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Chemical Vapor Deposition of Gallium Sulfide Thin Films

Seigi Suh and David M. Hoffman*

Department of Chemistry and Materials Research Science and Engineering Center, University of Houston, Houston, Texas 77204

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The compound $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$, a thermally stable solid with a low melting point, was used as a single-source precursor to gallium sulfide films in a low-pressure chemical vapor deposition process. Film depositions were carried out at substrate temperatures in the range 350−610 °C. The films were determined to have a Ga_2S_3 stoichiometry by Rutherford backscattering and energy-dispersive X-ray spectrometries. X-ray diffraction studies showed that the films deposited on glass, silicon, and YSZ (111) substrates were composed of γ-Ga_2S_3, α-Ga_2S_3, and highly oriented γ-Ga_2S_3, respectively.

Introduction

Gallium sulfide is currently of interest as a surface passivation material for GaAs,[1−4] and alkaline earth thiogallates, such as cerium-doped $Sr_2Ga_2S_5$, are promising materials for phosphor thin films in electroluminescent displays.[5−9] Chemists have contributed significantly to this area of research by synthesizing new molecular precursors to gallium sulfide and using the new precursors to prepare gallium sulfide films by chemical vapor deposition (CVD).

Barron and co-workers, for example, reported the atmospheric pressure CVD of cubic GaS from $[(t\text{-Bu})GaS]_4$, a molecule with a cubane-type structure.[10−13] They proposed that the formation of cubic GaS was influenced by the cube-based structure and the 1:1 Ga-to-S stoichiometry of the precursor. The same group also described the deposition of GaS with a distorted hexagonal wurtzite structure from $(t\text{-Bu})_2Ga(S_2CNMe_2)$.[14] More recently, O'Brien and co-workers reported the deposition of highly oriented cubic GaS films on glass by aerosol-assisted CVD using the complex $Ga(SOCNEt_2)_3$ as precursor.[15] Barron and co-workers also reported the atmospheric pressure CVD of amorphous Ga_2S_3 films at 475 °C and hexagonal GaS films at 400 °C from $[(t\text{-Bu})_2Ga(S\text{-}t\text{-Bu})]_2$.[13] The deposition of crystalline Ga_2S_3 films by CVD was first reported in 1995 by Smith et al.,[9] who prepared β-Ga_2S_3 by low-pressure CVD from $GaEt_3$ or $Ga(thd)_3$ and H_2S. Shortly thereafter, Hampden-Smith and co-workers[16] reported the preparation of α-Ga_2S_3 films by aerosol-assisted CVD from $Ga(SCOMe)_2Me(dmpy)$ and $Ga(SCOMe)_3(dmpy)$ (dmpy = 3,5-dimethlpyridine). Finally, O'Brien and co-workers recently described using $Ga(S_2CNMeHex)_3$ to deposit α-Ga_2S_3 films on GaAs(111) substrates at 500 °C by low-pressure CVD.[17]

As part of general synthetic studies leading to homoleptic group 13 alkoxide (Ga, In) and alkanethiolate (Al, Ga, and In) complexes,[18−22] we have synthesized gallium isopropyl thiolate, $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$.[21] This compound appeared to be a practicable gallium sulfide precursor in a conventional CVD process because of its ease of synthesis and desirable physical properties. In this paper, we describe the low-pressure chemical vapor deposition of high-quality α-Ga_2S_3 and γ-Ga_2S_3 films from $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$. The preparation of γ-Ga_2S_3 films has not been reported previously.

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Experimental Section

Film Deposition. Depositions were performed using a simple hot-wall home-built horizontal low-pressure chemical vapor deposition system equipped with mass flow controllers. The deposition chamber was constructed from 38 mm o.d. quartz tubing. A home-built tube furnace surrounded the reactor where the substrate platform rested. The substrate platform was made from a 9 cm length of 18 mm diameter molybdenum rod that had been cut in half lengthwise. The half-rod was milled so that it tapered from ~1 mm thick near the reactor inlet to 9 mm over a length of 5 cm. The deposition temperature was measured by using a thermocouple. Thermal contact between the substrate and the substrate platform was maintained by using silver paste.

