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BY METAL ORGANIC CHEMICAL VAPOR
DEPOSITION

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PRODUCTION OF STRONTIUM SULFIDE COATINGS BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION

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ABSTRACT

This work was focused on the MOCVD of the cerium-doped strontium sulfide (SrS:Ce) phosphor for use in thin film electroluminescent displays (TFELs). Following previous research on a small scale reactor, a feasibility scale-up using a commercially available reactor enlarged the size of the deposition area to a 4" diameter wafer or a 2" by 2" glass slide. Films were deposited from the reaction of Sr(thd)₂, Ce(thd)₄, and H₂S at 450 °C and 5 torr. This system employed a liquid delivery system for the accurate and repeatable delivery of the metal organic reagents. The deposition from this reactor was shown to be crystalline-as-deposited SrS with a (200) orientation, possibly a result of the thin nature of the coating and the involvement of (200) grains in the initial nucleation process. The wafers showed good uniformity, but had some thickness variation near the outer radius of the wafer resulting from the addition of H₂S from the outside edge. There were eighteen total deposition experiments, of which nine were characterized for EL performance. The highest brightness observed was 5 fL. The samples were exceedingly thin as a result of the fifteen fold increase in the surface area between the deposition reactors. Increasing the sample thickness to 7,000 Å or higher will dramatically increase the brightness of the emission.

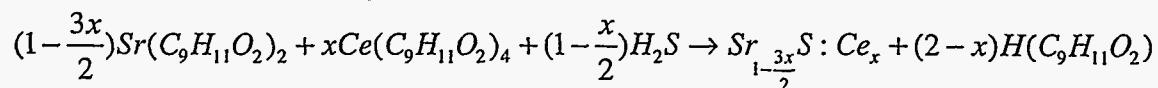
INTRODUCTION

During this research it was decided to focus the effort primarily on the MOCVD of the cerium-doped strontium sulfide (SrS:Ce) phosphor for use in thin film electroluminescent displays (TFELs). This decision was based on recent results of improved EL luminance and efficiency reported for this phosphor by research groups using other deposition techniques, such as molecular beam epitaxy (MBE),¹ and sputtering.² Both of these deposition techniques require high processing temperatures to achieve the enhanced luminance and efficiency values. In the case of the MBE process, a substrate temperature of greater than 600 °C is used, and, for the sputtering process, a post-deposition rapid thermal anneal of up to 800 °C is required. These high process temperature may limit the application of these processes to costly substrate materials such as quartz and sapphire.

An advantage of the MOCVD process investigated is the capability to prepare high quality phosphor films at temperatures below 600 °C.³ An objective of the program therefore was to demonstrate that high purity SrS films with good crystallinity could be grown at less than 600 °C using the MOCVD technique. This task also required the fabrication and testing of a large number of AC TFEL devices built on glass substrates and was done using a small scale reactor to demonstrate the feasibility of the material and the process. However, because the demonstration of luminescence on a small area thin film sample deposited using a research reactor does not guarantee that the MOCVD process can be transferred to a large production reactor, an another objective was added: an initial investigation of the feasibility of scale up.

EXPERIMENT

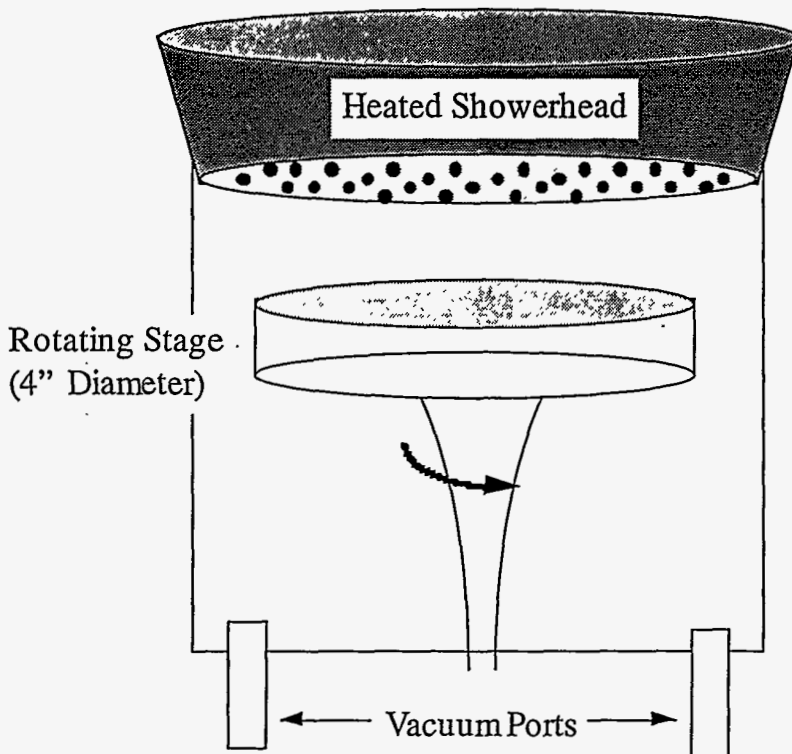
In order to keep the deposition temperature as low as possible, metal-organic reagents were selected for the deposition reaction. The metal-organic reagents were Sr(thd)₂ and Ce(thd)₄, where (thd) refers to 2,2,6,6-tetramethyl-3,5-heptadionate or C₁₁H₁₉O₂. Other gases that were used were hydrogen sulfide (H₂S) and Ar. The overall deposition reaction was of the form:



