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Title: Metal-Ogranic Chemical Vapor Deposition of the Blue Electro-Luminescent Cerium-Doped Calcium Thiogallate from a Liquid Reagent Delivery System

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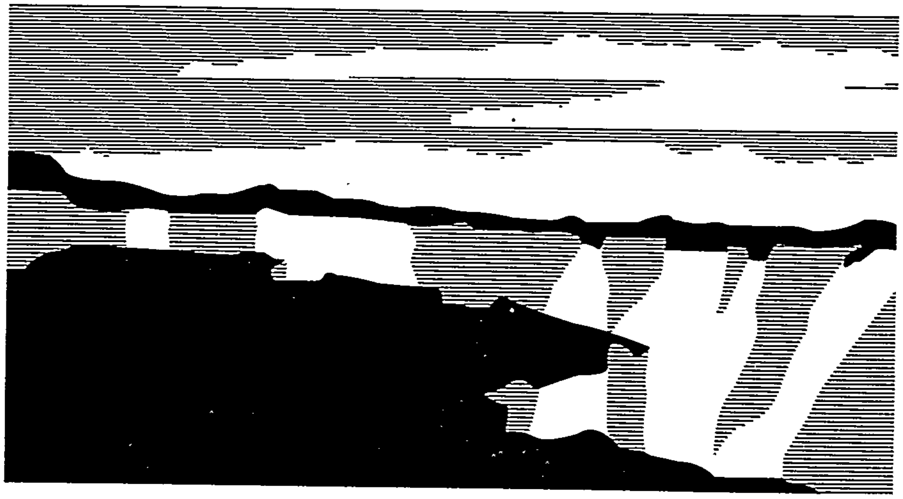

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MOCVD of the Blue Electro-luminescent Phosphor $CaGa_2S_4$:Ce from a Liquid Reagent Delivery System

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ABSTRACT

The deposition of CaS, Ga_2S_3, and $CaGa_2S_4$:Ce has been accomplished by MOCVD using $Ca(tmhd)_2$, $Ga(tmhd)_3$, and $Ce(tmhd)_4$, with bubblers and with a liquid delivery system to control the flows. Samples were primarily characterized using x-ray fluorescence and electro-luminescence measurements of the color and brightness. Deposition using the bubblers showed a definitive relationship between the $Ga(tmhd)_3$ bubbler temperature and the Ga XRF counts. The Ca conversion shows a tenuous relationship with the $Ca(tmhd)_2$ bubbler temperature, but the scatter of the data makes determining a correlation impractical. Use of the liquid delivery system is preferred to the bubblers because it delivered a reliable reagent flow without the same problems of degradation of the reagent over time. Analysis shows the CaS deposition is mass transport limited, while the Ga_2S_3 is limited by the deposition kinetics. However, application of these mechanisms to the $CaGa_2S_4$:Ce deposition system reveals that the $CaGa_2S_4$:Ce is independent of its components. Further, the deposition of $CaGa_2S_4$:Ce is found to be Ca rich under conditions which leads to low Ga/Ca ratios in the deposited film. This indicates that the conversion of Ca from $Ca(tmhd)_2$ was catalyzed by the slight presence of Ga in the form of $CaGa_2S_4$:Ce or Ga_2S_3 on the surface. The Ca is thought to be deposited as CaS:Ce since there is a shift in the EL color towards green under low Ga/Ca ratios. The Ca conversion is also found to approach values predicted by the CaS deposition mechanism under conditions which lead to high Ga/Ca ratios, implying that excess Ga_2S_3 is needed for the deposition of $CaGa_2S_4$:Ce without any CaS:Ce inclusions.

INTRODUCTION

The development of an efficient blue phosphor for use in thin film electro-luminescent displays is an important milestone in their deployment. It has been reported that Ce^{+3} doped alkaline earth thiogallate materials show blue emission with good chromaticity.[1] Cerium-doped calcium thiogallate ($CaGa_2S_4$:Ce) is such a material whose production has been and continues to be actively pursued. In the recent past, a full color VGA thin film electro-luminescent panel using $CaGa_2S_4$:Ce as the blue phosphor has been fabricated and tested.[1] The deposition of thiogallate films has been accomplished primarily using sputtering,[1] but $CaGa_2S_4$:Ce has also been produced by molecular beam epitaxy,[2] and multisource deposition.[3] However, with many of these processing techniques, a post-deposition anneal is needed to produce the crystallographic properties required for the optimum luminance. The extra annealing step also limits the possible glass substrates which can be used to high temperature compositions, adding to the overall cost of manufacturing. The process of metal-organic chemical vapor deposition (MOCVD) is especially well suited to deposit $CaGa_2S_4$:Ce because it is capable of producing high quality, crystalline material at processing temperatures below 600°C. Also, the relatively simple deposition equipment is attractive from a manufacturing standpoint because of its ease of integration to a manufacturing process. This paper covers the MOCVD of $CaGa_2S_4$:Ce for use as a blue phosphor in flat panel applications.

