those grown from \([(\text{Bu})_2\text{In}(\mu-\text{Se})\text{Bu}]_2\) to be indium rich, while those grown from \([(\text{Me}_2\text{Et})\text{In}(\mu_3\text{-Se})]_4\) are stoichiometric InSe. Transmission electron microscopy (TEM) indicates that the film morphology and crystallinity are highly dependent on the precursor and the deposition temperature. At low temperatures < 330 °C ball-like morphologies are observed, while deposition at 350 - 370 °C results in highly crystalline textured films. Use of \([(\text{Bu})\text{In}(\mu_3\text{-Se})]_4\) as the precursor at 320 - 420 °C results in indium metal films. The relationship between the precursor's structure and the film's morphology and chemical
composition are discussed. The efficacy of the single source precursor approach is considered with respect to elemental composition, phase formation, and film morphology.

The reaction of Ga(Bu)_3 with phenylphosphonic acid results in the formation of the unusual phosphonate bridged dimer, [(Bu)_2Ga(μ-O_2P(Ph)O)Ga(Bu)_2]_2, whose molecular structure consists of two four-coordinate and two three-coordinate gallium centers. While [(Bu)_2Ga(μ-O_2P(Ph)O)Ga(Bu)_2]_2 exists as the trans isomer in the solid state, it undergoes a trans to cis isomerization in solution, ΔH = 7 ± 1 kJ mol^-1 and ΔS = 25 ± 4 J mol^-1 K^-1.

The reaction of [(Bu)_2Ga(μ-Cl)]_2 with 1 molar equivalent of Na(S_2CNMe)_2 yields the di-tert-butyl gallium dithiocarbamate compounds (Bu)_2Ga(S_2CNMe)_2, R = Me (18), Et (20), nPr (22). The tert-butyl gallium bis-dithiocarbamate compounds, (Bu)Ga(S_2CNMe)_2, R = Me (19), Et (21), nPr (23), are formed as minor products. Separation of (Bu)_2Ga(S_2CNMe)_2 from (Bu)Ga(S_2CNMe)_2 may be readily accomplished by sublimation of the former. Compounds 18 and 20 are low melting point solids allowing their ready use as liquid precursors for MOCVD. The vaporization enthalpies (ΔH_v) have been determined, by thermogravimetric methods, for compounds 18, 20, 22, (Bu)_2Ga(S_2CNMe)_2 (24) and (secBu)_2Ga(S_2CNMe)_2 (25), and are dependent on both the identity of the substituents on gallium and the dithiocarbamate ligand. Inverse relationship is observed between the ΔH_v and the extent of branching of the gallium alkyl. The molecular structures of compounds 18 and 20 have been determined by X-ray crystallography. Gallium sulfide (GaS) thin films have been grown at 375 - 425 °C by atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) using compound 18. Characterization of the films by wavelength dispersive spectroscopy (WDS) microprobe analysis shows the films to have Ga:S compositions of 1:1 with a low degree of impurities (C < 3 %; O < 1 %). Gallium rich films were grown from compound 3 using AP-MOCVD and from compound 18 under reduced pressure. XPS studies of the GaS films additionally show an abundance of N on the surface, which has been confirmed to be present throughout the thin film by SIMS measurements. From X-ray diffraction (XRD) and transmission electron microscopy (TEM) the GaS films were found to be a new distorted hexagonal wurtzite phase (a = 4.590 Å, c = 6.195 Å).

The molecular structures of (Bu)Ga(S_2CNMePr)_2 (19) and (iPrO)Ga(S_2CNEt)_2 (26) have been determined. The variation in the geometries observed for bis-dithiocarbamate compounds of gallium, (X)Ga(S_2CNMe)_2 (X = Cl, iPrO, Bu) do not lie along the Berry pseudo-rotation pathway for the square-based pyramid to trigonal bipyramid geometrical transition. Instead, the structures appear to lie on an unusual ligand two-step, "Texas", pseudorotation mechanism which results in a highly distorted trigonal bipyramidal geometry.

The tert-butyl substituted compounds of gallium have been synthesized and characterized: [(Bu)_2Ga(μ-OCH(CF_3))_2]_2 (27), [(Bu)_2Ga(μ-O_2Ce)]_2 (28), [(Bu)_2Ga(μ-O_2CCF_3)]_2 (29), [(Bu)_2Ga(μ-OC(Ph)N(H))]_2 (30), [(Bu)_2Ga(μ-OC(Me)NPh)]_2 (31), [(Bu)_2Ga(μ-OC(Ph)NMe)_2] (32), [(Bu)_2Ga(μ-OC(Ph)NPh(Me)] (33), [(Bu)_2Ga(μ-OC(Ph)NPh(Me)] (34), [(Bu)_2Ga(μ-O_2S(CF_3))_2] (35), [(Bu)_2Ga(μ-Cl)]_2 Li(HO)Pr)_2 (36), and [Li(HO)Pr]_[(Bu)_2GaCl]_2 (37). X-ray crystallographic characterization was obtained for compounds 27 - 32 and 34 - 37. Compounds 36 and 37 exhibit three dimensional hydrogen bonded networks in which augmentation of the O-H-Cl hydrogen bond is proposed to be due to the increased acidity of alcohols bonded to the Lewis acidic lithium ions. A discussion of the dependence of the puckering of the chair-like conformation in eight-membered cyclic compounds of the Group 13 metals is presented.

