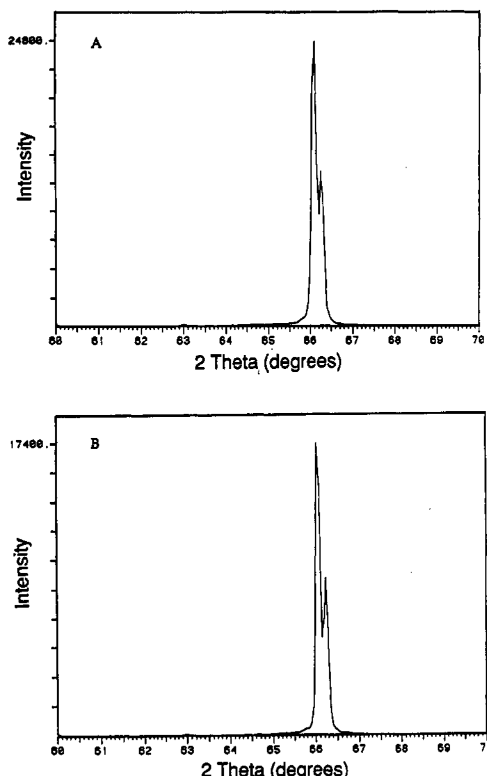

Figure 2. Single-crystal, X-ray diffraction pattern (A) for a 2.0-μm-thick film grown at 1×10^{-5} Torr and 475 °C and (B) for the (100) GaAs substrate.

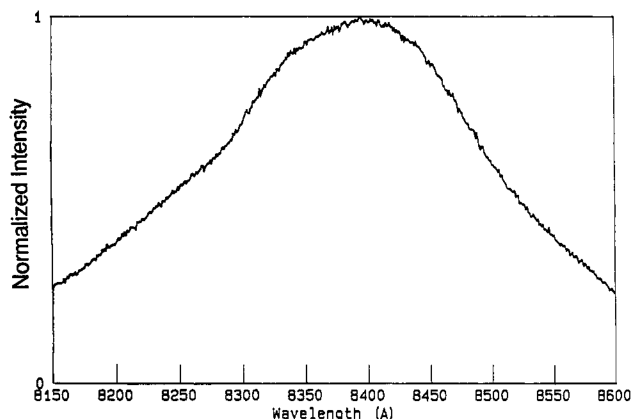

Figure 3. Photoluminescence spectra (4 K) of a 2.3-μm-thick film grown at 5×10^{-6} Torr and 500 °C.

Torr. The spectrum exhibits a single broad peak at 840 nm which arises from high concentrations of silicon and carbon in the film.[6] Inductively coupled plasma mass spectroscopy analysis of the precursor showed a high concentration (1000 ppm) of silicon. The silicon in the precursor probably originated from the stopcock grease used on the synthesis glassware. Steps have been undertaken to eliminate the use of stopcock grease during precursor synthesis. The carbon likely originated from the methyl ligands of the precursor. Several groups have investigated the use of $Ga(Me)_3$ and $Ga(Et)_3$ in CBE studies with both arsine and solid arsenic sources.[7] The films grown with $Ga(Me)_3$ typically contained greater than 1×10^{19} carbon atoms cm^{-3} whereas films grown from $Ga(Et)_3$ contained 10^{14}–10^{16} carbon atoms cm^3. Experiments are underway with $[Et_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ to determine how ligand structure and reactivity affect carbon impurity levels in the films.

Previous film growth studies[3] with $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ were conducted at pressures of 1×10^{-4} Torr. A significantly lower growth pressure was used herein, and it led to epitaxial films from the same precursor and at similar (500 °C) temperatures. We suspect that the lower pressure is necessary to eliminate prereaction of the precursor in the heated transfer line and/or in the gas region above the heated substrate. The role of prereaction in film crystallinity is currently under study.

(6) T. R. Block, University of Texas, private communication.
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Acknowledgment. This work was supported by the Army Research Office (Contract DAAL03-89-K-0164) and the Science and Technology Center Program of the National Science Foundation (Grant CHE-8920120). We also thank our colleagues in the Department of Chemistry at the University of Texas at Austin, Professors A. H. Cowley and R. A. Jones, for their input. The precursor used in this study was prepared by M. A. Mardones and J. W. Nail. The PL spectra were obtained by J. G. Neff.

Registry No. GaAs, 1303-00-0; $[Me_2Ga(\mu\text{-}t\text{-}Bu_2AS)]_2$, 106417-80-5.

