Conf-941016--1

LA-UR- 94-3179

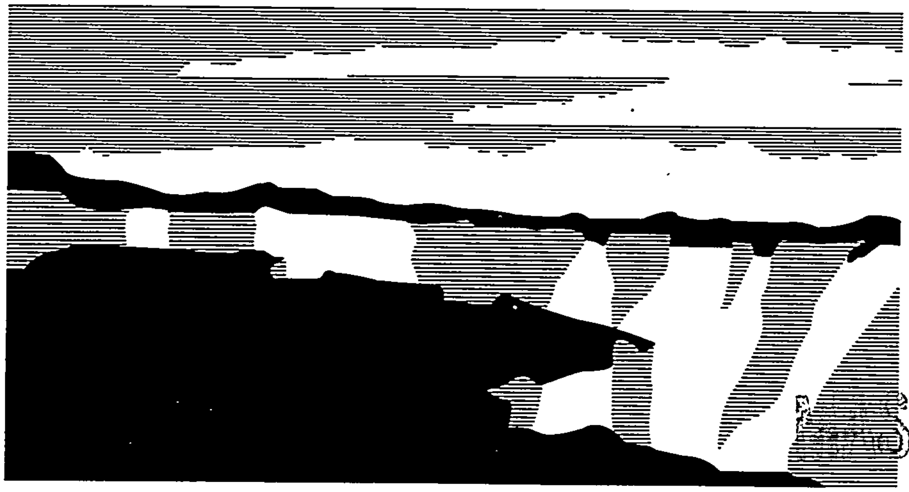
Title: MOCVD OF GALLIUM AND CALCIUM SULFIDES FOR IMPROVED PHOSPHOR PROCESSING

Author(s):
N. M. Peachey, MST-7
J. A. Samuels, MST-7
B. F. Espinoza, MST-7
C. D. Adams, MST-7
D. C. Smith, MST-7
R. C. Dye, MST-7
R. T. Tuenge, Planar
C. F. Schaus, Planar
C. N. King, Planar

Submitted to:
Proceedings of "Novel Techniques in Synthesis and Processing of Advanced Materials"
Rosemont, IL
October 3 - 6, 1994

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.



MASTER

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MOCVD OF GALLIUM AND CALCIUM SULFIDES FOR IMPROVED PHOSPHOR PROCESSING

N. M. Peachey, J. A. Samuels, B. F. Espanoza,
C. D. Adams, D. C. Smith, and R. C. Dye

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

and

R. T. Tuenge, C. F. Schaus, and C. N. King,

Planar Systems, Inc.
Beaverton, OR 97006

Abstract

Recently, doped calcium thiogallate ($CaGa_2S_4$) phosphors have been investigated for use in electroluminescent flat panel displays. The current technique used for the deposition of thin film calcium thiogallate is sputtering. Unfortunately, this requires a high temperature annealing process to provide the desired crystallinity of the phosphor. Recent efforts have focused on the possible use of metal-organic chemical vapor deposition (MOCVD) to produce the $CaGa_2S_4$ layer. The use of MOCVD provides an attractive alternative to sputtering since it does not require heating above the melting temperatures of the glass substrates used for the display panels. To accomplish this, the deposition of both Ga_2S_3 and CaS is investigated as these compounds are intermediate steps in the development of the phosphor deposition. Uniform, crystalline films of both Ga_2S_3 and CaS were deposited and the process shows promise for successful deposition of the $CaGa_2S_4$ phosphor.

Introduction

The lack of a satisfactory blue phosphor having sufficiently high luminances at low power has hampered the development of high resolution flat panel displays. Recently, a new series of blue emitting materials have been investigated for use in thin film electroluminescent (TFEL) devices.[1,2,3] These phosphors are based on a series of alkaline earth thiogallate host materials of the form MGa_2S_4:RE where M can be either calcium, strontium, zinc, or barium and RE is a rare earth ion. A full-color VGA TFEL panel using $CaGa_2S_4$:Ce as the blue phosphor has recently been fabricated and tested.[1] This FPD provided a luminance of 10 cd/m^2 at 60 Hz. The enhanced blue in this display allowed its color capabilities to approach those of the conventional CRT.