Previously, this group has reported the deposition of $CaGa_2S_4$:Ce using a traditional reagent bubbling techniques.[4] However, the use of this method is not optimal because of problems which are present with regards to the reproducibility of the experimental conditions. These problems are the result of several limitations such as changes in the surface area of the solid source and changes in the reagent chemistry from spending time at elevated temperatures. Also, from the prospective of understanding of the chemical processes with the deposition reactor, the traditional delivery method using the organometallic reagents has difficulties because the vapor pressures of these compounds have not been well defined. It is hoped that the liquid delivery system would eliminate these problems by providing reliable reagent delivery conditions from reagents which would be kept at room temperature.

EXPERIMENT

The deposition of $CaGa_2S_4$:Ce was done in a horizontal, warm wall reactor with a modified impinging jet injector. Heating was done by a quartz lamp which was focused on the backside of the substrate through a quartz window. Deposition was performed onto glass substrates coated with indium tin oxide, aluminum titanium oxide, and a thin zinc sulfide nucleation layer; the layered substrate allowed for color and brightness measurements to be made on the as-deposited material. All samples were deposited at 582°C and 5 torr; the reagent flow rates, H_2S and Ar flow rates, and deposition time were varied in the experiments. The principal characterization technique for these samples was x-ray fluorescence (XRF) and electroluminescence (EL). The deposition thickness for all of the samples were maintained at approximately 5000Å to allow for EL measurements.

The reagent flows were composed of $Ca(tmhd)_2$, $Ga(tmhd)_3$, and $Ce(tmhd)_4$, where the tmhd refers to 2,2,6,6-tetramethyl-3,5-heptanedionate. Gas flows of Ar were used as the carrier gas, and H_2S was used as the sulfur source. The delivery of the tmhd reagents was done using two methods. The first method was by saturating a carrier gas with the vapor from the reagent. The control of the flow rate was by the flow rate of the carrier gas and by the temperature of the bubbler. This setup introduced a large number of variables since each source's temperature and carrier flow rate had to independently controlled. The second method for reagent delivery was by the use of a commercially available liquid delivery system (LDS). The three source system (LDS-300B) was purchased from Advanced Technology Materials, Inc. For this system, the three sources contained $Ca(tmhd)_2$, $Ga(thmd)_3$, and $Ca(tmhd)_2$+$Ce(tmhd)_4$. The mixture of $Ca(tmhd)_2$ and $Ce(tmhd)_4$ in the last source was done to improve the resolution of the Ce doping in the deposition. The liquid sources consisted of the solid reagents which were dissolved into a common solvent. Delivery was then done by pressurizing the upstream side of the reservoirs with Ar, forcing the liquids out of a dip tube. The three sources were mixed in the controlled ratios using a series electric mixing valves, and the mixed liquid was then pumped to a remote vaporizer with a liquid pump. The liquid was vaporized from a frit located within the vaporizer and carried into the deposition reactor using a flow of Ar. H_2S was added to the reagent flow just prior to entry into the reactor.

RESULTS

The results of the thermal bubbling system were not particularly well suited for correlation to a deposition model since the vapor pressure of the $Ca(tmhd)_2$, $Ga(tmhd)_3$, and $Ce(tmhd)_4$ were not known. Thus, the flow rate and concentration of reagents which were delivered to the reactor could not be determined. However, it was possible to determine some empirical relationships between the bubbler conditions and the observed data from the XRF measurements. Primarily, there was a strong relationship between the Ga counts from the XRF and the temperature of the $Ga(tmhd)_3$ bubbler. This dependence is illustrated in Figure 1 for a series of runs done with a constant carrier gas flow rate of 10 sccm through the bubbler, constant H_2S flow rate of 20 sccm, constant system pressure of 5 torr, and at constant substrate temperature of 582°C.