Rapid Synthesis of GaP and GaAs from Solid-State Precursors

Randolph E. Treece, Gerald S. Macala, and Richard B. Kaner*

Department of Chemistry and Biochemistry and Solid State Science Center
University of California
Los Angeles, California 90024-1569

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The III–V compound semiconductors GaAs and GaP are well-known for their use in optoelectronic devices.[1] Bulk samples of these materials have been precipitated from solution and prepared by the decomposition of single-source solid-state precursors. Amorphous materials are typically made from solution. Cumberbatch and Putnis produced gallium arsenide by bubbling arsine through gallium nitrate solutions,[2] Byrne et al. reacted a monomeric arsinogallane with *tert*-butyl alcohol to produce GaAs,[3] and Lawrence made both GaAs and GaP in organic solutions from reactions between metal– or pnictide–tris(trialkylsilyl) derivatives and pnictide– or metal–trihalides, respectively.[4] Wells et al. used $GaCl_3$ and $(Me_3Si)_3As$ to both prepare bulk GaAs directly[5] and indirectly form the single-source precursor $AsCl_3Ga_2$, which upon heating decomposed to GaAs and $GaCl_3$.[6] Cowley et al. decomposed $[t\text{-}Bu_2Ga(\mu\text{-}AH_2)]_3$, where A = P or As, to form

(1) (a) Sze, S. M. *Phyics of Semiconductor Devices*, 2nd ed.; John Wiley and Sons: New York, 1981. (b) Streetman, B. G. *Solid State Electronic Devices*, 3rd ed.; Prentice Hall: New Jersey, 1990. (c) Grovenor, C. R. M. *Microelectronic Materials*; Adam Hilger: Philadelphia, 1989.
(2) Cumberbatch, T. J.; Putnis, A. *Mater. Res. Soc. Symp. Proc.* **1990**, *164*, 129.
(3) Byrne, E. K.; Parkanyi, L.; Theopold, K. H. *Science* **1988**, *241*, 332.
(4) Lawrence, D. W. U.S. Patent No. 4,798,701, Jan 17, 1989.
(5) (a) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4. (b) Wells et al. have also discussed routes to AlAs and InAs, as well as, GaAs: Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 45.
(6) Wells, R. L.; Hallock, R. B.; McPhail, A. T.; Pitt, C. G.; Johansen, J. D. *Chem. Mater.* **1991**, *3*, 381.

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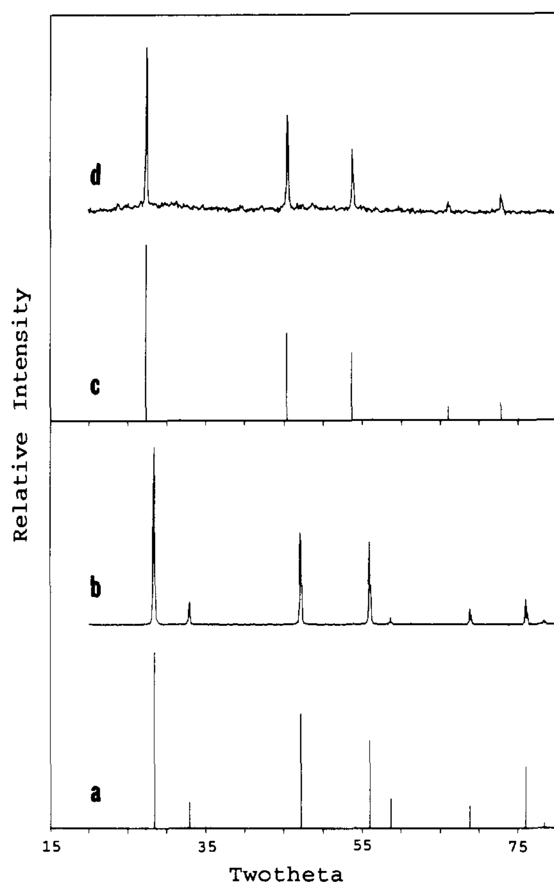
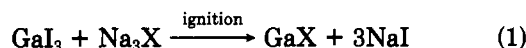


Figure 1. XRD patterns of (a) GaP standard,[10] (b) GaP from a 4400-mg reaction mixture of $GaI_3 + Na_3P$, (c) GaAs standard,[10] and (d) GaAs from a 4400-mg reaction mixture of $GaI_3 + Na_3As$.

polycrystalline GaP or GaAs.[7] We have investigated an alternative solid-state route to bulk III–V compounds. Herein is reported a rapid, low-temperature-initiated, precursor method for the synthesis of GaP and GaAs.