The method of depositing the phosphor onto the display panels in these test devices has been sputtering. Unfortunately the phosphor as deposited does not possess the crystalline properties required for optimum luminance. The crystalline structure is achieved by subsequent annealing of the deposited material. Although this post deposition anneal provides the desired crystal structure, it occurs above the melting temperature of ordinary glass. Consequently, the implementation of these phosphors requires the use of glasses capable of withstanding high temperatures, adding to the cost of the final display unit.

To circumvent this problem, other deposition techniques are being considered for the phosphor. One method under consideration is metal-organic chemical vapor deposition (MOCVD). This technique offers several advantages. First, it is a method in which rather complex thin film structures can be routinely deposited. Not only can the stoichiometry of the coating be controlled, but crystalline films can be obtained at deposition temperatures below 600°C. Second, the simple apparatus and reasonably high deposition rates also makes MOCVD attractive as a manufacturing processes. Consequently, this technique is promising as an alternative technique to obtain crystalline phosphors.

Calcium thiogallate has been previously investigated as a possible phosphor for conventional CRT screens.[4] This compound was formulated by grinding together stoichiometric amounts of the appropriate alkaline earth carbonates and rare earth oxides and heating the mixture in a hydrogen sulfide environment at around 1000°C. More recently, calcium thiogallate was synthesized by heating a stoichiometric mixture of Ga_2S_3 and CaS to 1400°C.[5] This research suggests that a possible approach for the MOCVD of the calcium thiogallate may be the controlled codeposition of Ga_2S_3 and CaS. To achieve this, the deposition of Ga_2S_3 and CaS were investigated separately.

Since the crystallinity of the calcium thiogallate resulting from the codeposition is an important issue, the crystallinity of the MOCVD films of the Ga_2S_3 and CaS precursors are also of interest. Ga_2S_3 displays a rather rich polymorphism in which the basic hexagonal arrangement of the sulfur atoms is largely unchanged. The various polymorphs arise from the differing placements of the gallium atoms and vacancies within the lattice. Two of the room temperature phases (α and β) are hexagonal while a third (α') is monoclinic. CaS has only one morphology, that of a face-centered cubic lattice. Both of these lattices are dominated by the structure of the sulfur atoms. Not surprisingly, the $CaGa_2S_4$ lattice is also defined by the sulfur arrangement.[4]

There have been few reported attempts at MOCVD of Ga_2S_3 and none which yielded crystalline material on amorphous substrates such as glass. Barron *et al.* report the MOCVD growth of Ga_2S_3 only as an undesirable product in an attempt to obtain cubic GaS.[6] In these depositions, when it was obtained the Ga_2S_3 was amorphous. Furthermore, the MOCVD and metalorganic molecular beam epitaxy[7] of gallium sulfide yielded low growth rates. Thus the successful implementation of gallium sulfide in the synthetic process of calcium thiogallate requires the consideration of both the possiblity of crystalline growth on amorphous substrates and the improvement of growth rates.

We report the MOCVD of both Ga_2S_3 and CaS. To the best of our knowledge, this is the first reported MOCVD of CaS. The experimental apparatus and analytical techniques are described followed by a discussion of the growth and crystallinity of the Ga_2S_3 and CaS films. The EL display architecture requires a transparent conductor layer and an insulating dielectric layer between the glass and the phosphor.[4] Consequently, following the successful deposition of the Ga_2S_3 and CaS films on glass, substrates having these underlayers were used. The deposition parameters of both compounds were investigated to provide the necessary control to produce the calcium thiogallate.

Experimental

The triethyl gallium ($GaEt_3$) and calcium bis-tetramethyl heptandionate ($Ca(TMHD)_2$) percursors were purchased from Stren Chemicals. $GaEt_3$ was received in a stainless steel bubbler and was used without futher purification. The $Ca(TMHD)_2$ was freshly sublimed and placed in a cleaned bubbler. All handling of the percursor was carried out in an inert (He) atmosphere. The gallium and calcium percursors were mixed with a carrier gas (argon) prior to entry into the reaction chamber. The hydrogen sulfide (H_2S) gas (99.5% purity) was obtained from Matheson while the ultrapure (99.995%) argon carrier gas was purchased from Air Products. The argon gas was further purified using a Purifilter (Semi Gas Systems) in the gas line prior to entering the precursor bubblers.