The precursor container was maintained at 63−65 °C, a temperature at which the precursor was a liquid. During depositions, three different sections of the precursor feed lines were maintained at temperatures ranging from 95 to 150 °C. The argon (UHP grade) carrier gas flow rate through the precursor bubbler was 400 sccm. After passing through the bubbler, the precursor/argon mixture was diluted with more argon (800 sccm) before entering the reactor. The typical deposition pressure was 1.0−1.1 Torr. Silicon substrates (Si(100)) with dimensions of approximately 1.5 cm × 2.0 cm were prepared for the film depositions by washing them with hexanes and then methanol before blow drying with a nitrogen stream. The glass and quartz substrates (1 mm thick) were prepared by washing them with soap, rinsing with distilled water and then methanol, and finally blow drying with a nitrogen stream.

Film Characterization. X-ray diffraction (XRD) studies were performed using Siemens D5000 diffractometers (Cu Kα radiation; 0.01° step size), and X-ray photoelectron spectroscopy (XPS) studies were carried out using a system (Physical Electronics PHI 5700 ESCA) equipped with a 5 keV Ar^+ sputter gun. The electron-energy analyzer was referenced to the Au $4f_{7/2}$ line at 84 eV. X-ray photoelectron spectra during depth profile analyses were collected using a standard Al Kα source. The width was set at 11.75 eV throughout. The base pressure was 2×10^{-8} Torr during sputtering. After sputtering into the bulk, spectra were collected using a monochromated Al source at a pass energy of 11.75 eV. The base pressure was below 10^{-9} Torr. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) data collection was accomplished using a JEOL JSM-6330F instrument. The film thicknesses used in the growth rate calculations were obtained from SEM cross-sectional views. Transmittance spectra were collected on a Varian Carry 8452A diode array spectrophotometer. Rutherford backscattering spectrometry (RBS) data were collected by Dr. Yongqiang Wang at the Ion Beam Analysis Facility, University of Minnesota. The beam was 2 MeV $^4He^+$, and the total charge collected for the spectrum was 10 μC at 10 nA. The RBS detector (fwhm = 18 keV, Ω = 4.16 msr) was located at 165°. The backscattering data were analyzed locally by using the commercial program RUMP.

Results and Discussion

Gallium isopropyl thiolate, $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$,[21] was used as the film precursor in this study. This compound combines several attributes that make it an excellent precursor candidate. It has, for example, a low melting point (59−60 °C), and therefore it can be converted easily to a liquid in a conventional bubbler assembly. The use of liquid precursors is preferred to solids in CVD processes because liquids can be delivered inexpensively at a uniform rate to the reactor by using simple bubblers and mass flow controllers. Importantly, $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ can be distilled without decomposition, which also ensures uniform delivery to the reactor, and it is only moderately air sensitive, which makes precursor handling simple. In addition, $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ is synthesized easily in moderate yield from inexpensive reagents (eq 1), and it can be purified by vacuum distillation.[21]

Table 1. Compositions and Growth Rates of Films Deposited at Various Temperatures on Silicon from $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$

deposition *T* (°C)	S/Ga[a]	growth rate (Å/min)[b]
350	1.47	70
400	1.48	82
450	1.48	89
500	not measured	94
550	1.48	97
610	1.48	93

[a] From RBS spectra. The error is estimated to be ±0.05. [b] Thicknesses obtained by cross-sectional SEM. The error is estimated to be ±5%.

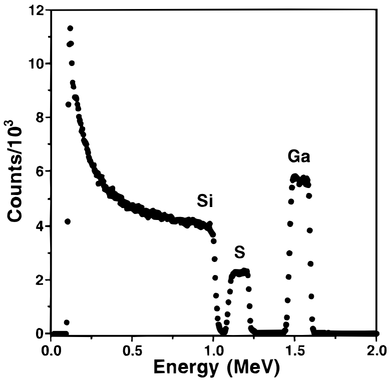

Figure 1. Rutherford backscattering spectrum for a Ga_2S_3 film (≈2250 Å) deposited on silicon at 400 °C.

$$GaCl_3 + 3LiN\text{-}i\text{-}Pr_2 \rightarrow Ga(N\text{-}i\text{-}Pr_2)_3 \xrightarrow{\text{excess } i\text{-PrSH}} [i\text{-}Pr_2NH_2][Ga(S\text{-}i\text{-}Pr)_4] \xrightarrow[\text{vacuum}]{70\ °C} [Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2 \quad (1)$$

Low-pressure CVD using $[Ga(S\text{-}i\text{-}Pr)_2(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ as a single-source precursor gave shiny films at substrate temperatures of 350−610 °C. Film compositions and growth rates are presented in Table 1.

