

PHOSPHOR SCREENING

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INTRODUCTION

Most phosphor literature discusses the luminescent properties of phosphors and very few discuss the methods of fabricating phosphor screens. However, phosphor screening is used whenever one wants to apply a phosphor to a substrate whether it is for fluorescent lighting systems, monochrome or color CRTs, used in consumer electronics or in the military. Thus, phosphor screening used in emissive displays is applicable to FEDs, Plasma Displays, Electroluminescent displays, Vacuum Fluorescent displays, Xray intensifiers and fluorescent lamps. We can consider Phosphor Screening as an interdisciplinary technology involved with fabricating luminous coatings and using at least the following disciplines; Physics, Chemistry, Optics, Vacuum Science and Graphic Arts. This paper is a discussion of some of many screening methods used both historically and at the present time. We hope that this paper can be used by the reader to review alternative methods under consideration and consider new methods.

LIST OF SCREENING METHODS

This paper discusses a list of Screening methods which include; 1. Painting, 2. Gravity Settling, 3. Settling with compression, 4. Slurry, 5. Slurry with Segregation, 6. Dusting, 7. Photo-tacky Dusting, 8. Thin Screen Evaporation/Sputtering, 9. Screen Printing, 10. Pressed Printing, 11. Pulsed Laser Deposition, 12. Centrifugal, 13. Electrophoretic, 14. Spraying , 15. Electrostatic Dusting, 16. Tape Transfer, 17. Reactive Deposition, 18. Reactive Evaporation, 19. RF Sputtering with Ion-Implantation of activators, 20. MOCVD, 21. Atomic Layer Epitaxy

PAINTING

The painting techniques are used for dials, indicators, signs etc. There are three classifications of luminescent paints. They are Fluorescent, Phosphorescent and Self-luminous. They can be Organic or inorganic in nature and are used with a vehicle such as lacquers or oils. Paints as well known can be applied by used of brush, roller and sprays. Details at times can be obtained through the use of stencils. Here the luminescent paint may be applied to selected areas of a substrate. Paints can also be applied via off-set printing methods. These fluorescence and phosphorescent paints can be excited via IR, visible or UV radiation . In the self luminous paints the source of the excitation is a radioactive material (ex. Radium) mixed with the paint.

SETTLING (Gravity Settling)

Settling is a well known method. Screening methods have been used by a number of authors for example Pringsheim, Hopkinson and Donofrio & Rehkopf (refs 1, 2 and 3). A nice description of settling can be found in a GTE Sylvania publication (ref 4). This technique describes the settling of phosphor slides which requires phosphor, a 1% barium acetate solution (in water), PS-6 potassium silicate & DI water. One recipe is to add 34 ml of the 1%

barium acetate to the settling chamber (6»x 6»x10»). Weight out about 0.9 grams of phosphor and dispense the phosphor in 100 ml and 34 ml of PS-6 in an Erlenmeyer flask. Shake the suspension and pour it in the settling solution. It is suggested that you allow the solution to settle for 20 minutes before decanting the supernatant liquid. We could either do this by draining or by pouring the solution out of the chamber. Dr. Niel Yocom (ref 19) in his 1996 talk on phosphor screening discussed nine steps to settling and aluminizing a phosphor screen; 1. Settle phosphor on face plate, 2. Liquid cushion is decanted and siphoned off. 3. Dry Screen, 4. Bake Screen, 5. Rewet screen, 6. apply filming material on to of water., 7. Remove water, 8. Evacuate and evaporate the Aluminum layer, 9. Bake out screen.

SLURRY

The slurry method has been described by Norihiro Tatayama of Sony (ref 5). One of his recipes is to use 100 g of phosphor, 0.6g of Aerosil, with 5 g of PVA and 0.5g of ADC (ammonium dichromate) and 100g of water. A quantity of this mixture is deposited near the center of the face of a CRT panel and by rotation and tilting the slurry is spread over the inside of the face plate.