Ga_2S_3

The MOCVD of Ga_2S_3 was carried out in a reaction chamber designed specifically for this application. The experimental setup is shown in Figure 1. Eight inch vacuum flanges were used to construct a reaction chamber approximately two inches wide. The dimensions of the chamber were such that 2" X 2" panels mounted parallel to the flanges could easily be coated. Each flange was fitted with a quartz window to allow radiant heating of the substrate by quartz-halogen lamps. The quartz-halogen lamps provided a means of heating the substrates quickly and evenly, both of which are necessary to efficiently manufacture uniform coatings. Since many commercial MOCVD processes incorporate radiant heating, upscaling this process should be rather straightforward. Varying the power supplied to the lamps provided an effective method of controlling the temperature. The substrates were held firmly against a rectangular piece of unpolished silicon cut to the same dimensions as the glass substrates. This prevented deposition on the reverse side of the substrate and aided in heating the glass in preparation for deposition. The chamber pressure was maintained at 5 torr while the precursors used were H_2S and $GaEt_3$. Immediately following deposition, the triethyl gallate flow was reduced to zero while the hydrogen sulfide flow was maintained until the substrates had cooled to below 50°C. This was done to prevent the loss of sulfur from the film during the cooling process. The depositions were done at a variety of substrate temperatures between 450 and 600°C.

CaS

The deposition of CaS was conducted in a horizonal hot-walled reactor shown schematically in Figure 2. This reactor provided a larger degree of temperature control than did the radiant reactor. The $Ca(TMHD)_2$ bubbler, argon carrier gas, and all tubing were heated to prevent condensation of precursor material prior to entry into the chamber. The $Ca(TMHD)_2$ and the H_2S gases entered the reactor mixing zone through separate

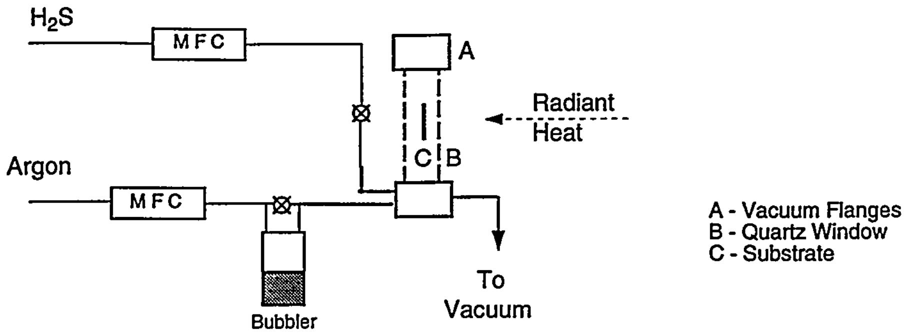


Figure 1. Schematic diagram of the apparatus used in the MOCVD of the Ga_2S_3

inlet ports at flow rates of 200 sccm and 100 sccm respectively. The base pressure of the reactor was maintained at 5 torr. The initial depositions were made on silicon substrates. These substrates were cleaned with distilled water followed by a methanol rinse. They were then heated to deposition temperatures under vacuum. Following the successful deposition of CaS on silicon, glass substrates were used. The substrates were placed at a 45° angle to the incoming reactants. Depositions were carried out over an hour period. These were run with the precursor heated to 220°C and 240°C while the substrate temperatures ranged from 400°C to 600°C. Samples were allowed to cool under a flow of argon to 80°C before being removed from the reactor. CaS was also deposited in the radiant reactor to establish that such depositions were possible.

