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CONF-971201--

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Submitted to:

Proceedings of the 1997 Fall Materials
Research Society Meeting
December 1-5, 1997
Boston, MA

MASTER

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MOCVD OF FIELD EMISSION PHOSPHORS USING A LIQUID DELIVERY SYSTEM

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ABSTRACT

Thin film phosphors for field emission displays show the potential to overcome the life-limiting problems that traditional powders face because of their high surface areas. By depositing a fully dense thin film, the surface area can be dramatically reduced, while the electrical and thermal conductivity is increased. Metal organic chemical vapor deposition offers the ability to deposit high quality, dense films that are crystalline-as-deposited and at temperatures low enough to allow for inexpensive glass. Deposition has been produced from mixtures of $\text{Y}(\text{tmhd})_3$, TEOS, $\text{Tb}(\text{tmhd})_3$, and O_2 using a liquid delivery system. Coatings were shown to be composed of Y, Si, and Tb by x-ray fluorescence, but x-ray diffraction did not show any crystallinity. Excitation using radioluminescence produced a peak in the visible green at approximately 540 nm, indicative of the excitation of a Tb^{3+} . The morphology of the deposition was smooth, with surface features on the order of one micron and below. Some limited microcracking was also observed from the morphology because of the thermal expansion mismatch.

INTRODUCTION

The concept of a field emission display (FED), where a visible emission is produced from the interaction of a rare earth dopant in a host lattice with an electron beam, has been proposed for many years. It is in fact very similar in structure to that of a cathode ray tube or a television set. Cathodoluminescent (CL) phosphors have been well developed and have been used for the last 30 years in full color CRT and TV sets. However, the requirements for the phosphor and phosphor environment are much different for field emission displays, and the CL phosphors for CRTs and TVs are not applicable to FEDs. Primarily, because CRTs are operated at high accelerating voltages, on the order of 13 to 30 kV, significant spacing is required between the anode and cathode to prevent a vacuum breakdown and arcing. Reducing this distance between the anode and cathode is one of the main driving forces for flat panel displays and has led to the development of new phosphors that can be operated at lower voltages, allowing a spacing on the order of 1 mm while operating at 2 to 4 kV.^{1,2}

To date, most of the work in phosphors for field emission displays has been in the area of powders. While powders do present some attractive advantages in terms of simplicity of synthesis, several problems with the performance have been noted. The largest of these is the degradation mechanism that phosphors undergo while being excited by an electron beam. This electron-stimulated surface chemical reaction leads to the formation of a dead layer at the surface of the particle, reducing the luminance of the phosphor, and to the formation of gaseous components, eroding the vacuum between the anode and cathode.³ However, by producing a thin film instead of a powder, the surface area can be reduced because the material would be fully dense. A thin film would also have the advantage of improved thermal and electrical

dense. A thin film would also have the advantage of improved thermal and electrical conductivity, and the adherence would be improved in the event of arcing from the cathode and rough handling from usage.

The choice of phosphor to be deposited for this program was terbium-doped yttrium silicate ($\text{Y}_2\text{SiO}_5:\text{Tb}$) because of its bright green color and, most importantly, low luminance saturation at high current densities.⁴ The process of metal organic chemical vapor deposition (MOCVD) was selected because it is well suited to produce these low voltage phosphors in a thin film form at a low deposition temperature. These depositions are typically high quality and crystalline-as-deposited with high densities obtainable. Further, by working at reduced temperatures, inexpensive glass can be used, an important advantage from a manufacturing prospective.

EXPERIMENT

The deposition of $\text{Y}_2\text{SiO}_5:\text{Tb}$ was accomplished in a hot wall reactor using a liquid delivery system purchased from MKS Instruments (Model DLI-25B). This system is shown schematically in Figure 1. The choice of reagents was $\text{Y}(\text{tmhd})_3$, TEOS, and $\text{Tb}(\text{tmhd})_3$, where (tmhd) refers to 2,2,6,6-tetramethyl-3,5-heptadionate or $\text{C}_{11}\text{H}_{19}\text{O}_2$ and TEOS is tetraethyl orthosilicate or $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$. The oxygen source was from O_2 gas, and Ar gas was used as a carrier and diluent. Deposition reactions were accomplished at pressures below 30 torr and at temperatures below 650°C . Quartz slides and silicon wafers were used as the substrates, but both caused some difficulty in the analysis of the deposition using x-ray fluorescence because the Si peak was convoluted with signal from the substrate.

Figure 1. Schematic of the MOCVD system.

The reagents were combined into a single source, or reagent cocktail, for use in the liquid delivery system. This process involved the determination of a single solvent that was capable of dissolving all three reagents. However, because TEOS is a liquid at room, either the $\text{Y}(\text{tmhd})_3$ or the $\text{Tb}(\text{tmhd})_3$ had the limiting solubility. Toluene (C_7H_8) was found to be an acceptable solvent, capable of dissolving all the reagents to some amount. All reagent cocktails were mixed in a glove box using dry toluene and loaded into the liquid source container before being attached to the system. In the liquid delivery system, this reagent cocktail was pumped to a remote vaporizer, located just prior to the deposition system. The vaporizer was kept at approximately 150°C so that the liquid would be converted into a gas which could then be transported into the reactor using an Ar flow. The substrate was supported on a boron nitride holder within the closest zone of a three zone furnace. By-products of the reaction were removed from the end of the reaction tube. A vacuum pump was used to operate at reduced pressures.