SLURRY (with segregation)

Tatsyama, Yamazaki, Kato & Teshima of Sony developed a cascaded slurry system in which the Silicate concentration was higher on the glass substrate side than the electron gun side to reduce the effects of aging (ref. 5).

DUSTING

There a number of ways to do dusting. Hopkinson (in 1946 ref 2) calls this «Dry Spraying» and sprays the phosphor in to a wet or dry binder. Another possible dusting technique is one in which the phosphor is either allowed to fall on or is projected on a prepared surface. Another option is to have , the phosphor material agitated through a sieve or muslin gauze upon the plate which has been coated with some kind of binder like sodium silicate. T. V. Rychlewski (ref 6) developed a method by which, the phosphor can also be dusted more vigorously via a dry powder spray system on to a wet photo-resist (prior to exposure) as part of a screening method to fabricate color CRT screens.

DUSTING (2) Photo-tacky Method

In 1984 Hitachi (ref. 7) announced a dusting method in which phosphors would be dusted on (photo-tacky) coated dry surface. Then the exposure to UV would allow the coating to become tacky and this tacky nature of the surface coating would cause the phosphor in the exposed areas to be attached to the surface. This process did not use the Di-chromated PR but a Diazonium salt.

SETTLING (with compression)

In 1995, Oki & Ozawa (ref. 8) discussed the use of Settling with normal sedimentation techniques and using a mechanical press machine to reduce the voids in the screen for high

resolution uses. They state that this method produces weak cathodo-luminescence similar to that obtained from thin film screens.

THIN FILM SCREENS EVAPORATION or SPUTTERING

It has been shown that high resolution screens can be made by evaporating or sputtering the phosphor on the substrate. Because of selective evaporation usually sputtering is chosen for the generation of very thin phosphor screens. Magnetron sputtering of ZnGa_2O_4 on to BaTiO_3 ceramic sheets has been reported for use in thin film Electro-luminescent devices . Some of the process conditions were; RF power of 80 W, the target to substrate distance was 25mm, Argon gas and substrate temperature of 275 deg C was used. The achieved screen thickness was 1.5 microns. It has been shown that an Electroluminescent film can be made by vacuum evaporation methods. Velthaus used five sources to do reactive multi-source deposition (RMSD). In this technique they showed that they could form a SrS:Ce, Cl, Ag, Mn thin layer phosphor on the required substrate

SCREEN PRINTING

One of the oldest methods of making a phosphor screen is by screen printing techniques. A tight but spring-like cloth or metal mesh is used with areas blocked by a lacquer and aligned above a substrate to be coated. The slurry mix is then mechanically pressed through the selected areas of the mesh on to the substrate and the mesh springs back to its original position after the phosphor paste is applied. By photographic printing of patterns on a mesh, very fine patterns can be screen printed. This method has been used in the past with phosphor screens for EL panels, watch dials etc. Fujitsu recently mentioned that they use this method for Plasma Display screen fabrication.

PRINTING WITH COMPRESSION

In 1992 Morikawa et al (ref. 10) discussed a method to achieve a smoother and better aging screen using a printing method plus screen compression. This compression method allows the manufacturer to achieve higher packing densities They prepared phosphor in a paste and screen printed a layer of about 20 microns thick. It appears that the printing involves compression of the paste more than silk screening. However, no quantitative compression data was given and only the statement was made that it was pressed strongly. Morikawa claims that this method gives a screen which has improved aging characteristics compared to settling.

PULSED LASER DEPOSITION

Greer et al in 1994 reported (ref 11) on Pulsed Laser Deposition (PLD) of phosphor screens used in helmet mounted displays (HMD). They use a rastered laser with a wavelength of 248 nm to scan targets of Yttrium Aluminum Gallium Garnet phosphors and by ablation, deposit these materials on to sapphire substrates. This method used a screen growth rate of one micron per hour. Screens of thickness up to 8 microns were fabricated. Work is being done in 1997 by Singh at the University of Florida on Pulsed Laser Deposition (PLD) of FED phosphors. This work is addressing the deposition of Y, La & Ga oxy-sulfide phosphors.