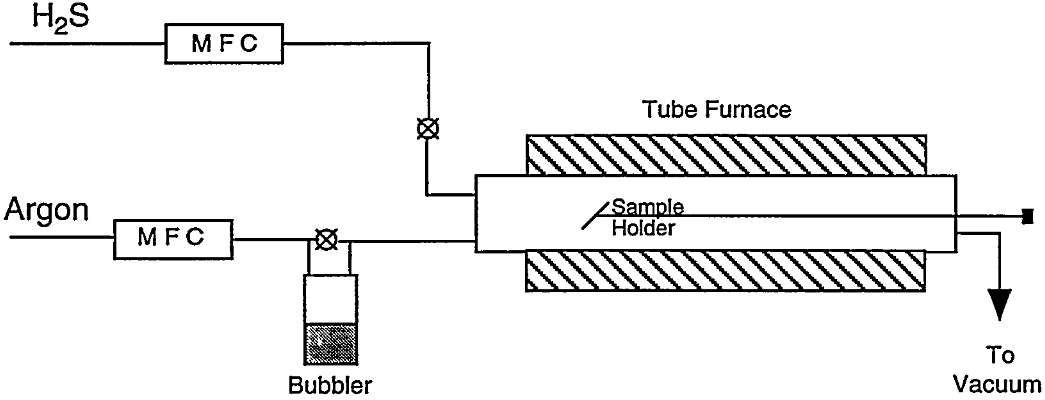


Figure 2. Schematic diagram of the apparatus used in the MOCVD of CaS

Characterization

The thn films were characterized by a variety of techniques. The degree of crystallinity and crystal morphology were established by powder (thin film) X-ray diffraction powder patterns. The samples were continually rotated during the data acquisition. The X-ray diffraction was performed using a Rigaku Rotoflex rotating anode tube utilizing Cu Kα radiation and an Inel CPS 120 position sensitive detector.

The stoichiometry and thickness of the deposited layer was investigated with Rutherford backscattering spectroscopy (RBS). A 2 MeV ion beam ($^4He+$) was used in the RBS analysis. Surface characterization was studied with electron microscopy using a Philips CM30 transmission electron microscope (TEM) and a Jeol JSM-6300FXV scanning electron microscope (SEM). Routine thickness measurements were obtained using profilometry.

Results and Discussion

Ga_2S_3 films deposited on glass substrates could be obtained using a deposition time of two minutes. Although the metal thermocouples in contact with the glass substrate indicated temperatures of approximately 500°C during deposition, it is unlikely that the substrate was actually that hot since it is a much poorer absorber than the metal thermocouple. The glass substrates were backed with unpolished silicon to provide more uniform heating of the substrates and to prevent deposition on the reverse side. The X-ray results for the films indicated a high degree of crystallinity and the pattern corresponded to that of α-phase Ga_2S_3. A typical powder diffraction pattern is given in Figure 3.

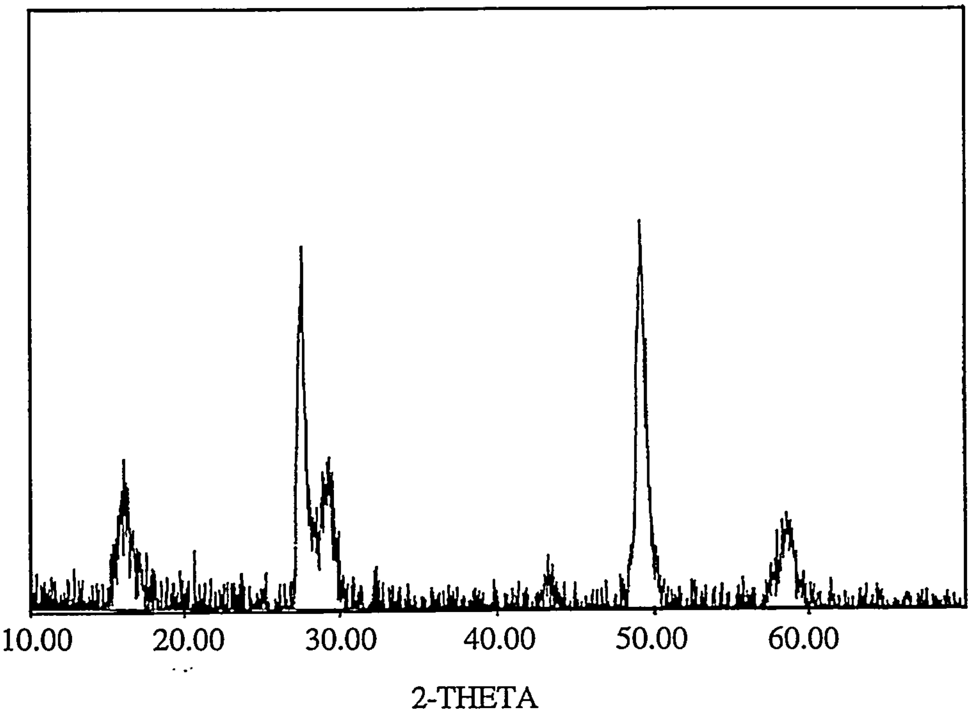
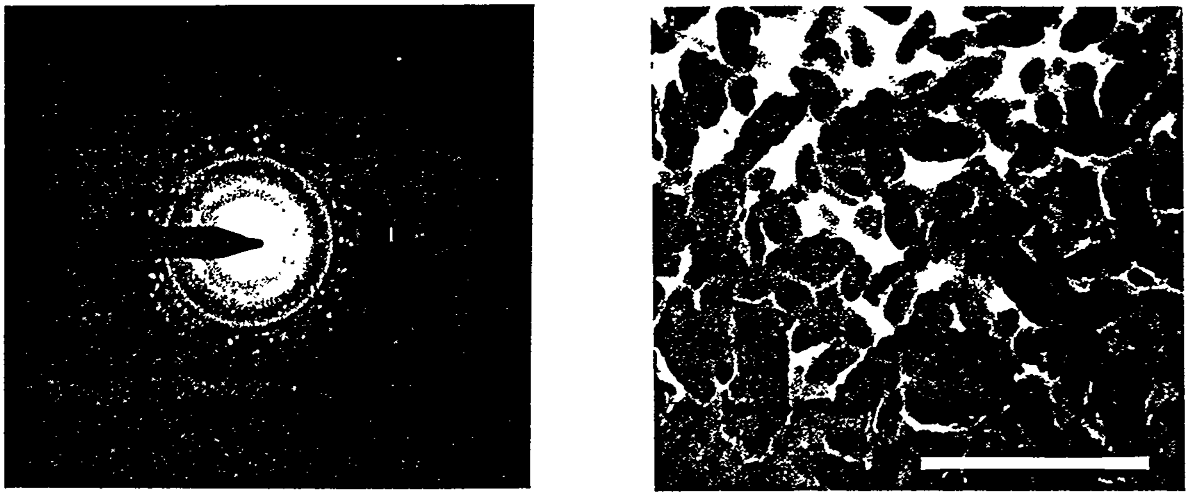