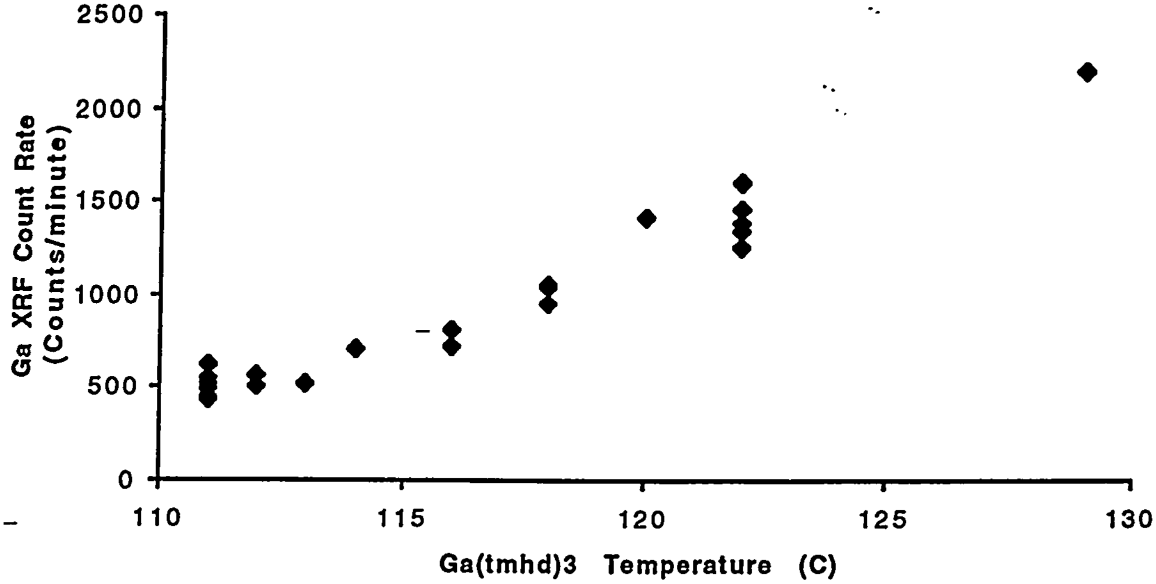

Figure 1. The XRF count rate for Ga increases rapidly with the Ga(tmhd)3 temperature.

The form of the data shown in Figure 1 was expected because of the sensitivity of the $Ga(tmhd)_3$ vapor pressure to the temperature within the bubbler. The information shown in this graph was attempted to be related to a possible deposition model. However, it was difficult to determine its form and rate constant without the vapor pressure data because there are more unknowns than equations. It was possible to fit an empirical equation to the data shown that could be used to predict the amount of Ga deposition which could be expected from particular conditions. The fit of the natural log of the Ga XRF count rate against the $Ga(tmhd)_3$ bubbler temperature gave an intercept of -4.07 (±0.51) and a slope of 0.092 (±0.004) with a standard deviation of 0.109 and an R^2 of 95.3% (R^2_{Adj} of 95.1%). Converting this result into an exponential equation gives a formula as Ga XRF Count Rate = $0.0171 \cdot \exp[0.0927 \cdot \{Ga(tmhd)_3$ Temperature$\}]$.

A similar analysis using the Ca conversion as a function of the Ca(tmhd)$_2$ bubbler temperature was attempted and is shown in Figure 2.