Crystalline powders of GaP and GaAs are produced in seconds from the solid-state metathesis reaction



$$GaI_3 + Na_3X \xrightarrow{\text{ignition}} GaX + 3NaI \qquad (1)$$

where X represents phosphorus or arsenic. The gallium iodide and sodium pnictide precursors[8] are ground individually and then mixed in equimolar quantities. The mixture is ignited with a hot filament in a bomb similar to those used in calorimetry experiments.[9] The products are ground with a mortar and pestle in a He-filled drybox and then washed in air with methanol and diethyl ether to remove the NaI and any unreacted starting reagents. The isolated products are dried on a vacuum line. GaP made by this method is a fine yellow powder, while GaAs is a gray powder displaying a metallic luster. Powder X-ray diffraction[10] (XRD) shows that both materials are phase pure, and they assume the well-known sphalerite (cubic-ZnS) structure with lattice constants of a = 5.446 (1) and 5.654 (1) Å, respectively. These can be compared to literature values of 5.448 (GaP) and 5.6538 Å (GaAs).[11] Representative XRD patterns of the crystalline GaP and GaAs formed in these metathesis reactions are presented in Figure 1.

These ignited precursor reactions are highly exothermic and quite rapid. The enthalpy of the precursor reaction used to produce GaP is −138 kcal/mol, as calculated from Hess' law.[12,13] Optical pyrometry reveals that the temperatures generated in this reaction are in excess of 750 °C within seconds of initiation. These temperatures are certainly sufficient to vaporize or melt the reactants, thereby overcoming solid-state diffusion barriers to reaction. A molten reaction flux is formed, including the byproduct sodium iodide (mp(NaI) = 661 °C), which allows for material diffusion and rapid formation of more products and byproducts. This in turn generates more heat. The rapid heating is followed by rapid cooling of the flux: within 10 s the reaction mixture cools to room temperature.

The extent of reaction depends on the amount of time the reaction flux is held at elevated temperatures. This is illustrated by varying the amount of the precursor mixtures. When a 1.0 mmol (~550 mg) reaction mixture of GaI_3 and Na_3P is ignited, optical microscopy reveals red phosphorus in the product. However, ignition of an 8.0 mmol (~4400 mg) reaction mixture leads to GaP powder in which no red phosphorus is observed. The larger reaction mixtures are better insulated against heat loss to the surroundings. Increased insulation retains more of the heat generated by the reaction keeping the core of the reaction flux at elevated temperatures longer than can be maintained by a smaller reaction mixture.

Regardless of the amount of the precursor mixture, the initial steps in these reactions appear to include a breakdown of the GaI_3 lattice. It is quite likely that melting and/or vaporization of the gallium iodide increases surface contact, thereby initiating the precursor reactions. Gallium iodide is a high vapor pressure, molecular solid[14] with low melting (212 °C) and sublimation (345 °C) temperatures.[13] On igniting a mixture of GaI_3 and Na_3As a whisp of yellow vapor characteristic of $GaI_3(g)$ is visible immediately prior to the highly exothermic reaction.

The breakdown of the GaI_3 lattice is followed by the formation of the sodium iodide byproduct. The formation of three moles of NaI accounts for 90% of the reaction enthalpy, and the initial surface reaction is expected to be an important aspect of the self-propagating nature of these reactions, as the reactions can be initiated by grinding the reagents together by mortar and pestle. The extent of initial surface reaction was examined by lightly grinding, but not initiating, a reaction mixture of GaI_3 and Na_3As in a mortar and pestle. An XRD pattern of the reaction mixture reveals the formation of partially crystalline NaI. This shows that some initial surface reaction occurs, but

(7) Cowley, A. H.; Harris, P. R.; Jones, R. A.; Nunn, C. M. *Organometallics* **1991**, *10*, 652. Cowley et al. have also deposited films of GaAs and InP from single-source precursors, such as $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ (used to prepare GaAs): Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248–6249.

(8) The gallium iodide is made from the elements at ca. 300 °C in sealed Pyrex tubes and then purified by direct vapor transport in a 300 °C–room temperature gradient. The sodium pnictides are prepared by heating stoichiometric amounts of the elements in sealed glass tubes for 5 h at 500 °C, opening the tube, and grinding the contents in a He-filled drybox, reloading and sealing the contents under vacuum and reheating for an additional 5 h at 500 °C. *Caution*: The sodium pnictides are toxic and highly reactive to air and water.

(9) Bonneau, P. R.; Wiley, J. B.; Kaner, R. B. *Inorg. Synth.*, submitted.

(10) The XRD patterns are obtained on a G.E. powder diffractometer with Ni-filtered Cu Kα radiation, scanning in steps of 0.05° 2θ at a step of 5 s/step. The lattice constants are determined by linear regression, referenced to an internal standard of tungsten powder.

(11) *Powder Diffraction File*; Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data, Swarthmore, PA, 1986, file no. 12-191 (GaP) and file no. 32-389 (GaAs).

(12) *JANAF Thermochemical Tables*, 3rd ed.; Lide, Jr., D. R., Ed.; American Chemical Society and American Institute of Physics, Inc.: New York, 1985.