Figure 3. X-ray diffraction powder pattern of Ga_2S_3 on glass substrate

The TEM results, shown in Figure 4, confirmed the degree of crystallinity of the films, yielding selected area diffraction (SAD) images which contained not only concentric ring patterns indicative of microcrystallites but also distinct spots from larger crystals (Figure 4a). These films consisted of granular material as shown by the TEM images in Figure 4b. The stoichiometry was confirmed to be Ga_2S_3 by RBS and the thickness of the films was found to vary between 14,000 and 500 Å depending on the deposition conditions. No residual carbon was detected by the RBS. A typical RBS spectrum is shown in Figure 5. These deposition rates are considerably higher than those reported earlier.[6,7]

Following the successful deposition of Ga_2S_3 on glass substrates, gallium sulfide was deposited on glass having the conductive and dielectric layers suitable for FPDs. These substrates were again backed with an unpolished silicon wafer. The deposited films showed the same morphology and crystalline characteristics of those on the glass slides. A cross-section TEM (Figure 6a) shows the columnar structure of the Ga_2S_3 on the TFEL panel glass. No amorphous ring is observed in the selected area diffraction pattern of this film indicating that the films are highly crystalline (Figure 6b).



(a) (b)

Figure 4. (a) Selected area diffraction of the Ga_2S_3 as deposited on the glass substrate. (b) A bright field image of the grains comprising the film. Distance marker denotes 500 nm.