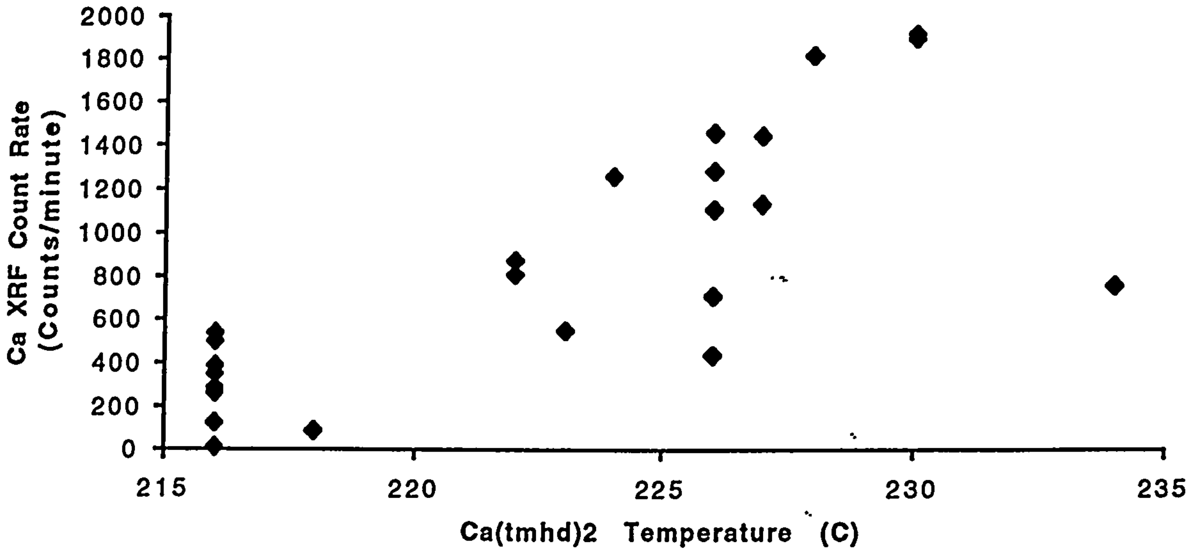

Figure 2. The Ca XRF count rate shows a lot of scatter but has an overall upward trend.

There does appear to be an upward trend in the XRF count rate as the bubbler temperature was increased, but the amount of scatter in the data made it difficult to use this data to predict how the deposition would change based on the bubbler temperature. Further, the repeatability of the Ca deposition was not of sufficient precision to place much trust in the observed data. There are several possible explanations which have been offered for these difficulties. The most probable is that the Ca(tmhd)$_2$ bubbler was run at the highest temperature and frequently would clog at the valve due to condensation of the reagent. Also, there are some questions regarding the stability of the Ca(tmhd)$_2$ as a function of the time at temperature; some possible breakdown of the reagent might have occurred, adding to the uncertainty of the flow rate. These problems were part of the desire to change the reagent flow system to that of the liquid delivery system.

The second method of reagent delivery was by the use of the LDS. This method improved the ability to repeat the deposition conditions from day to day, eliminating the uncertainty that surrounded the heating of the bubblers and the nature of the reagent within the bubbler. Also, the LDS allowed for precise control of the inlet reagent conditions so that the deposition mechanisms could be better determined. Initial experiments with the LDS were designed for the deposition of the single phase components of the thiogallate: CaS and Ga_2S_3. The deposition of these compounds allowed for mechanisms to be determined for both reactions. These mechanisms could then be compared against the observed deposition rate of $CaGa_2S_4$:Ce to check for independence of the reaction. However, since independence has never been practically observed under CVD conditions, the same analysis could be used to examine conditions which led to or away from independence.

The results of the CaS deposition show that the reaction is in a mass transport limited regime by virtue of the fact that the deposition rate is a function of the total flow rate (Q_{total}).[4-5]

This relationship is illustrated in Figure 3. In this figure the deposition rate is plotted against the $[Ca(tmhd)_2] \cdot Q_{Total}^{1.5}$.

