

Chemical vapor deposition of cubic gallium sulfide thin films: a new metastable phase

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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., $\text{Na}_3\text{P}_x\text{As}_{1-x}$, or $\text{Al}_x\text{Ga}_{1-x}\text{I}_3$. 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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Chemical Vapor Deposition of Cubic Gallium Sulfide Thin Films: A New Metastable Phase

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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.

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

<i>hkl</i>	<i>d</i> , Å		<i>hkl</i>	<i>d</i> , Å	
	calcd	measd		calcd	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 precursors⁴ 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*-Bu)GaS]₄,⁷ whose volatility (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*-Bu)GaS]₄ indicates that no significant fragmentation of the Ga₄S₄ 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

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Table II. Comparison of d Spacings (\AA) of Previously Reported GaS Phases with That Formed by Chemical Vapor Deposition Using $[(t\text{-Bu})\text{GaS}]_4$ as a Single Source Precursor

hexagonal (30-576) ^a			rhombohedral (40-1030) ^{b,c}			present work	
d	I/I_0	hkl	d	I/I_0	hkl	d	hkl
7.742	93	002					
3.870	76	004					
3.106	100	100	3.093	100	10 $\bar{1}$	3.11	111
3.046	85	101					
2.882	12	102	2.751	34	01 $\bar{4}$	2.70	002
2.662	48	103					
2.582	13	006					
2.423	26	104	2.279	36	01 $\bar{7}$		
2.193	52	105	2.131	8	018		
1.985	8	106					
1.937	3	008					
1.803	90	107	1.870	23	1010	1.83	022
1.794	72	110	1.799	27	110		
1.747	9	112	1.754	23	0111/113		
1.644	3	108	1.633	14	116	1.64	113
1.553	9	200				1.56	222
1.545	10	201					
1.523	1	202					
1.487	6	203					
1.473	11	116					
1.441	4	204					
1.388	9	205				1.37	004
1.331	2	206					
1.316	4	118					

^a Reference 12b. ^b Reference 13. ^c Always formed in the presence of Ga_2S_3 .

a vapor phase process. We describe herein the formation of a new metastable cubic phase of gallium sulfide by the low temperature MOCVD deposition using the cubane precursor $[(t\text{-Bu})\text{GaS}]_4$.

$[(t\text{-Bu})\text{GaS}]_4$, which is a white air-stable solid, is introduced into a horizontal laminar flow Pyrex MOCVD system¹⁰ operated at atmospheric pressure. Argon was used as the carrier gas at 1 L min^{-1} through a resistively heated zone. Deposition studies were carried out between 380 and 550 °C with the precursor heated to 225 °C.

Deposition was carried out on a variety of substrates, including, borosilicate glass, p-type (100) oriented silicon, KBr, GaAs, and Mo transmission electron microscopy (TEM) grids. No appreciable difference in the film morphology as a function of substrate was noted. The coating adhered well to all substrates (Scotch Tape test).

Rutherford backscattering (RBS) analysis (2.5 MeV He^{2+}) was performed on films deposited on Si wafers. A film thickness of ca. 2800 Å for 16 h deposition time indicated a deposition rate (if a linear deposition rate is assumed) of the order of 0.05 Å s^{-1} . TEM analysis¹¹ of the films was enabled by the production of electron transparent (<1000 Å) films by a short duration (~1 h) deposition onto Mo grids and/or KBr single-crystal plates. (On immersion in deionized water the films float off easily and may then be scooped onto standard TEM grids for observation.)

The microstructural features and chemical composition of the deposited films were observed to be dependent on the temperature in the hot-walled reactor. Films deposited at ca. $380 \pm 10 \text{ °C}$ were largely amorphous as evidenced by electron diffraction and were of the chemical composition Ga:S in a ratio of ca. 1:1 (50:50, ± 2) as indicated by energy dispersive X-ray (EDX) analysis (N.B. light elements $Z < 11$ could not be detected in this system). Films deposited at $400 \pm 10 \text{ °C}$ again displayed Ga and S in a