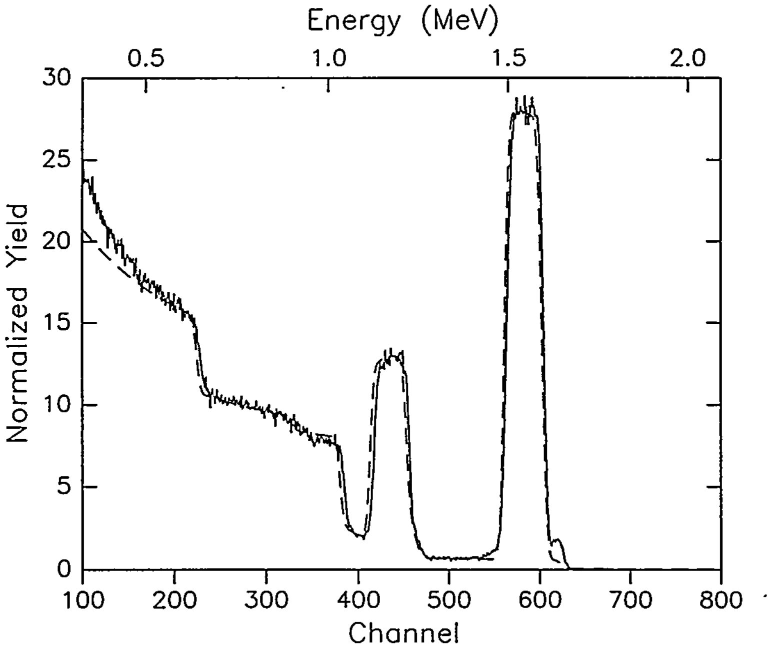
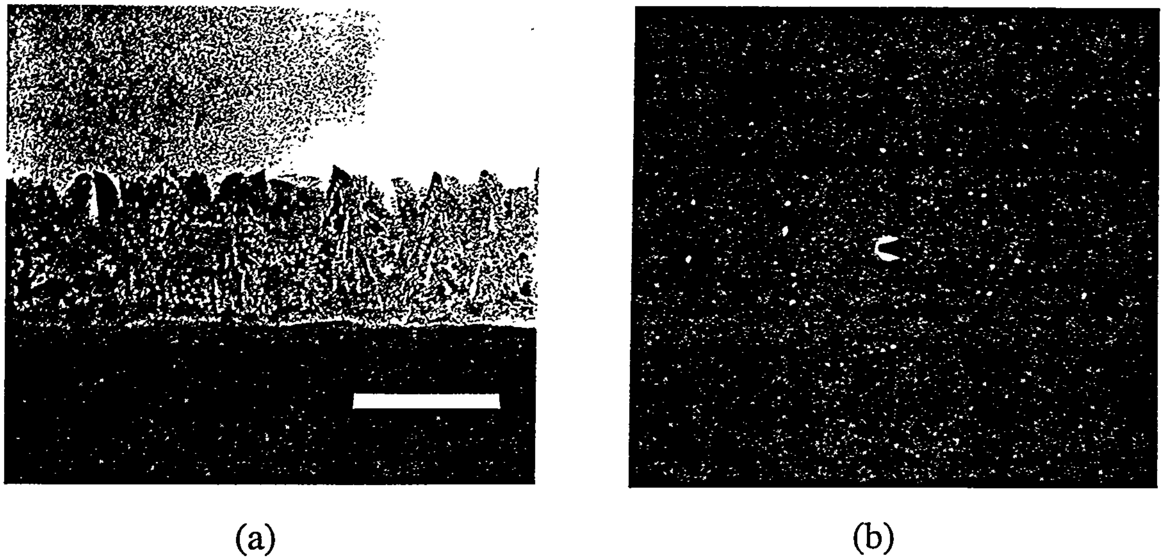


Figure 5. Rutherford backscattering spectrum of Ga_2S_3 on glass. Solid line (—) is the experimental spectrum, dashed line (--) is the calculated spectrum

More controlled deposition of Ga_2S_3 was achieved by reducing the precursor flows into the reaction chamber. Consequently, subsequent depositions were made on the panel glass keeping the hydrogen sulfide flow at 100 sccm and argon carrier gas flow through the triethyl gallate at 10 sccm. Observing that the best films on the glass blanks were grown at around 500°C, a series of depositions were attempted on the panel glass at temperatures higher than 500°C. The deposition time for all of these films was 30 minutes. The results, listed in Table I, show that film growth decreases with increasing temperature in this temperature region. However, X-ray diffraction line-width analysis indicated that the crytallinity is largely unchanged.