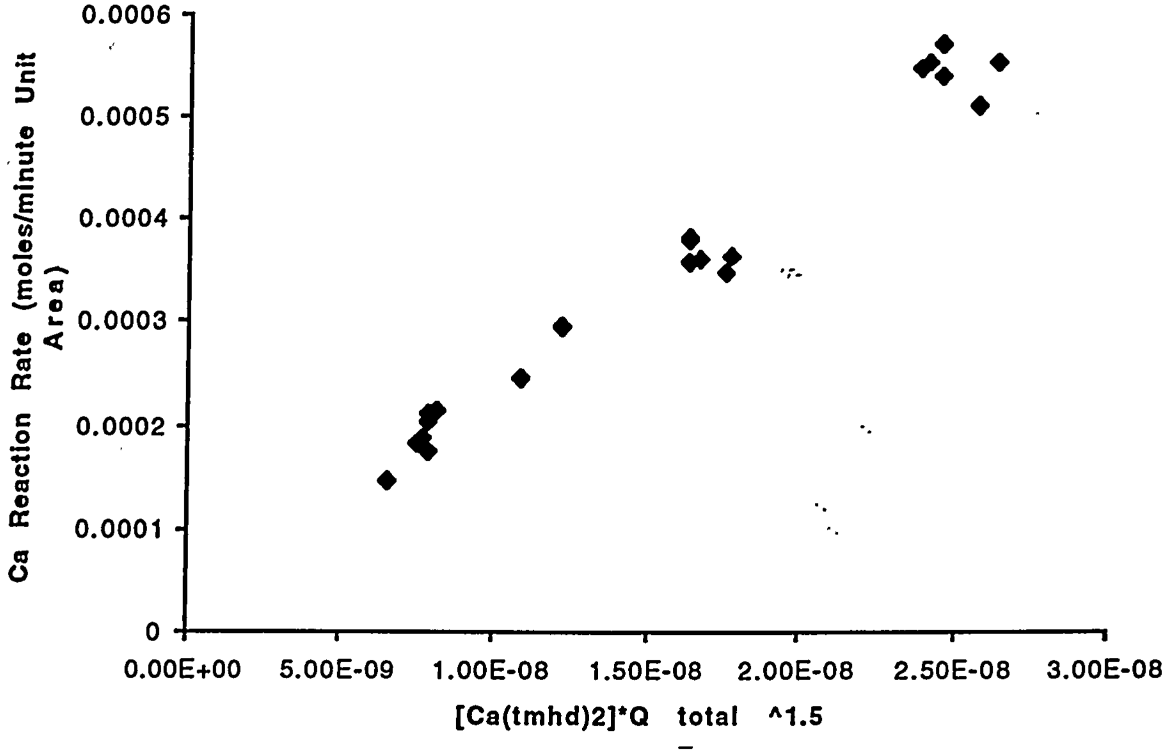

Figure 3. The Ca reaction rate is a function of the $[Ca(tmhd)_2]*Q_{Total}^{1.5}$, indicating a mass transport controlled deposition mechanism.

The no constant-regression of this expression provides a mass transport coefficient for the deposition of $2.210x10^4$ $minutes^{0.5}/(liters^{0.5} \cdot$Unit Area), where the Unit Area is the fluoresced area in the XRF measurement. The standard error of the regressed coefficient was $0.0342x10^4$; the standard deviation of the fit was $2.87x10^{-5}$ moles/(minute·Unit Area); and coefficient of determination (R^2) was 97.5% and R^2_{Adj} was 97.4% . The expression for the deposition of CaS in moles/(minute·Unit Area) could then be described for conditions of constant pressure and surface temperature and by:

$$J_{CaS} = J_{Ca,PRED} = 2.210x10^4 \cdot [Ca(tmhd)_2] \cdot Q_{Total}^{1.5} \tag{1}$$

The deposition of the single phase Ga_2S_3 required a different mechanism than the CaS deposition. Within the range of parameters studied, the Ga_2S_3 deposition was best described by a kinetic deposition model that allowed for suppression of the deposition at higher $Ga(tmhd)_3$ concentrations. This mechanism is much different than the mass transport model used for the CaS. This kinetic relationship is illustrated in Figure 4, where the Ga conversion rate is plotted against $Ga(tmhd)_3$ concentration at three different flow rates of H_2S. The three different H_2S flow rates are shown as different plotted shapes.