The cumbersome chemical reaction results from the charge compensation for the substitution of Ce^{3+} in the place of Sr^{2+} . For every atom of cerium dopant present in the crystalline SrS film, half of a vacancy must be present in the lattice. As such, the formula for the deposition may be appropriately written as $Sr_{1-1.5x}V_{0.5x}S:Ce_x$.

The delivery of these reagents was done with a commercially available liquid delivery system, purchased from Advanced Technology Materials (Danbury, CT). In this process, the metal organic reagents were stored dissolved into a solvent and were metered to a remote vaporizer, just prior to the reactor. The reagent flow that resulted from the vaporizer was then directed into the system. This type of reagent system allowed for both accurate and repeatable reagent delivery conditions, a problem that can result from traditional thermal sublimation of metal organic reagents.

The experimental depositions were conducted in a commercially purchased reactor, Model 400 S manufactured by the Spire Corporation. This system utilized both a rotating stage and



showerhead reagent delivery to achieve microelectronics quality deposition. Thickness variations of less than 10% were expected across the sample. Its sample stage was capable of handling a 4 inch (10 mm) diameter wafer; a second sample holder was machined to allow a 2" by 2" glass slide or two 1" by 2" glass slides. The total deposition area in this reactor was 81 cm².

Samples were loaded into the chamber through a load-lock so that the deposition chamber was guarded from secondary contamination from the air. Sample rotation was accomplished using a Ferrofluidics feed through and was computer controlled to allow rotation in both

Figure 1. Schematic of the Spire Reactor.
directions at a variety of speeds. An schematic of the deposition chamber is shown in Figure 1.

RESULTS

There were a total of 18 experiments run using the Spire Reactor for the deposition of SrS:Ce from $Sr(thd)_2 + Ce(thd)_4 + H_2S$. These samples were characterized using a variety of techniques, but the most used were x-ray fluorescence (XRF), x-ray diffraction (XRD), and Rutherford backscatter spectroscopy (RBS). The use of XRF provided very quick and non-destructive information regarding the chemical composition of the film; XRD was used to characterize the samples for their crystalline qualities, such as preferred orientation and growth directions. Selected samples were measured for their EL performance. One of the primary reasons for using MOCVD was that the crystalline-as-deposited films could be deposited at relatively low temperatures. As such, the deposition temperature was kept below 600 °C to allow for the use of low temperature glass as the substrate material. The ease of deposition for SrS:Ce allowed a substrate temperature of 450 °C.

The uniformity of the samples was also measured on a 4" silicon wafer using optical characterization at Planar Systems. Two diagonals of five equidistant points each were taken; a graph of these points is shown in Figure 2. The variation across the diagonal was approximately 300 Å from the center to the edge. Most likely this variation resulted from the addition of the H₂S from the outside edge of the wafer. In this geometry, the concentration of the H₂S would be much higher at the edge of the wafer and would drop off toward the center of the wafer. The only method through which H₂S could make its way