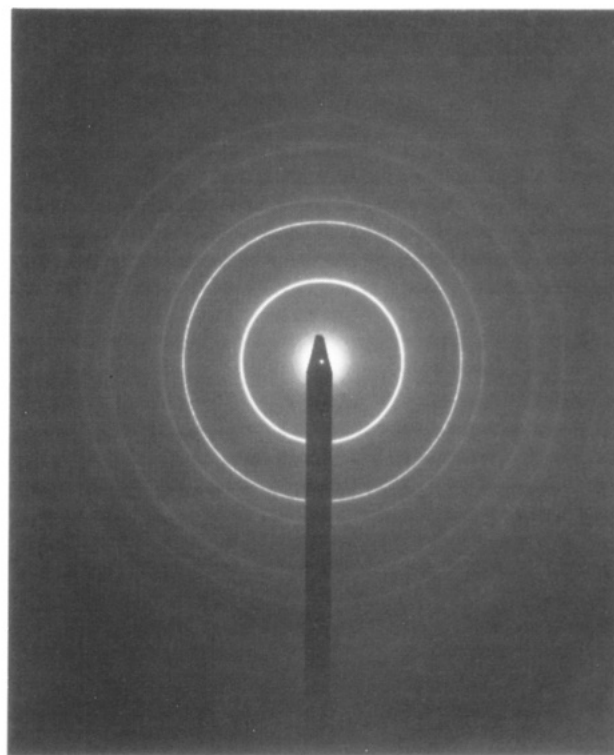


Figure 1. Selected area diffraction pattern of GaS film. N.B. rings of low intensity are barely visible on micrograph.

ratio of ca. 1:1 and, furthermore, gave the resulting diffraction pattern shown as Figure 1. Table I gives the calculated interplanar d spacings from this pattern and the corresponding peak assignment assuming a face-centered cubic (fcc) lattice with a lattice parameter $a = 5.37 \text{ Å}$ (expected peak positions are also included for comparison). While noting the coincidence of peak positions with those of the known phases of GaS, it must be pointed out that our electron diffraction patterns display well-defined rings, indicative of a randomly oriented polycrystalline sample. The large number of expected peaks not observed

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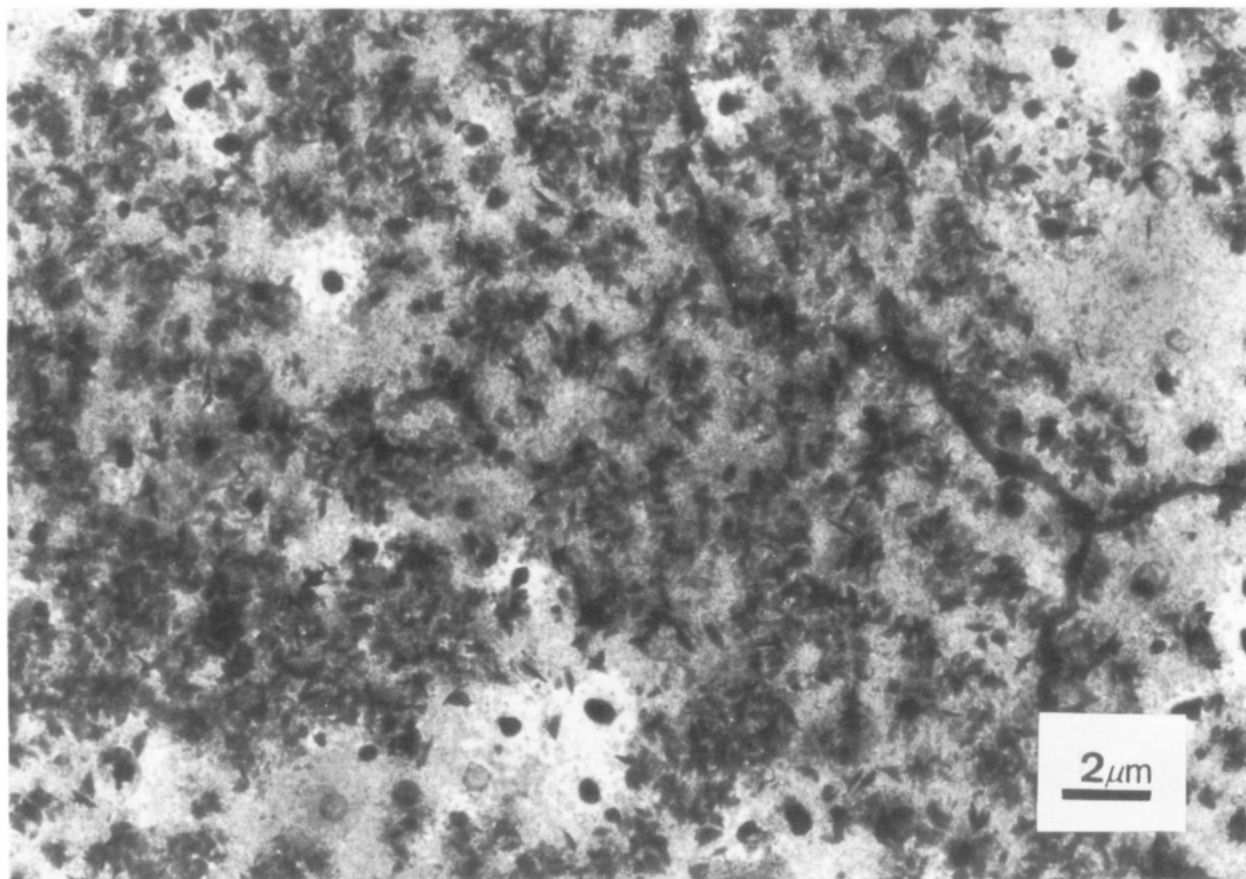
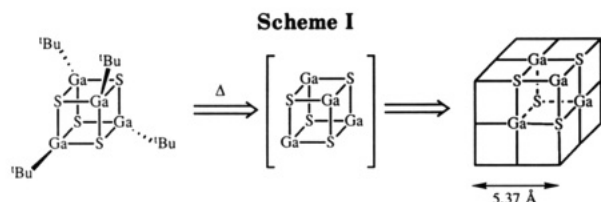