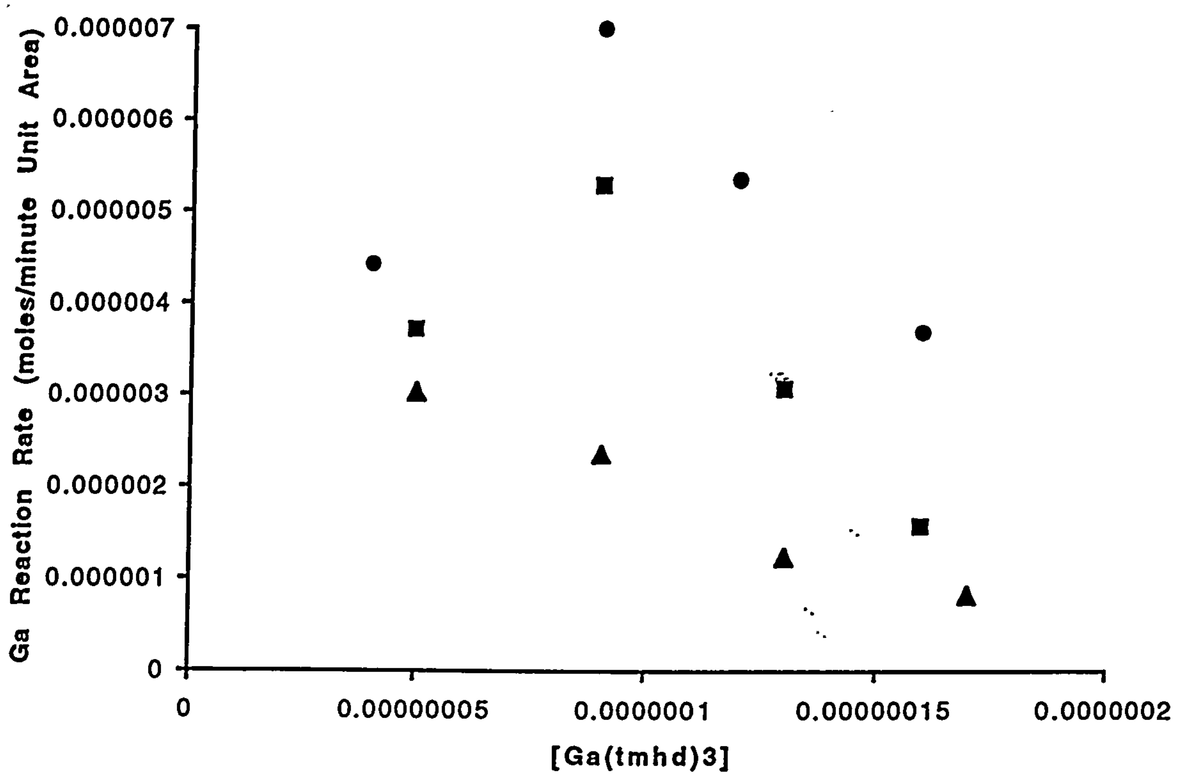

Figure 4. The Ga reaction rate is shown versus the [Ga(tmhd)$_3$] for 20 sccm(▲), 30-sccm(■), and 40 sccm(●) H_2S.

From the data in this plot, it was anticipated that a Langmuir Hinshelwood model would be needed to allow for an inhibition mechanism.[6] The regression of this data had a kinetic coefficient of 2.153×10^4 liter^3/(Mole^2·minute·Unit Area) with a standard error of 0.7035×10^4, and an inhibition coefficient was found to be 2.691×10^{14} liter^2/Mole^2. For this regression, R^2 was 92.6% and R^2_{Adj} was 91.9%, indicating an accurate representation of the data. The deposition of Ga_2S_3 in moles/(minute·Unit Area) may be described by an empirical formula as:

$$J_{Ga_2S_3} = J_{Ga,PRED} = \frac{2.951x10^{12} \cdot [Ga(tmhd)_3] \cdot [H_2S]^2}{1 + 4.255x10^{14} \cdot [Ga(tmhd)_3]^2} \quad 2$$

If the deposition of the $CaGa_2S_4$:Ce is indeed an independent addition of the two constituent reactions, then the overall deposition rate may then be described by the expression:

$$J_{CaGa_2S_4} = J_{CaS} + J_{Ga_2S_3} \quad 3$$

However, if the deposition was not independent, then the reaction rate must be described using a different reaction rate. The method that was used to compare the two independent mechanisms employed the use of the difference between the observed Ca and Ga rates ($J_{Ca,OBS}$ and $J_{Ga,OBS}$) and the predicted Ca and Ga deposition rates ($J_{Ca,PRED}$ and $J_{Ga,PRED}$) such that:

$$\Delta_{Ca} = J_{Ca,OBS} - J_{Ca,PRED}$$
$$\Delta_{Ga} = J_{Ga,OBS} - J_{Ga,PRED} \quad 4$$

Of these two variables, the Δ_{Ca} is of higher interest since the conversion of extra Ca into even the slightest amount of CaS instead of $CaGa_2S_4$ is detrimental to the EL color of the deposition. CaS tends to shift the color towards the green. Extra Ga_2S_3 acts as a dead phase under EL conditions, reducing the brightness, but does not affect the EL color.

The influence of the deposition on Δ_{Ca} is shown in Figure 5. Within this plot, Δ_{Ca} is plotted against the molar ratio of Ga to Ca in the film based on calibrated XRF measurements.