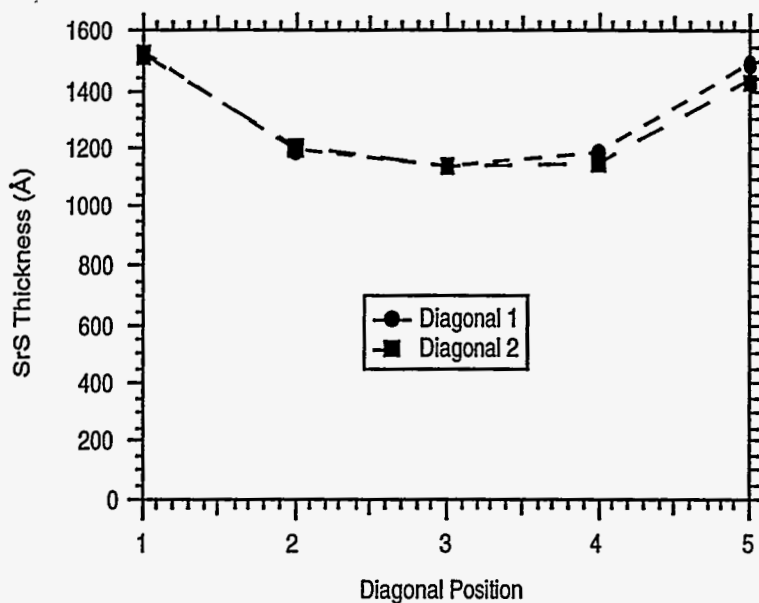


Figure 2. Uniformity of deposition on a 4" Si Wafer. Deposition on 2"x2" slides was done between points 2 and 4.

into the sample center would be through concentration diffusion, along with some forced convection from the sample rotation. However, changes in the rotation speed did not statistically affect the deposition thickness, based on the XRF measurements and standard deviation of such. Future work on this system will deal with a system modification to accommodate these variations.

The XRD characterization has shown that the deposition was crystalline and again matched up to JCPDS Card 8-489. A sample XRD pattern is shown in Figure 3. These samples again

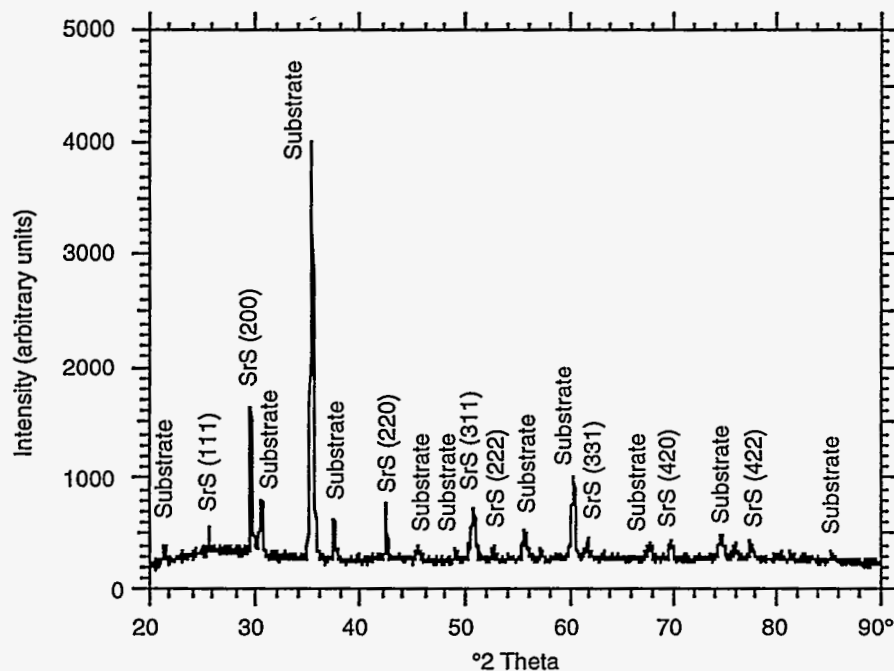


Figure 3. XRD pattern of SrS deposited in the Spire Reactor.

have shown preferred orientation in the (200) direction, resulting from their thin coatings and the prominent role of (200) oriented grains in the nucleation process. An estimation of the lattice parameter was calculated from three samples that were deposited at different times: 45, 75, and 90 minutes. The result of this regression gave values of 6.0168, 6.0181, and 6.0214 Å, respectively, compared with a published value of 6.020 from JCPDS Card 8-489. These differences indicate an enlargement of the average size of

the unit cell as the deposition thickness increased. Most likely, this can be attributed to a reduction in the residual stresses in the film as the deposition growth process becomes less competitive due to the enlargement of grains and reduction in the number of active growth grains.

Some scanning electron microscopy was also performed on samples from the Spire Reactor. A sample of the surface morphology is shown in Figure 4. In general, surfaces were composed of sharply faceted grains, typically with a square cross section. The grain size was well below a micron in width, as might be expected due to the limited amount of competitive growth that could be accomplished with the thin deposition. This sample was also examined using quantitative