(13) *CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, Fl, 1983.

(14) Wells, A. *Structural Inorganic Chemistry*, 5th ed.; Claredon Press: Oxford, England, 1986.

it does not generate sufficient heat to initiate a self-sustaining reaction. While there are some clues as to the initiation of these reactions, the intermediate stages are very difficult to determine. Emission spectroscopy of the bright flash generated by the ignition of reactions should provide some answers as to the species present in the brief, hot reaction flux.

The preparation of other III–V compounds from analogous precursor reactions are under investigation. Ternary materials such as Ga(P, As) and (Al, Ga)As should also be able to be produced by this method using the appropriate precursors, e.g., $Na_3P_xAs_{1-x}$, or $Al_xGa_{1-x}I_3$. Although these highly exothermic reactions lead to crystalline products, it may be possible to control particle size by the addition of a heat sink.[15] Solid-state precursors offer an exciting synthetic route for many types of materials.

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Registry No. GaI_3, 13450-91-4; Na_3P, 12058-85-4; Na_3As, 12044-25-6; GaP, 12063-98-8; GaAs, 1303-00-0; Ga, 7440-55-3; I_2, 7553-56-2; Na, 7440-23-5; P, 7723-14-0; As, 7440-38-2; NaI, 7681-82-5.

(15) Bonneau, P. R.; Jarvis, Jr., R. F.; Kaner, R. B. *Nature* 1991, *349*, 510.

Chemical Vapor Deposition of Cubic Gallium Sulfide Thin Films: A New Metastable Phase

Andrew N. MacInnes, Michael B. Power, and Andrew R. Barron*

Department of Chemistry and Materials Research Laboratory
Harvard University
Cambridge, Massachusetts 02138

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The low-temperature deposition of thin-film materials from molecular precursors has been an area of increasing interest since the first studies by Manasevit over 20 years ago.[1,2] In principle, metal–organic chemical vapor deposition (MOCVD) offers significant advantages over physical vapor deposition (PVD) methods, for example, simple apparatus, mild process conditions, control over composition, high deposition rates, and possible large scale processing. However, one drawback with the more traditional molecular precursors is that many are toxic and/or pyrophoric. Thus, much effort has been aimed at the development of new stable precursors,[3] in particular those containing all the desired elements in a single molecule.

Table I. Measured *d* Spacing for Deposited GaS Films Compared to Calculated Values for Fcc Lattice, *a* = 5.37 Å

hkl	d, Å calcd	d, Å measd	hkl	d, Å calcd	d, Å measd
111	3.10	3.11	133	1.23	1.22
002	2.69	2.70	024	1.20	1.18
022	1.90	1.83	422	1.10	1.08
113	1.62	1.64	333/511	1.04	1.06
222	1.55	1.56	440	0.95	0.93
004	1.34	1.37	531	0.91	0.90

Such compounds have been termed single source precursors[4] and have successfully been employed for the growth of a wide variety of thin films.

Although not as extensively studied as the III/V compound semiconductors, there has been increasing interest in group III–chalcogenides because of their possible application as semiconductors, semimetals, photoconductors, and light emitters.[5] Additional work on gallium and indium sulfide has been prompted by their use as passivation layers on GaAs and InP, respectively.[6] As part of our ongoing research in this latter area we have recently reported the synthesis and structural characterization of the first gallium chalcogenide cubane, $[(t\text{-Bu})GaS]_4$,[7] whose volatilty (sublimed 225 °C at 760 mmHg) and gallium–sulfur ratio make it a suitable candidate as a single source precursor for GaS.

Perhaps the most significant advantage (and one that has only recently been appreciated) that CVD has over other methods is the production of metastable materials. Most CVD processes operate far from equilibrium conditions, so that kinetically, rather than thermodynamically, favored products are produced.[8] Since the mass spectrum of $[(t\text{-Bu})GaS]_4$ indicates that no significant fragmentation of the Ga_4S_4 cubane unit occurs, an important question arises: *Does the molecular structure of the precursor control the crystal structure of a solid state product?* Such an effect has been previously observed for the solid-state pyrolysis of organometallic compounds;[9] however, to our knowledge no such control has been reported for

* Author to whom all correspondence should be addressed.

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(2) Manasevit, H. M. *J. Cryst. Growth* 1981, *55*, 1.
(3) For recent review articles see: (a) Jones, A. C. *Chemtronics* 1989, *4*, 15. (b) Bradley, D. C. *Chem. Rev.* 1989, *89*, 1317. (c) Girolami, G. S.; Gozum, J. E. *Mater. Res. Soc. Symp. Proc.* 1990, *168*, 319. (d) Cowley, A. H.; Jones, R. A. Angew *Chem., Int. Ed. Engl.* 1990, *28*, 1208.
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