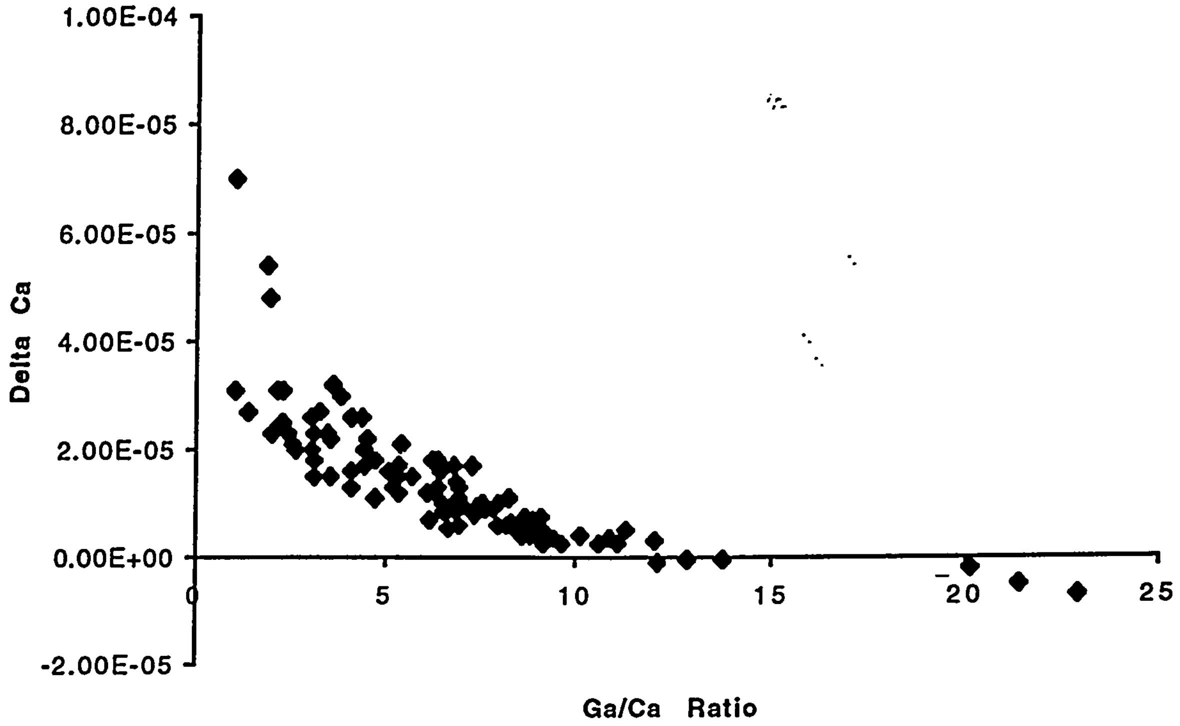

Figure 5. The difference between the observed and predicted Ca reaction rate increases to more positive values at lower Ga/Ca ratios.

The data shows that as the Ga/Ca ratio is reduced, Δ_{Ca} becomes larger (and is positive). This would indicate that at conditions which lead to a low Ga/Ca ratio, the conversion rate of Ca is increased to values over those expected for the single phase material, almost as if it was catalyzed by the slight Ga presence on the surface. However, at higher Ga/Ca ratios the value of Δ_{Ca} approaches zero and appears to turn slightly negative at high ratios. This would indicate that at the high ratios the conversion of Ca from $Ca(tmhd)_2$ approaches that seen from the CaS deposition system. Further, it suggests that the presence of an extra Ga_2S_3 layer is necessary for the deposition of $CaGa_2S_4$:Ce, and at conditions which lead to lower Ga/Ca ratios the Ca is converted not only into $CaGa_2S_4$:Ce but also into another Ca containing compound. The extra Ca containing phase is expected to be CaS.

When the same Ga/Ca ratio is compared to the EL color, this relationship is enhanced. In Figure 6, Δ_{Color} is defined as:

$$\Delta_{Color} = \sqrt{(CIE_x - 0.15)^2 + (CIE_y - 0.20)^2}$$

This quantity may be visualized as the linear distance away from the desired blue color with a CIE_x of 0.15 and a CIE_y of 0.20, is plotted against the Ga/Ca ratio.