Rutherford backscattering spectrometry spectra for films deposited at 350, 400, 450, 550, and 610 °C on silicon (e.g., Figure 1) indicated that within experimental error they each had a stoichiometry of Ga_2S_3. Carbon and oxygen peaks were not observed in any of the spectra, indicating low carbon and oxygen contamination levels (<1 atom %). Consistent with the RBS results, EDS analyses for the films deposited on silicon at 400 and 550 °C indicated they were composed of material having S/Ga ratios in the range of 1.43−1.47 (three separate areas of each film were selected for analysis).

X-ray photoelectron data for the films deposited at 350, 400, and 550 °C on silicon indicated there was carbon and oxygen on the surface of the films, but virtually no carbon or oxygen was detected after sputtering into the bulk. An X-ray photoelectron spectrum for a film deposited on silicon at 400 °C recorded after sputtering for 5 min is shown in Figure 2. The peaks at 108.43 and 105.10 eV are assigned to Ga $3p_{1/2}$ and $3p_{3/2}$ transitions, respectively. These values are lower than those reported previously for Ga_2S_3 (110.4 and 106.8 eV)

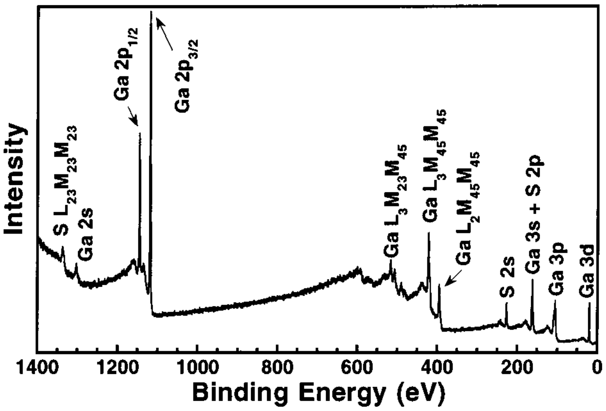

Figure 2. X-ray photoelectron spectrum of a Ga_2S_3 film deposited at 400 °C after argon ion etching.

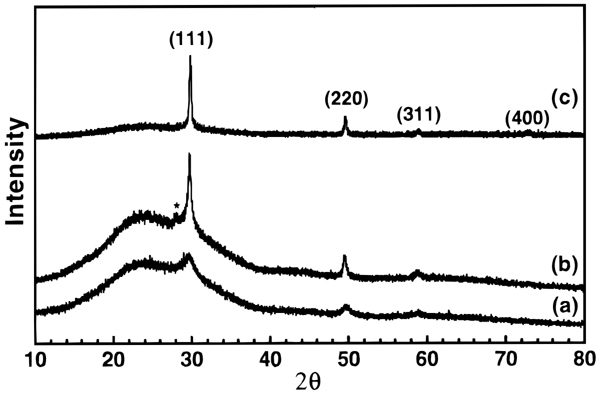

Figure 3. X-ray diffraction patterns for films deposited on glass at 400 (a), 500 (b), and 610 °C (c). The hump at low angle is due to the glass substrate.

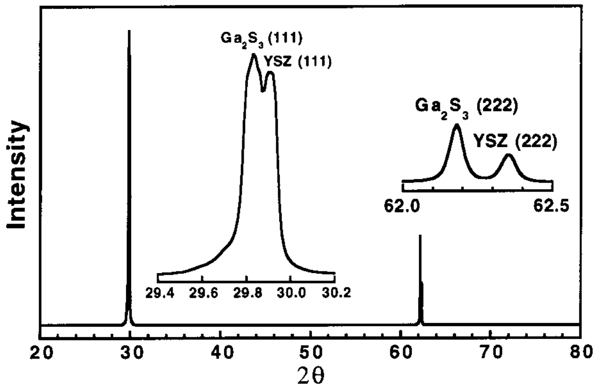

Figure 4. X-ray diffraction pattern for a film deposited on YSZ (111) at 610 °C. The insets show the detail in the peak regions.