Figure 2. Bright-field image of GaS film. Note dark "growth plumes" in film.



(see Table II) essentially disallows the known phases as being present in the films. In contrast, all the peaks expected from the proposed fcc structure are the sole reflections observed. The diffraction pattern thus obtained is not consistent with the presently known hexagonal¹² and rhombohedral¹³ GaS (or Ga₂S₃) phases.¹⁴ The interpretation and significance of this will be detailed later. The corresponding microstructure of the film deposited at 400 ± 10 °C is shown in Figure 2. It is interesting to note the large number of "growth plumes" evident, indicative of the evolution of a structure from the prior amorphous matrix. Films deposited at higher temperatures, 450 ± 10 °C and 500 ± 10 °C, were found to suffer considerable sulfur loss resulting in the deposition of an amorphous gallium matrix containing between 0 and 20% sulfur.

The formation of this previously unreported cubic phase of GaS may readily be explained in terms of retention of the cubane precursor core in the deposited film (Scheme I). This distorted cubic core [Ga-S-Ga = 82.1 (1)°, S-Ga-S = 97.3 (1)°] presumably "relaxes" under appropriate conditions in the deposited film and begins to rearrange into a cubic lattice. The resultant structure would thus

be expected to be an NaCl-type lattice exhibiting face-centered cubic reflections, as is observed.

X-ray photoelectron spectroscopy (XPS)¹⁵ was utilized to analyze the quality of deposited films and indicated the total absence of both carbon¹⁶ and oxygen after a short argon ion sputter process designed to remove adventitious hydrocarbons and surface oxidation products. The Ga 2p^{3/2} and Ga 2p^{1/2} peaks were recorded at 105.24 and 108.67 eV, respectively (calibrated to Au 4f^{7/2} at 84.0 eV). This is a lower binding energy than has been reported elsewhere¹⁷ for GaS (106.2 and 108.6 eV) or Ga₂S₃ (106.8 and 110.4 eV). It is of worthy note that the XPS analysis resulted in degradation of the film as evidenced by a marked sulfur loss on exposure to the photon (X-ray) beam.

It is clear from these results that a new metastable GaS phase has been deposited from a predesigned molecular motif. Work is in progress to understand the mechanism of film formation and its subsequent transformation to the thermodynamically stable phase.

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(16) Transmission IR spectral analysis of the deposited films indicate the absence of both C-H and Ga-H stretching bands, consistent with the high film purity. An approximately 2000 Å thick film was deposited at 400 °C onto an NaCl infrared plate and transferred under inert atmosphere to an FT-IR spectrometer. The obtained spectrum (4000–700 cm⁻¹) showed no evidence for Ga-H or Ga-H₂ stretches previously reported (2070 and 1930 cm⁻¹, respectively). Similarly, no C-H stretches were observed (2000–2500 cm⁻¹); see Kouvetakis, J.; Beach, D. B. *Chem. Mater.* **1989**, 1, 476.