Table I. Deposition thickness of Ga_2S_3 at several different temperatures

Substrate Temperature (°C)	Film Thickness (µm)
570	0.47
600	0.37
645	0.33

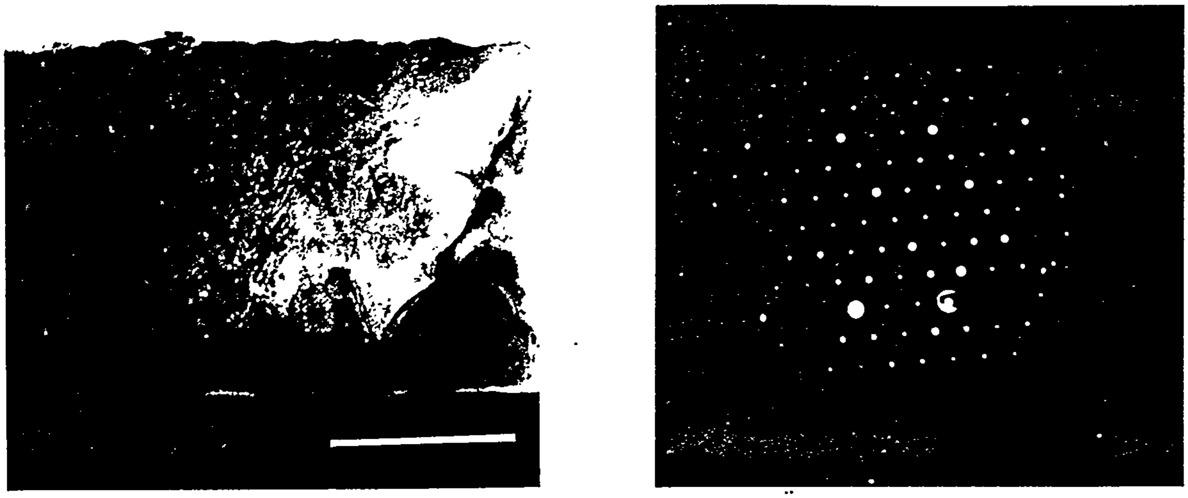

(a)

(b)

Figure 6. (a) TEM cross-section view of Ga_2S_3 on TFEL panel glass. Distance marker denotes 500 nm. (b) Selected area diffraction of the Ga_2S_3 layer.

While it is unclear larger crytallites are necessary for the development of the calcium thiogallate phosphor, post deposition annealing of the Ga_2S_3 does increase crystal size. Several substrates on which the thiogallate was deposited were annealled at approximately 850°C. Cross-section samples of this film were prepared and investigated by TEM. Selected area diffraction of some crystallites provided nearly single crystal diffraction patterns as shown in Figure 7. Dark field analysis showed that the crystals were typically 1000 to 5000Å in length.

The deposition of CaS on either glass or silicon produced a highly crystalline film when the substrate temperatures were maintained between 400°C and 500°C. The X-ray diffraction (Figure 8) demonstrates this crystallinity. Film composition was determined by RBS on a representative sample and yielded a Ca:S ratio of one.



(a) (b)

Figure 7. (a) TEM cross-section view of annealed Ga_2S_3 film on TFEL panel glass. Distance marker denotes 500 nm. (b) Selected area diffraction of the Ga_2S_3 layer.

Table II. CaS film thickness after 1 hour deposition time

Precursor Temperature (°C)	Substrate Temperature (°C)	Film Thickness (µm)
220	400	0.15
220	500	0.16
240	400	0.36
240	500	0.35

Deposition rates of CaS are significantly lower than those of Ga_2S_3. This is primarily due to the lower volatility of the solid $Ca(TMHD)_2$ as compared to the liquid $GaEt_3$. A comparison of film thickness as a function of substrate and precursor temperture is given in Table II. These data show that while film thickness is independent of substrate temperature, the precursor temperature can greatly influence film growth. The fact that at constant deposition time and flow rates, the film thickness is independent of substrate temmperature indicates that precursor transport may be the rate limiting step under these conditions.

Depositions at 600°C produced no detectable film growth at either precursor temperature. This may result from the product forming in the cooler regions of the chamber or, more likely, the substrate temperature is high enough to cause desorption of the precursor before reaction can occur.

