Conf-9505157--2

LA-UR- 95-1181

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Submitted to:
Presentation at SID 1995
Orlando, FL
May 1995
Article to appear in SID 1995 Digest

Los Alamos
NATIONAL LABORATORY

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CRYSTALLINE-AS-DEPOSITED CAGA$_2$S$_4$:CE VIA LOW-TEMPERATURE METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

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Abstract

A metal-organic chemical vapor deposition (MOCVD) process for the growth of crystalline-as-deposited cerium doped calcium thiogallate ($CaGa_2S_4$:Ce) at substrate temperatures less than 600°C has been developed. Blue-green electroluminescence was observed with a luminance of ~2 cd/m^2 at 40 volts above threshold using 60 Hz drive frequency. Threshold voltages were approximately 200 V.

Introduction

The feasibility of full-color thin film electroluminescent (TFEL) display panels has recently been demonstrated as a result of the development of a new saturated blue electroluminescent (EL) emitter based on an alkaline earth thiogallate phosphor host.[1] The full-color TFEL displays, however, have not yet reached their potential due to insufficient brightness. A white areal luminance of 30 cd/m^2 was reported for a 320.256 full color TFEL display.[2] This luminance level, which is close to the 35 cd/m^2 ANSI standard for minimum white luminance in display panels has yet to be achieved for the larger VGA-size full color TFEL displays. A luminance improvement by a factor of two is needed in the blue phosphor to meet the white luminance standard for VGA displays.

Nearly all blue thiogallate phosphor work focuses on low-temperature deposition of noncrystalline films with subsequent crystallization by rapid thermal processing (RTP). While thiogallate films readily crystallize at 650°C, luminance increases strongly at higher temperatures.[3] RTP of thiogallate phosphors at temperatures greater than 650°C requires an expensive, high-temperature glass substrate. For color EL displays to be commercially competitive, it is necessary either to find a low-cost, high-temperature glass substrate or to lower the processing temperature. The more technically-feasible route is the latter. One way to reduce the processing temperature is to deposit the thiogallate phosphor in crystalline form. Post annealing can be eliminated by using a metal-organic chemical vapor deposition (MOCVD) approach in which the phosphors are deposited directly in crystalline form.

MOCVD of $CaGa_2S_4$:Ce had not been reported prior to our entry into the field. Based on the phase diagram and the existence of metal-organic precursors for Ga_2S_3-, CaS- and CeS_x-related compounds, it was expected that $CaGa_2S_4$:Ce could be deposited by MOCVD at substrate temperatures of less than 600°C. Our approach to the growth of $CaGa_2S_4$:Ce was to investigate the growth of the subunits of this material, i.e. Ga_2S_3, CaS and CeS_x, and to integrate these processes for the deposition of the phosphor.

GaS and Ga_2S_3 can be deposited from a number of gallium complexes.[4,5] Atmospheric pressure CVD using [(*t*-butyl)GaS]$_4$ yields cubic GaS near-epitaxially grown at less than 400°C on GaAs. At higher substrate temperatures, Ga_2S_3 is deposited along with a, as yet unidentified, Ga rich material. Deposition with Ga(S-*t*-butyl)$_3$ under similar conditions as the cubane precursors in combination with H_2S yields Ga_2S_3. Depositions employing trialkyl gallium complexes and a sulfur source yield Ga_xS_y materials. This approach has been used for the epitaxial growth of $CuGaS_2$ by MOCVD.[6]

Calcium metal-organics have been used with great success in the growth of a variety of oxide materials.[7,8] Employing analogous calcium compounds, CaS has been deposited by atomic layer epitaxy at 450°C. High purity, polycrystalline CaS, with some orientation along the (220) can be deposited from Ca(2,2,6,6-tetramethyl-3,5-heptanedionate)$_2$, Ca(thd)$_2$, and hydrogen sulfide (H_2S).[9] With this background, it appeared feasible that deposition of CaS could be accomplished by more conventional CVD processes.

Cerium sulfide growth has been pursued in analogy to the growth of Group 2 sulfides using similar β-diketonate complexes. Depositions employing Ce(thd)$_4$ and H_2S yield an amorphous sulfur containing material whose characterization is quite incomplete.[10] Ce(thd)$_4$ is employed as the Ce precursor in the ALE growth of SrS:Ce for use as an EL phosphor.[11,12] Given the similarity to the Group 2 chemistry, the success in deposition of CeO_2 from the β–diketonate complexes and the precedent for the incorporation of Ce in the ALE growth of SrS:Ce the likelihood of success for Ce incorporation with the MOCVD process was quite high.