The vapor phase structures of Al(Bu)_3 and Ga(Bu)_3 have been investigated by gas phase electron diffraction and consist of planar three-coordinate monomers. Salient structural parameters (r_a) include: Al-C = 2.005(3) Å, Ga-C = 2.034(2) Å. The geometry and ligand orientation are controlled by inter-ligand interactions for both compounds. The structure of Ga(Bu)_3 as determined by ab initio calculations [MP2/6-31G(*) level] is in good agreement with the electron diffraction structure. A comparison of the ab initio calculated structure [MP2/6-31G(*)] of In(Bu)_3 with the structures of Al(Bu)_3 and Ga(Bu)_3 suggests the former's photochemistry is not due to structural factors.
Reaction of Ga(\(\text{Bu}\))\(_3\) with the 1,3-diphenylamidine [PhN(H)C(H)=NPh, H-dpam] yields monomeric (\(\text{Bu}\))\(_2\)Ga(dpam) (38). The partial hydrolysis of 38 results in the isolation of (\(\text{Bu}\))\(_2\)Ga(\(\mu\)-dpam)(\(\mu\)-OH)Ga(\(\text{Bu}\))\(_2\) (39), whose structure consists of a gallium dimer in which the amidine and hydroxide ligands bridge two Ga(\(\text{Bu}\))\(_2\) moieties. Reaction of [Me\(_2\)Ga(\(\mu\)-Cl)]\(_2\) with H-dpam results in the complex [H\(_2\)-dpam][Me\(_2\)GaCl\(_2\)] (40). The solid state structure of 40 indicates the presence of a hydrogen bonded cation-anion complex, in which the core has a twisted eight-membered ring configuration. The versatility of amidines as both chelating and bridging ligands to gallium is discussed with respect to the predominance of bridging and chelating modes of coordination of carboxylates and triazenes, respectively. Reaction of 2-(methylamino)pyridine (H-map) with Ga(\(\text{Bu}\))\(_3\) allows for the isolation of (\(\text{Bu}\))\(_2\)Ga(map) (41). In contrast, reaction with [(\(\text{Bu}\))\(_2\)Ga(\(\mu\)-Cl)]\(_2\) and [Me\(_2\)Ga(\(\mu\)-Cl)]\(_2\) yields the Lewis acid base adducts, (\(\text{Bu}\))\(_2\)GaCl(H-map) (42) and Me\(_2\)GaCl(H-map) (43), respectively. Reaction of compound 43 with PrNH\(_2\) does not result in the deprotonation of the H-map ligand, but ligand metathesis and the formation of (\(\text{Bu}\))\(_2\)GaCl(NH\(_2\)-Pr) (44).

Hexanethiol (C\(_6\)H\(_{13}\)SH), phenylphosphonic acid [PhP(O)(OH)\(_2\)], and 3-bromo-benzoic acid (3-BrC\(_6\)H\(_4\)CO\(_2\)H) have been reacted with \(\{100\}\)-GaAs surface which have been pretreated with an acid etch and an ammonium sulfide reactive passivation layer. The chemically reacted surfaces have been characterized by X-ray photoelectron spectroscopy (XPS) and advancing contact angle measurements using H\(_2\)O and hexadecane. As predicted from simple model compounds, [(\(\text{Bu}\))\(_2\)Ga(\(\mu\)-X)]\(_2\), the thiol and phosphonic acid ligands allow for uniform surface layers, while the carboxylic acid is geometrically unsuited to binding the surface of GaAs.

**Impact/Navy Relevance**

We have successfully demonstrated that a molecular model approach to the choice of suitable surface binding groups. This will allow for the passivation and chemical modification of semiconductor nano-particles with the view to the development of new device structures. The control of solid state materials structure and morphology will allow for greater control over properties via chemical synthesis rather than process conditions.

**Technology Transfer**

No new technology transfer is ongoing.

**References**

N/A

**Subcontractors**

None

**Productivity**


Molecular structures of [(\(\text{Bu}\))\(_2\)Ga(\(\mu\)-O\(_2\)CPh)]\(_2\), [(\(\text{Bu}\))\(_2\)Ga(\(\mu\)-O\(_2\)CC\(_6\)H\(_4\)-3-CN)]\(_2\), [(\(\text{Bu}\))\(_2\)Ga(\(\mu\)-SC\(_6\)H\(_5\))]\(_2\): the efficacy of oxygen and sulfur donor ligands for binding to GaAs and GaS surfaces. A. Keys, S. G. Bott, and A. R. Barron, *Polyhedron*, 1998, 17, 3121.

Molecular structures of (tBu)Ga(S\textsubscript{2}CN\textsuperscript{a}Pr\textsubscript{2})\textsubscript{2} and (tPrO)Ga(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}: an example of an unusual ligand pseudorotation. A. Keys, S. G. Bott, and A. R. Barron, *J. Chem. Cryst.*, 1998, 28, 629.