CENTRIFUGAL

In this method a phosphor suspension in solution is by centrifugal action deposited on a faceplate (ref 12). It has been reported that 1» CRT screens, a stable phosphor suspension is made with a fine grain (less than 5 micron particle size) phosphor, a binder , electrolyte and in some cases a dispersing agent. The settling in the centrifuge is at 3000 rpm for 2 minutes to 4000 rpm for 3 minutes. Screens of optimum screen weight of about 0.6 mg/cm² for 5 KV electrons was found using P20 phosphor with an average particle size of 1.9 microns. Recently (1997 ref 13) Zupanc - Metzner and Zumer reporter on a centrifugal technique in which the used a suspension containing (1.8 micron) P43 phosphor, Barium Acetate, Potassium silicate and a surfactant. They reported good electron aging with a screen weight of 1.0 mg/cm² at a screen thickness of approximately five particle diameters and an anode voltage of 5 KV.

ELECTROPHORETIC

Electrophoretic (or Cataphoretic) phosphor coatings are used for high resolution displays. Schesinger (ref. 14) explained the method by which a conductive coated glass face plate is put in a solution of a phosphor and electrolyte and a metallic anode (situated about two inches from the face plate). When a DC electric current of 20 ma is passed through the solution the phosphor screen is deposited on the cathode. However it is known that this effect is dependent on phosphor and coatings on the phosphor. Cataphoretic screen is presently being used by Imaging & Sensing Technology Corp. (IST) for their high resolution CRTs used in military applications. In 1996 Russ et al reported the use of vertically separated electrodes (one evaporated Aluminum and the other Platinum mesh). They used a suspension of ZnS:Ag (P-11) and 10⁻³ M Mg(NO₃)₂ in IPA. They used an applied voltage of 500V for 100 sec.

THREE COLOR CATAPHORETIC COAT

In 1996 Kurinee & Sluzky (ref 15) described a means of Tri-color Cataphoretic Screening. In 1997 Hung, You, Park, Choi and Kim of Samsung reported on the electrophoretic deposition of color phosphors on a four inch full color FED. The deposition suspension used color phosphors whose particle size was between 1 - 3 microns. A uniform thickness of 4-8 microns was achieved. In May 1997, Schermerhorn, Sweeney & Wang from Electro Plasma and Park, Park and Kim from Samsung (ref 16 & 17) discussed the use of Electrophoretic deposition of color phosphors for Plasma Display screens through the use of metalized recessed regions or cavities.

SPRAYING

Wet or Dry phosphor can be sprayed on a substrate. The wet phosphor method is similar to paint spraying. The nozzle of the spray gun can be changed to spray at various spray angles depending on the distance from the substrate and other constraints. A pressure pot is used just in any spray system to keep the pressure constant to the spray gun. In the dry system, the dry phosphor is sprayed on the screen face whose surface is coated with an adhesive binder. Here, we have two methods (as mentioned by Hopkinson), a wet binder and dry binder can be used. In wet spraying, we can also use an organic binder (discussed previously under dusting) such as nitrocellulose or PVA. We can also use a binder which becomes tacky under UV radiation

bombardment. Presently the spray method is used by at least one manufacturer to fabricate «LCD Backlights ». The six interior side of the lamp housing is spray coated with a UV excitable phosphor.

ELECTROSTATIC SPRAY/DUST

Thomson Electronics has discussed a method (called the Electrophotographic method) using a phosphor spray or dusting in which the phosphor is charged and blown against a charged screen surface. The phosphors are then fixed to allow further processing. There are numerous patents discussing this method. In one method (ref 18) a tribo-electric gun is used to charge the phosphor. The phosphor is fed to the panel using a hopper, an auger to transfer the material from the hopper to the venturi chamber. The venturi chamber dispenses the charged phosphor to the latent image on the panel.

TRANSFER TAPE

Another screening method mentioned by Dr. Yocom (ref 19) is the transfer Tape method. Here the phosphor is coated on a tape base with a layer to contain phosphor. Under the phosphor is a release layer and the phosphor and binder are pressed onto a substrate. The base tape is removed leaving the phosphor and binder.