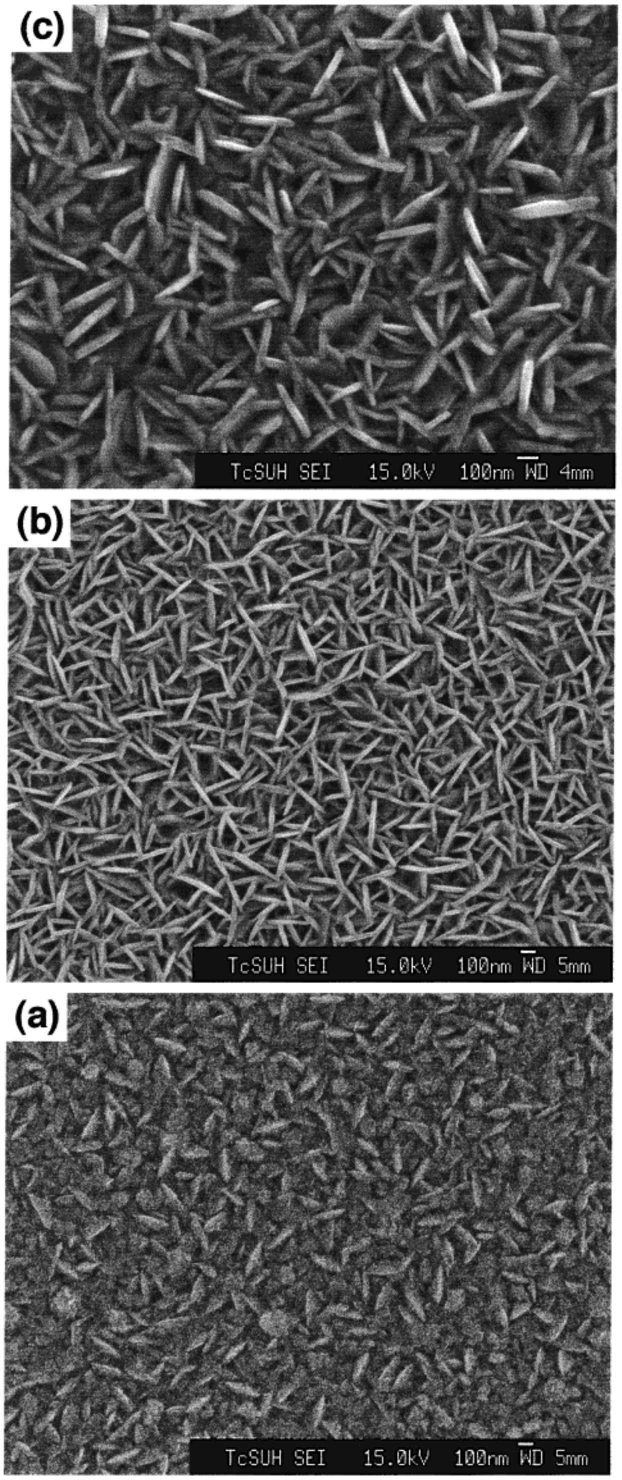

Figure 5. Scanning electron micrographs of Ga_2S_3 films on silicon at 400 (a), 500 (b), and 610 °C (c).

and “Ga_2S_2” (108.6 and 106.2 eV),[23] but close to the values of 108.67 and 105.24 eV given by Barron et al. for a GaS film deposited from $[(t\text{-Bu})GaS]_4$.[11,12]

Film growth rates, which were calculated from film thicknesses obtained from cross-sectional SEM views, increased from 70 Å/min at $T_{dep} = 350$ °C to 97 Å/min at $T_{dep} = 550$ °C (Table 1), all at constant bubbler and feed line temperatures. Growth rates were not optimized, but higher growth rates were observed when the bubbler temperature was increased; for example, when the bubbler was heated to 80 °C, the growth rate more than doubled to ≈220 Å/min at $T_{dep} = 550$ °C. These growth rates are higher than those reported for GaS films deposited from $[(t\text{-Bu})GaS]_4$ in an atmospheric pressure CVD process (≈3 Å/min; $T_{dep} = 380-550$ °C; precursor sublimed at 225 °C)[11] and $(t\text{-Bu})_2Ga(S_2CNMe_2)$ (≈6 Å/min; $T_{dep} = 425$ °C; bubbler temperature = 100 °C),[14] but lower than those for α-Ga_2S_3 films deposited from $Ga(S_2CNMeHex)_3$ in a low-pressure CVD process (≈500 Å/min; $T_{dep} > 475$ °C; bubbler temperature = 225 °C).[17]

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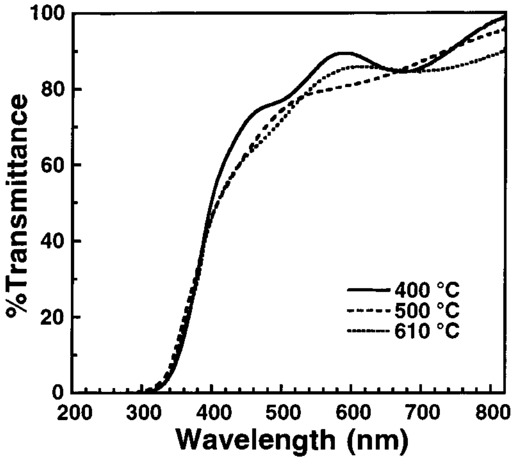

Figure 6. Transmittance spectra for Ga_2S_3 films deposited on quartz at 400, 500, and 610 °C.