However, the addition of additional hydrocarbons to the reagent stream is the cause of some concern because it could provide a source for carbon and hydrogen in the films. Such inclusions can have a negative impact on the luminescent properties of the material. As a result, additional oxygen was critical to ensure that all of the hydrocarbon molecules were burned in the gas phase. Significant amounts of carbon are typically detectable as a brownish color in the normally translucent film and are visible to the naked eye. No browning was observed in any of the deposition.

RESULTS

Deposition from the MOCVD reactor was, in general, of good quality. Chemical characterization of the deposition using x-ray fluorescence (XRF) showed that Y, Si, and Tb were present on the surface. The results were not calibrated to an absolute molar amount that could be used to determine the ratio of Y to Si and the doping amount of Tb. However, future plans are under way to develop those relationships by calibrating against information from Rutherford Backscatter Spectroscopy. Notwithstanding, the relative numbers from the XRF are still valid in an attempt to understand the performance of the deposition reaction.

Of interest in the deposition system is the positioning of the sample in the reactor relative to the reagent injector. This is an important parameter because of the high reactivity of the

TEOS in the hot wall environment. In an early design of the system, the reagents were not kept separate prior to entering the reactor, and the TEOS was found to have completely depleted before reaching the sample, usually in the form of a spiderweb of SiO_x . A redesign was made to keep the $\text{Y}(\text{tmhd})_3$, TEOS, and $\text{Tb}(\text{tmhd})_3$ separate from the O_2 flow until well inside of the furnace. In keeping with the

design, an optimum distance from this injector had to be determined relative to the maximum deposition rate. For this a series of four experiments were performed, each positioning the sample at a different distance from the injector. The results of these runs is shown in Figure 2 as the Y XRF counts against the distance; in this figure the 0" point refers to the background Y XRF counts taken from an uncoated sample. The Y peak was used because it was completely resolved and had a strong intensity while the Si peak was convoluted with counts from the glass slide beneath it and the Tb peak was relatively small and did not have good counting statistics. Based on the information, a distance of 3" was determined to be the best distance from the injector. This position gave the maximum distance to allow for proper heating of the reagents in the reactor with the minimum depletion to the walls of the reactor.

Samples from this system were also examined using x-ray diffraction (XRD) for their crystalline structure. XRD did not show the presence of any crystalline material, just the amorphous hump from the quartz substrate. This observation was a surprise because the samples did show emission when excited using a 254 nm UV lamp. Typically, amorphous materials do not show PL emissions because the crystal structure of the host lattice is important to the local environment of the dopant atom. A possible explanation is that the deposition XRD pattern was obscured by the quartz hump because the thickness was not sufficient to produce a strong diffraction pattern.

Selected samples were also examined using radioluminescence (RL), a process where the material is excited using x-rays and the resulting luminescence is characterized. The RL data for two samples, along with a blank quartz slide is shown in Figure 3. Both samples show an emission peak in the visible green at around 540 nm as would be expected for the excitation of a Tb^{3+} dopant. The absolute intensity is not calibrated for this system, but the relative intensity for Sample 187 is slightly higher than 188, presumably due to a thicker deposition.

Sample 187, which showed a good emission spectrum, was also analyzed using scanning electron microscopy (SEM) to determine the surface morphology. This micrograph is shown in Figure 4. The surface has a smooth characteristic to it, with surface features on the order of one micron or less. That size range is a smaller than optimum. Previous experience in the deposition of thin films for electroluminescent displays has shown that larger grain sizes give enhanced brightnesses. However, due to the relatively low deposition temperature and relative stability of the $\text{Y}(\text{tmhd})_3$ and $\text{Tb}(\text{tmhd})_3$, enhanced grain growth may not be possible without a significant post deposition anneal. Also seen in Figure 4 is a slight amount of microcracking on the surface. This is attributed to the difference in the thermal expansion of the deposition and the quartz. Such a difference may be moderated by the presence of an indium tin oxide layer, necessary to act as a transparent conductor, and/or by changing the type of glass away from quartz, which has little or no thermal expansion.

Figure 4. Surface morphology of the $\text{Y}_2\text{SiO}_5\text{:Tb}$ deposition shows smooth features with some limited microcracking of the surface.

CONCLUSIONS

The MOCVD of $\text{Y}_2\text{SiO}_5\text{:Tb}$ films from a mixture of $\text{Y}(\text{tmhd})_3$, TEOS, $\text{Tb}(\text{tmhd})_4$, and O_2 has been accomplished for the production of thin film field emission phosphors. The reagent flows in this system were controlled using a liquid delivery system from a single source reagent cocktail. These coatings have deposited on quartz slides and silicon wafers at temperatures below 650°C and pressures below 30 torr. The deposition has shown the presence of Y, Si, and Tb by x-ray fluorescence, but the deposition has not been shown to be crystalline based on XRD. Radioluminescence of the deposition revealed an emission peak in the visible green at around 540 nm, as would be expected from the excitation of a Tb^{3+} dopant. SEM micrographs of

the surface morphology showed a relatively smooth surface with features below one micron in size. A limited amount of microcracking was also observed on the surface, presumably due to the difference in thermal expansion between the deposition and the quartz substrate.

ACKNOWLEDGMENTS

The authors wish to acknowledge the work of Norm Elliot for the SEM micrographs and Wayne Cooke for the RL spectra, both of Los Alamos National Laboratory.

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M98004391

Report Number (14) LA-UR--97-5025
CONF-971201--

Publ. Date (11) 199803
Sponsor Code (18) DOE/EM, XF
UC Category (19) UC-1391, DOE/ER

DOE