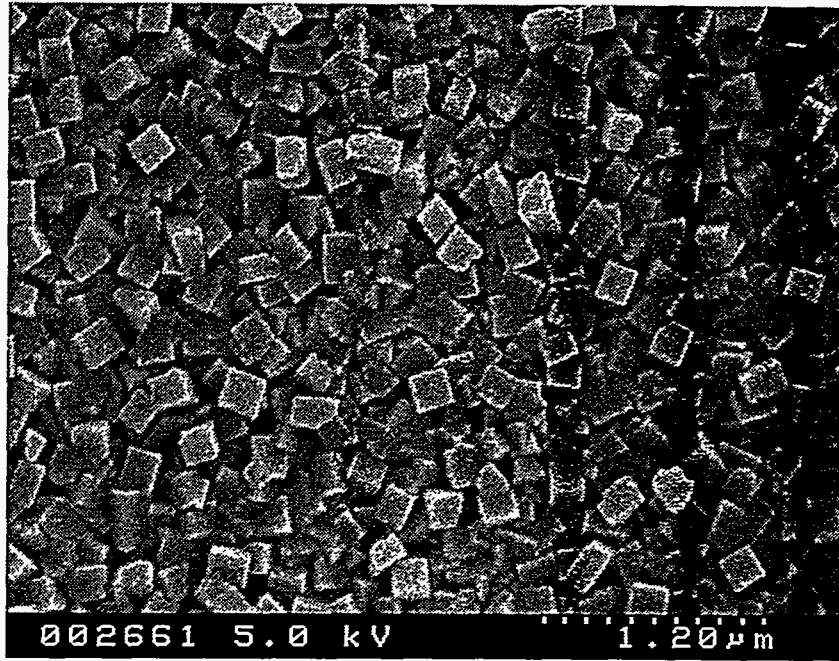


Figure 4. Micrograph of the surface morphology of as-deposited SrS:Ce.

microprobe analysis to determine the thickness and chemical make-up of the deposition. The results of the thickness determination agreed within the standard deviation with those produced by the RBS analysis of the same sample, approximately 2,000 Å. The chemical composition of the deposition produced a value that was slightly off stoichiometry and Sr rich. However, this sample had experienced some time in the ambient atmosphere from the RBS and x-ray analysis and probably had off-gassed volatile S, leading to a Sr rich calculation from the microprobe characterization.

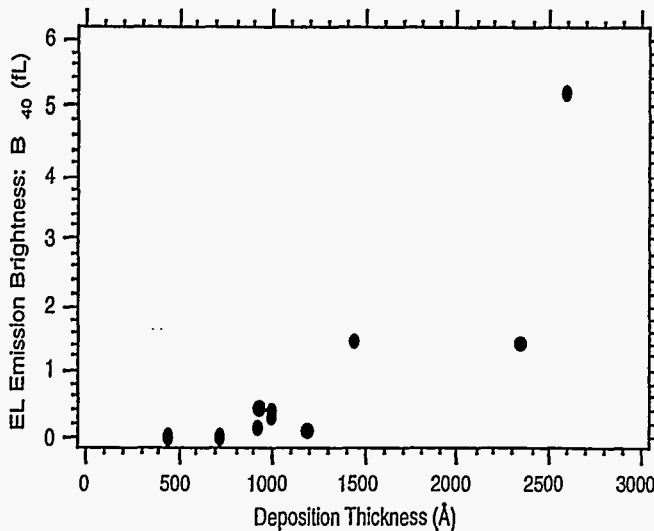


Figure 5. The brightness at 40V over threshold increases with the deposition thickness.

The luminescence of the samples from this reactor have not been as good as those seen from the smaller system. The highest observed brightness has been 5 fL with CIE coordinates of (0.292, 0.506). Other samples have had brightnesses of 2 fL and below. However, this lack of performance is attributable to the thinness of the samples. In fact, the highest brightness was measured from the thickest sample (2,250 Å). There is a nearly linear relationship between the deposition thickness and the luminescence brightness, as shown in Figure 5. It is expected that increasing the deposition thickness to 7,000 Å or above will increase the brightness

of the samples by at least three times.

CONCLUSIONS

The deposition of SrS:Ce was carried out using Sr(thd)₂, Ce(thd)₄, and H₂S precursors in a large commercially purchased system. The use of the Spire Reactor enlarged the size of the deposition area to a 4" diameter wafer or a 2" by 2" glass slide. This system utilized a commercial liquid delivery system for the reliable control and delivery of the reagent gases. The deposition from this reactor was shown to be crystalline SrS with a (200) orientation, possibly a result of the thin nature of the coating and the involvement of (200) grains in the initial nucleation process. The wafers showed good uniformity, but had some thickness variation near the outer radius of the wafer resulting from the addition of H₂S from the outside edge. There were eighteen total deposition experiments, of which nine were characterized for EL performance. The highest brightness observed was 5 fL. The samples were exceedingly thin as a result of the fifteen fold increase in the surface area from the reactor scale-up. Increasing the sample thickness to 7,000 Å or higher is expected to dramatically increase the brightness of the emission.

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