Results

CaS

MOCVD reactors used for the growth of CaS were previously described by Peachey, et. al.[13] CaS was deposited using Ca(thd)$_2$ in an argon carrier gas and H_2S. Argon to H_2S ratios were approximately 1:1 with reactor pressures of 1 to 10 torr. The substrate temperature was varied from 400 to 600°C. Substrates used were glass, silicon, and EL substrates with an aluminum-titanium oxide (ATO) insulator layer. At lower temperatures, <500°C, deposition rates appeared to be transport limited. At substrate temperatures above 500°C, growth rates decreased dramatically with increasing temperature. The films produced were highly crystalline with x-ray diffraction patterns that matched well with cubic CaS. Film composition was determined by RBS with representative samples and yielded a Ca:S ratio of 1. Carbon and oxygen contents of the films were found to be near the detection limit of AES and XPS, < 3%.[14]

Ga_2S_3

Thiogallate (Ga_2S_3) was grown from either $GaEt_3$ or Ga(thd)$_3$ using an argon carrier gas and H_2S. Gas ratios were approximately 1:2, argon:H_2S. Crystalline films were produced at substrate temperatures of 500 to 645°C on glass, silicon, and EL substrates with an ATO insulator layer at 1 to 10 torr. Films were crystalline by X-ray diffraction with the pattern matching β–Ga_2S_3. This was confirmed by selective area electron diffraction. Transmission electron micrographs shows that large crystallites, 300 Å, formed during deposition. Selected area electron diffraction yielded concentric ring patterns indicating microcrystallites but also distinct spots from larger grains. RBS confirmed a stoichiometry of Ga_2S_3. As in the case of CaS, carbon and oxygen levels were near the detection limits of AES and XPS.[14]

$CaGa_2S_4$:Ce

The MOCVD of $CaGa_2S_4$ was accomplished by combining the CaS and the Ga_2S_3 processes.[13] Crystalline material could be deposited on EL substrates with an ATO insulator layer at temperatures greater than 550°C. While deposition does occur at lower temperatures, the material is amorphous by x-ray diffraction. By carefully controlling the bubbler temperatures and the argon flow rates through the metal-organic complexes, thin films with nominal stoichiometries of $CaGa_2S_4$ as determined by RBS and x-ray fluorescence could be produced. AES and XPS indicated no significant increase in the carbon and oxygen content for the ternary films as compared to the binary materials.[14]

Cerium was doped into the $CaGa_2S_4$ by introducing Ce(thd)$_4$ into the MOCVD process. Inclusion of the cerium precursor does not appear to perturb the MOCVD process with crystalline material being produced at temperatures greater than 550°C (Fig. 1). AES and XPS showed no increase in carbon or oxygen content from that of the undoped $CaGa_2S_4$.[14]

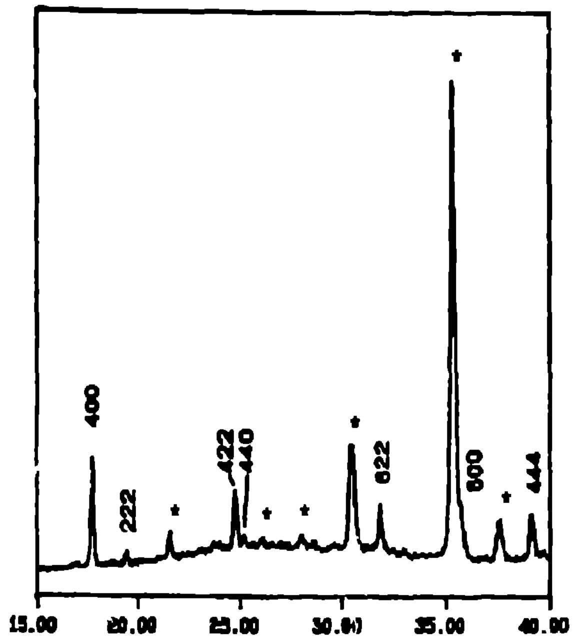

Figure 1. XRD of as deposited $CaGa_2S_4$:Ce on an EL substrate with an ATO insulator layer. Substrate temperature = 590°C. $CaGa_2S_4$:Ce features are indexed. Substrate features are indicated by an *.