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Mercury Intercalates of Titanium Disulfide: Novel Intercalation Compounds

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Relatively little is known about the intercalation of mercury into transition metal dichalcogenides (TMDs),^{1,2} even though the high volatility of Hg relative to other metallic intercalants¹⁻⁶ and its ability to form clusters⁷⁻¹⁴ suggest that the properties of these materials may be interesting. Therefore, this initial study was undertaken to help elucidate the reaction chemistry, thermal behavior, and structural features of this relatively unexplored system. As described below, we have found that Hg_xTiS_2 is indeed an unusual intercalation compound in all these respects.

Nearly stoichiometric TiS_2 ($\text{Ti}_{1.002}\text{S}_2$) was used as the host.¹⁵ Triply distilled Hg (<5 ppm foreign metals) and

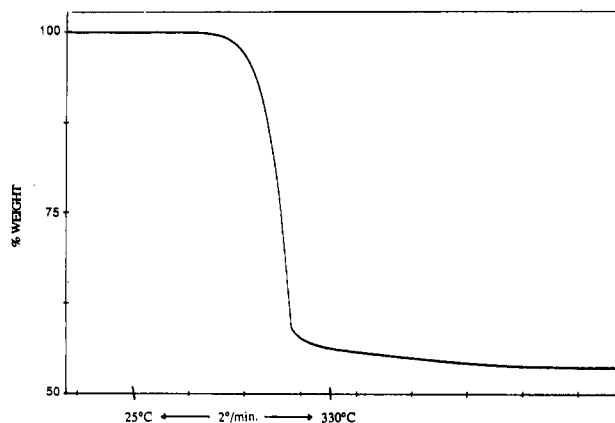


Figure 1. TGA of $\text{Hg}_{0.48}\text{TiS}_2$ using argon as the flow gas.

TiS_2 were loaded into quartz ampules in a drybox, evacuated to $<10^{-4}$ Torr at -196°C , and flame sealed. The gradual uptake of Hg by the host is apparent at ambient temperature. Samples were homogenized by annealing for 2 days at 320°C , followed by slow cooling to ambient temperature.

Sample compositions ($x = 0.27, 0.48, 0.75, 1.03, 1.25$, and 1.29 for Hg_xTiS_2) were determined by thermogravimetric analysis (TGA) with a $40\text{ cm}^3/\text{min}$ argon flow. It is interesting to note that the compositional limit of $x = 1.29$ corresponds to that expected if hexagonally-close-packed elemental Hg monolayers completely fill the guest layers.

Both TGA and X-ray powder diffraction (XPD) demonstrate the thermal reversibility of the intercalation process. TGA of Hg_xTiS_2 shows that Hg begins to slowly deintercalate at about 170°C , and substantial deintercalation occurs only above 250°C and is complete at 330°C (Figure 1). This behavior is distinct from elemental Hg, which volatilizes above 90°C . TGA of the oxidation of the regenerated host at 900°C reveals that it has essentially the same stoichiometry as the original host.^{15,16} XPD of the deintercalated host indicates that it is also similar structurally to the original host. A slight expansion in c (0.003 \AA) and some peak broadening were observed for the regenerated host, which can be attributed to slight disorder in host-layer registry.¹⁶

The XPD patterns observed for Hg_xTiS_2 , where $1.29 \geq x \geq 1.00$, are almost identical and are characteristic of stage-one monolayer compounds having a 2.96-\AA occupied layer expansion. For example, the diffraction pattern for $x = 1.25$ can be primarily indexed to a monoclinic unit cell, with $a = 5.9209(8)\text{ \AA}$, $b = 3.4074(9)\text{ \AA}$, $c = 8.8662(12)\text{ \AA}$, and $\beta = 102.352(14)^\circ$, suggesting a change from AB to ABC sulfur stacking during intercalation. This indexing of the pattern accounted for 28 of the observed 38 reflections, which includes all of the major peaks as well as the first seven $(00l)$ reflections. This cell can be viewed as a slight monoclinic distortion of a trigonal unit cell, with an 8.66-\AA layer repeat distance. However, the above fit for $x = 1.25$ does not take into account reflections from an incommensurate Hg sublattice, which may be the origin of the 10 extra, relatively weak, reflections. Such incommensurability is indicated by the unusual composition observed for the fully intercalated stage-one compound ($\text{Hg}_{1.29}\text{TiS}_2$), where there are insufficient guest sites (one per Ti) to accommodate all of the guest species.

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