X-ray diffraction patterns for 4000−4500 Å films deposited at 400, 500, and 610 °C on glass are shown in Figure 3. The film deposited at 400 °C produced broad peaks, indicating poorly formed crystals, but at the higher deposition temperatures, the peaks sharpened. The films deposited at 500 (Figure 3b) and 550 °C (not shown) consisted primarily of randomly oriented cubic $\gamma\text{-Ga}_2\text{S}_3$ (JCPDS 43-0916). In the films deposited at 500 and 550 °C, a peak was also observed at $2\theta = 27.9°$ (the starred peak in Figure 3b) corresponding to a spacing of 3.20 Å. This peak probably arose from the $(\bar{3}12)$ reflection of monoclinic $\alpha\text{-Ga}_2\text{S}_3$ (JCPDS 30-0577). The X-ray diffraction pattern for the film deposited at 610 °C (Figure 3c) was consistent with cubic $\gamma\text{-Ga}_2\text{S}_3$ having some preferred (111) orientation. Attempts to grow highly oriented cubic $\gamma\text{-Ga}_2\text{S}_3$ (a = 5.17 Å)[14] films on YSZ (111) (a = 5.15 Å)[24] at 550 and 610 °C were successful, as indicated by the diffraction pattern shown in Figure 4.

A scanning electron micrograph for a film (≈3500 Å) deposited at 400 °C on silicon (100) suggested the film surface consisted of randomly oriented poorly defined crystals (Figure 5a). In contrast, 3500 and 2500 Å films deposited on silicon at 500 (Figure 5b) and 610 °C (Figure 5c), respectively, had platelike morphologies with the plates standing on edge with respect to the substrate surface (approximate edge dimensions: 300 × 2400 Å (500 °C) and 350 × 3000 Å (610 °C)). The stoichiometries of these films were confirmed to be Ga_2S_3 by RBS and EDS (see above), but the platelike film morphology suggested that the films were not composed of cubic $\gamma\text{-Ga}_2\text{S}_3$, which was the material deposited on glass substrates. An X-ray analysis of the film deposited on silicon at 610 °C confirmed that it, in fact, was composed of monoclinic $\alpha\text{-Ga}_2\text{S}_3$ and not cubic $\gamma\text{-Ga}_2\text{S}_3$. These results show that the crystalline form of Ga_2S_3 deposited from $[\text{Ga(S-}i\text{-Pr)}_2(\mu\text{-S-}i\text{-Pr)}]_2$ is strongly dependent on the substrate.

Transmission spectra for 2500−3500 Å films grown on quartz at 400, 500, and 610 °C are shown in Figure 6. The % transmittance and absorption edges did not vary appreciably with the deposition temperature. Optical band gaps were calculated from the absorbance data by plotting $(\alpha E)^2$ vs E and extrapolating the linear portion of the curve to $\alpha^2 = 0$, where α is the absorption coefficient and E is the photon energy. At the three deposition temperatures, the band gaps were 3.47−3.48 eV. These values are close to those reported previously for $\alpha\text{-Ga}_2\text{S}_3$ (3.42 eV).[25,26]

Conclusion

Low-pressure CVD using $[\text{Ga(S-}i\text{-Pr)}_2(\mu\text{-S-}i\text{-Pr)}]_2$ as a single-source precursor gave Ga_2S_3 films at substrate temperatures of 350−610 °C. The crystalline form of the gallium sulfide was strongly dependent on the substrate with the deposition producing $\gamma\text{-Ga}_2\text{S}_3$ on glass, $\alpha\text{-Ga}_2\text{S}_3$ on silicon (100), and highly oriented $\gamma\text{-Ga}_2\text{S}_3$ on YSZ (111). These results, coupled with the high thermal stability, high volatility, low melting point, and inexpensive and easy synthesis of the $[\text{Ga(S-}i\text{-Pr)}_2(\mu\text{-S-}i\text{-Pr)}]_2$ precursor, suggest that this is a promising system for the deposition of gallium sulfide films by chemical vapor deposition. Studies that are directed to the synthesis of a more practical liquid precursor analogous to $[\text{Ga(S-}i\text{-Pr)}_2(\mu\text{-S-}i\text{-Pr)}]_2$ and its use to deposit passivating coatings on GaAs substrates are under way.

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