REACTIVE DEPOSITION

Cusano (ref. 20) in 1962 reported the vapor reaction for fabricating ZnS phosphor layers. His apparatus is seen in the figure above. In 1955 Cusano reported a process using equipment similar to that seen above but having an additional heater for the Zinc and activator powder. Here the substrate to be coated is heated to temperatures from 400 - 700 deg C. The material is added so that the vapor components will «be continuously present in the same proportion». One mixture used to make ZnS:Mn was ; 25g Zn, 12.5 g ZnCl₂ and 0.38 g MnCl₂. H₂S is continuously present during the formation of the phosphor layer. This apparatus was used to make high resolution CRT screens . These screens had a thickness of 10 - 20 microns or more. Cusano also showed that this method could also be used for electroluminescent screens.

REACTIVE EVAPORATION

It has been recently reported by Daud et al (ref 21) that transparent thin films of Y₂O₂S:Eu have been made as a film in situ (as seen above) . In contrast to Cusano's work, in this method, the Yttrium metal was evaporated on to the substrate using an E-Beam gun. Excited SO₂ was introduced while simultaneously heating a crucible of EuCl₂ powder

RF SPUTTERING AND ION IMPLANTATION

This method of forming phosphor screens is similar to RF sputtering except the activator Ion is implanted. Minami et al fabricated TFEL devices with ZnGa₂O₄:Mn. Here the activated phosphor was fabricated from RF sputtering (using Argon gas, RF power of 80 W and substrate temp of 275 deg C) from a target containing ZnO, Ga₂O₃, MnO₂, EuCl₃ etc. In 1997 N.M.Kalkhoran et al (ref 22) reported their work in looking at methods to form thin film

electroluminescent screens by rf sputtering. They were able to implant ZnGa_2O_4 thin films on a flexible polyimide substrate with Mn, Eu to get green and red phosphor screens (resp.). The un-doped host material was used for the blue screen.

METAL ORGANIC CHEMICAL VAPOR DEPOSITION

In 1995 Smith et al (ref 23) described their formation of $\text{CaGa}_2\text{S}_4:\text{Ce}$ phosphor by MOCVD methods. Here Calcium metal-organics were used in the form of $\text{Ca}(\text{2,2,6,6-tetramethyl-3,5-heptanedionate})_2$ called $\text{Ca}(\text{thd})_2$. The CaS was deposited using $\text{Ca}(\text{thd})_2$ in an argon carrier gas and H_2S with reactor pressures from 1 to 10 Torr. Substrates were glass, silicon and coated EL substrates at temperatures from 400-600 deg C. The Ga_2S_3 and CaS formation was combined with the use of $\text{Ce}(\text{thd})_4$ to obtain the $\text{CaGa}_2\text{S}_4:\text{Ce}$ phosphor.

ATOMIC LAYER EPITAXY

In their 1997 book on Display Systems by MacDonald and Lowe (ref 24) they discussed the formation of a luminescent screen for Alternating Current Thin film Electroluminescent Displays. This system developed by Suntola et al. involves (and similar to Cusano's reactor method) exposing of a substrate at high temperature (500 Deg C) to low pressure «chemical precursors». So to obtain ZnS:Mn layer, the process is to apply Zn and Mn. Then the reactor is evacuated and Sulfur is introduced. The cycle is then started again Whereas, in Cusano's Vapor Reactor method the screen was continuously formed. Here the screen is built up as a number of layers.

CONCLUSIONS

As we have seen, the methods used to prepare phosphor screens is a the choice which is dependent on performance characteristics, geometry and the cost (both in materials, equipment and in process). This paper, briefly describes many different screening methods and shows how they are in part, built on each other. From a historical perspective the line between preparing phosphor screens and fabricating phosphors is becoming very faint. Many new methods described in this paper are fabricating the phosphor on the substrate and thus forming the phosphor and the screen together. It is hoped that this work in showing the diversity of phosphor screening methods which have been used will help the Screening Engineer and Screening Scientists in giving them direction for future improvements.

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