Doping levels of 3-10%, with respect to calcium, produced material that showed blue to blue-green photoluminescence. EL test structures were fabricated with the MOCVD prepared $CaGa_2S_4$:Ce using ATO and BTO (barium tantalum oxide) for the lower and upper insulator, respectively. Blue-green electroluminescence was observed. A range of chromaticities from x = 0.14, y = 0.28 to x = 0.17, y = 0.33 were measured reflecting variations in stoichiometry and Ce dopant concentration from sample to sample. A representative EL emission spectrum for MOCVD $CaGa_2S_4$:Ce is shown in Figure 2. The two characteristic Ce emission bands were observed with the more intense feature having a maximum at 459 nm. An EL luminance of ~2 cd/m^2 was observed 40 volts above threshold using 60 Hz drive frequency. Threshold voltages were approximately 200 V.

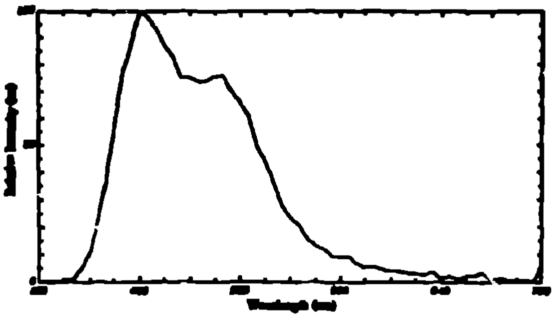

Figure 2. Electroluminescent emission spectrum for MOCVD $CaGa_2S_4$:Ce.

Discussion

A comparable low-temperature deposition process for crystalline $SrGa_2S_4$:Ce has been recently reported.[15] Crystalline-as-deposited $SrGa_2S_4$:Ce has been prepared by MBE at substrate temperatures between 400 to 600°C. The crystallinity of this material is comparable to that observed for MOCVD $CaGa_2S_4$:Ce. Both photoluminescence and electroluminescence were observed for the MBE $SrGa_2S_4$:Ce films. A maximum EL luminance of 3 cd/m^2 at 1kHz was observed 80 V above a threshold voltage of 275 V. The L_{40} EL luminance of 2 cd/m^2 at a drive frequency of 60 Hz achieved for the MOCVD $CaGa_2S_4$:Ce films in the present work is more than an order of magnitude improvement over the $SrGa_2S_4$:Ce prepared by MBE.

The chromaticity coordinates of the MOCVD $CaGa_2S_4$:Ce are higher than those for sputter deposited $CaGa_2S_4$:Ce.[1] The blue-green luminescence observed for MOCVD $CaGa_2S_4$:Ce may be the result of a high Ce dopant concentration or the presence of a second EL active impurity phase. The EL emission spectrum gave no clear indication of a third emission band; this might be anticipated if a second EL active impurity phase were present. What was observed was that the relative intensity of the lower energy features in the EL emission spectrum were greater for the MOCVD $CaGa_2S_4$:Ce than for the sputter deposited material.[1] As the Ce dopant concentration is decreased the chromaticity should shift toward the blue. While no impurity phases were observed via X-ray diffraction, further investigations are being conducted by transmission electron microscopy and selected area electron diffraction. Neither the Ce doping nor the MOCVD process have been optimized. With optimization the luminance, threshold voltage and chromaticity should dramatically improve.

Conclusion

Chemical vapor deposition using ß-diketonates or organometallic precursors in combination with H_2S does produce the desired materials. Crystalline binary and ternary metal sulfides are deposited within the temperature limits necessary for flat panel display production (<600°C). The MOCVD of crystalline, cerium activated thiogallate film at temperatures less than 600°C would eliminate the need for costly high temperature substrates and post-deposition anneal processing in the production of TFEL devices. Such a CVD process would scale for deposition of the phosphor over large areas for high volume manufacturing of full-color TFEL panels. With continued improvement in the MOCVD process and the deposited material, color EL could achieve performance equal to that of the active matrix LCDs with lower manufacturing costs.

Acknowledgment

We gratefully acknowledge the Advanced Research Projects Agency and the Department of Energy for support for this work.

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