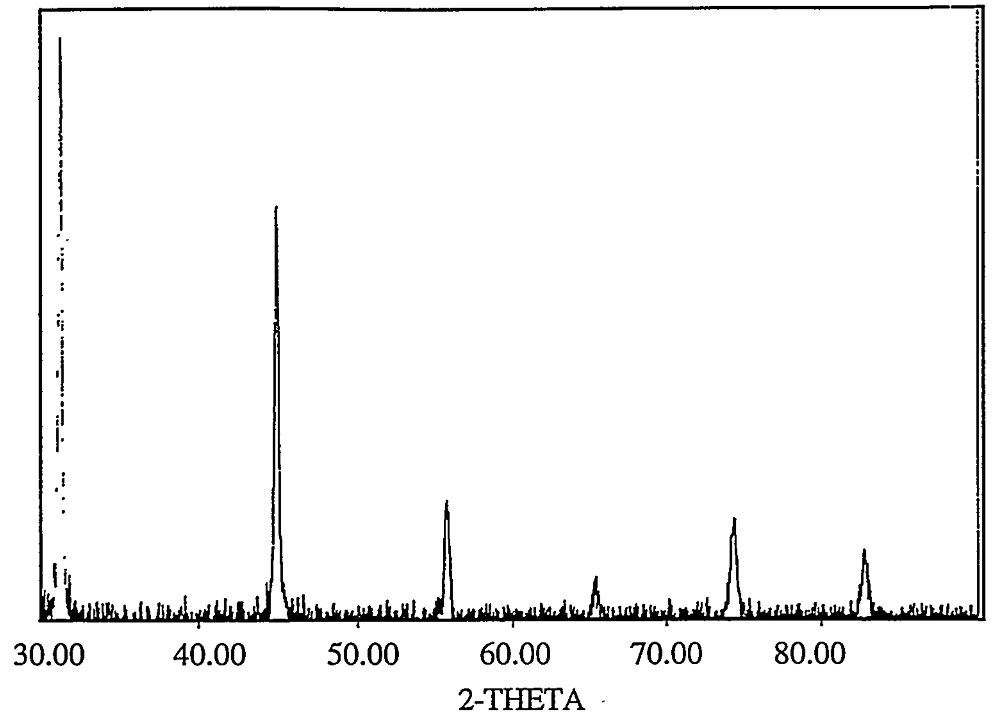


Figure 8. X-ray diffraction powder pattern of CaS on glass substrate.

Conclusions

The objective of this research was to establish the conditions for crystalline deposition of both gallium and calcium sulfides on amorphous substrates. This is in preparation of the crystalline MOCVD deposition of calcium thiogallate phosphors. Highly crystalline Ga_2S_3 films were deposited on FPD panel substrates using the MOCVD process. Furthermore, the growth temperatures were low enough to allow the use of cheaper glass substrates. Raising the temperature of the substrates above approximately 570°C did not improve the Ga_2S_3 crystallinity and yielded a slower growth rate.

The calcium sulfide was also deposited onto amorphous substrates. Like the Ga_2S_3, these films are highly crystalline. Although the growth rates are less than those observed in the Ga_2S_3 deposition, they are nonetheless high enough to be useful commercially. Furthermore, raising the precursor temperature above 240°C will increase the film growth rate.

With the refinement of the MOCVD parameters for the crystalline deposition of Ga_2S_3 and CaS, it is possible to design the stoichiometric codeposition of these materials to form $CaGa_2S_4$. The deposition of Ga_2S_3 can be controlled by varying the flow rate of the $GaEt_3$ precursor. To demostrate this, the precusor flow was cut by half while the substrate temperature was maintained at 570°C. The resulting film had a thickness of 0.22 μm. This is almost half the film thickness observed for the deposition at the same temperature listed in Table I. As shown in Table II, the deposition rate of the CaS can be effectively controlled by varying the precursor temperature. The crystallization of the $CaGa_2S_4$ from a mixture of Ga_2S_3 and CaS has previously been demonstrated.[4] All three compounds are formed from variations of the cubic sulfur structure. The differing compounds result from the arrangements of the cations and accompanying vacancies in the sulfur lattice.

References

---

[1] W. A. Barrow, et al. "A New Class of Blue TFEL Phosphors with Application to a VGA Full-Color Display", SID 93 Digest, 24 (1993) 761-764.

[2] L. V. Pham, et al. "Electrical Characterization of Blue Electroluminescent Devices", SPIE--The international Society for Optical Engineering, ed. P. S. Friedman, 2174 (1994) 190-199.

[3] S. S. Sun, R. T. Tuenge, J. Kane, and M. Ling, J. Electrochem.Soc. in press.

[4] T. E. Peters, and J. A. Baglio, "Luminescence and Structural Properties of Thiogallate Phosphors Ce^{+3} and Eu^{+2}-Activated Phosphors. Part I, J. Electrochem. Soc., 119 (1972) 230-236.

[5] N. I. Yagubov, T. N. Guliev, P. G. Rustamov, and E. T. Azizov, "Interaction Studies in CaS-Ga_2S_3 System", Mat. Res. Bull., 25 (1990) 271-276.

[6] A. N. MacInnes, M. B. Power, and A. R. Barron, "Chemical Vapor Deposition of Gallium Sulfide: Phase Control by Molecular Design", Chem. Mater., 5 (1993) 1344-1351.

[7] N. Teraguchi, F. Kato, M. Konagai, and K. Takahashi, "Growth of III-VI Compunds Semiconductors by Metalorganic Molecular Beam Epitaxy", Japanese Journal of Applied Physics, 28 (1989) L2134-L2136.