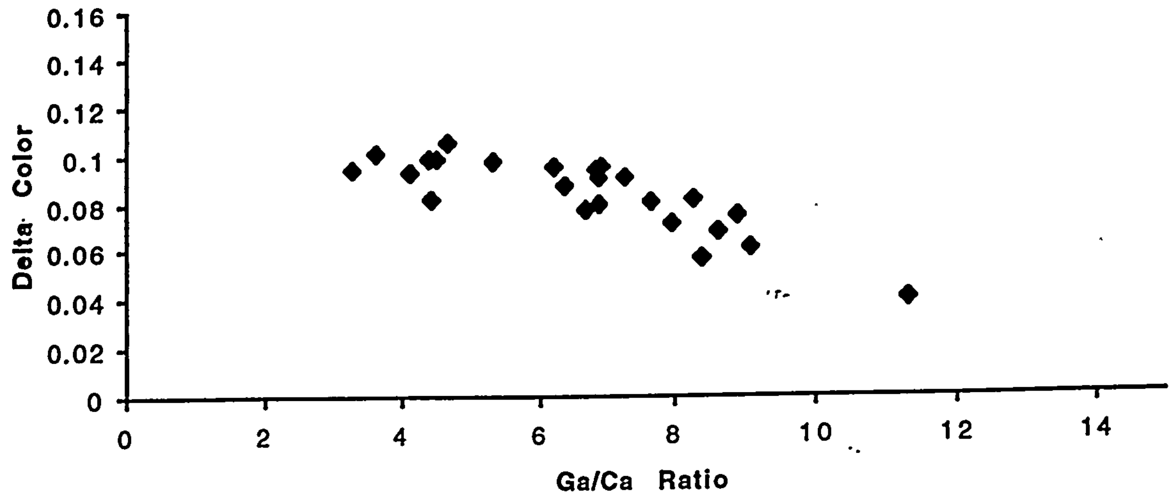

Figure 6. The Delta color, which is the deviation in the EL color from the desired blue color, decreases with increases in the Ga/Ca ratio.

The figure shows a statistically significant downward trend in the data, indicating that the EL color at low Ga/Ca ratios is shifted away from blue. This would be consistent with the possible inclusion of CaS:Ce in the film which cause the samples to EL at a greenish color and shift the value of Δ_{Color} to higher values as the color becomes more green. Unfortunately, the conditions which take the EL color towards the desired values serve to diminish the brightness since the Ga_2S_3 serves as a dead phase under EL conditions.

From these findings, it is possible to observe that using the present substrate system and deposition system, higher amounts of Ga are needed to promote the reaction of Ca into $CaGa_2S_4$:Ce and to minimize the conversion of Ca into the non-desirable CaS:Ce phase. The higher amounts of Ga are thought to be in the form of a Ga_2S_3 layer which either provides the necessary surface for the nucleation and growth of $CaGa_2S_4$:Ce or converts into $CaGa_2S_4$:Ce from the reaction with an intermediate Ca species. Future studies into this system will explore the initial stages of nucleation and growth using this substrate surface and will also explore the nucleation and growth behavior with other surfaces to determine optimum conditions for deposition.

CONCLUSIONS

The deposition of CaS, Ga_2S_3, and $CaGa_2S_4$:Ce has been accomplished by MOCVD from $Ca(tmhd)_2$, $Ga(tmhd)_3$, and $Ce(tmhd)_4$. Reagent flows were controlled using both bubblers and a liquid delivery system, and samples were primarily characterized using XRF and EL. The bubblers show an exponential trend between the $Ga(tmhd)_3$ bubbler temperature and the Ga XRF counts. This relationship could then be used as an empirical prediction tool for future depositions. The Ca conversion did not have the same correlation; the scatter in the plot of $Ca(tmhd)_2$ bubbler temperature against Ca XRF counts made any empirical equations error prone. The use of the liquid delivery system is preferred because of the accuracy and repeatability of the reagent delivery and the reduction of possible thermal transformations in the reagents. The analysis of the constituent systems (CaS and Ga_2S_3) shows that the CaS deposition is mass transport limited while the Ga_2S_3 is limited by the deposition kinetics. Application of the single phase mechanisms to the $CaGa_2S_4$:Ce deposition system reveals that the $CaGa_2S_4$:Ce deposition mechanism is independent of its components. Further, the deposition of $CaGa_2S_4$:Ce is found to be Ca rich under conditions which lead to low Ga/Ca ratios in the deposited film. This indicates that the conversion of Ca from $Ca(tmhd)_2$ is catalyzed by the presence of Ga in the form of $CaGa_2S_4$:Ce or Ga_2S_3 on the surface. The Ca is thought to be deposited as CaS:Ce since there is a shift in the EL color towards the green under low Ga/Ca ratios. At higher Ga/Ca ratios, the Ca conversion rate approaches values predicted using the CaS deposition expression, implying that extra Ga, presumably present in the form of Ga_2S_3, is necessary for the deposition of $CaGa_2S_4$:Ce without any CaS inclusions. However, the Ga_2S_3, which is observed as necessary to improve the EL color, diminishes the brightness because it acts as a dead phase under EL conditions.

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INTRODUCTION

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