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PHOSPHORS FOR FLAT PANEL EMISSIVE DISPLAYS

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ABSTRACT

An overview of emissive display technologies is presented. Display types briefly described include: cathode ray tubes (CRTs), field emission displays (FEDs), electroluminescent displays (ELDs), and plasma display panels (PDPs). The critical role of phosphors in further development of the latter three flat panel emissive display technologies is outlined. The need for stable, efficient red, green, and blue phosphors for RGB full color displays is emphasized.

INTRODUCTION

A. DISPLAYS IN THE INFORMATION AGE

Technology for flat panel displays (FPDs) has evolved rapidly in the past several years as demand has continued to increase.¹ In 1992 Hitachi predicted that the burgeoning market for displays would exceed \$40 billion by the year 2000. Displays for video applications can be grouped arbitrarily into three general sizes: small (up to 14" diagonal), medium (up to 35" diagonal), and large (greater than 35" diagonal). We shall not discuss small nonvideo displays that rely on vacuum fluorescent, liquid crystal, or light emitting diode technologies such as those used for alphanumeric indicators. Small video displays are used, for example, as monitors for laptop computers and as monitors for military displays. For portable, battery operated displays, the devices must be lightweight, thin, and efficient. Liquid crystal displays (LCDs) currently hold 90 to 95% of the market for small flat panel displays. The flat panel emissive display technologies that could challenge this technology are field emission displays (FEDs) and electroluminescent displays (ELDs). Medium size displays are employed commonly as television sets and as desktop computer monitors. Owing to their relatively low cost, stable performance, and good visual output, cathode ray tubes (CRTs) are the dominant technology. It would be advantageous to replace these bulky monitors with thinner, lighter, more portable flat panel displays. The FED,

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ELD and plasma display panel (PDP) are potential challengers along with LCDs if technical barriers to size scale up can be overcome. Large displays are used typically in big venues, such as, military command centers, meeting halls, public facilities, and classrooms. Projection displays based on CRTs and LCDs are the most common technologies. Monochrome PDPs have been available for over 20 years and have found niche markets in medical, commercial, and military displays.² Desirable attributes of new large displays include full color, high resolution (for use as direct view high definition televisions, HDTVs), and readability in bright light. Phosphors are one key to further development of flat panel emissive display technologies. The properties and performance of phosphors exhibit a wide variability. The choice of phosphor type and deposition method provides a great opportunity to improve the performance of a display.

B. PHOSPHORS: KEYS TO EMISSIVE DISPLAYS

Phosphors are materials that emit visible light when excited by photons or electrons. It is convenient to describe phosphors in terms of a host, activator, and coactivator. Phosphor hosts are typically crystalline oxides or sulfides. Activators are typically lanthanide ions, transition metal ions, or molecular complexes. Coactivators are ions that increase luminescent efficiency of the activator. Phosphors are generally sprayed, shaken, or screen printed in powder form onto the faceplate of a display in small dots or stripes (pixels) that are on the order of 0.3 mm for CRT applications. For some applications they are deposited as thin films. In general full color displays contain red, green, and blue (RGB) pixels. The use of RGB in full color applications dictates that three separate materials, all of which meet the necessary criteria for operation in a display, must be developed for each full color display technology. Important figures of merit for traditional applications of phosphors (in CRTs) include:³ chromaticity (color) specified as CIE coordinates, peak wavelength of visible emission, luminous efficiency (W/W or lm/W), persistence (decay time for the light output after the input energy is removed), and maintenance (luminance of phosphor relative to that when the screen was first excited). Another important benchmark is luminance. A standard CRT produces a maximum luminance of approximately 100 foot Lamberts (fL) for white light. The white luminance is composed of 10 fL blue, 25 fL red, and 65 fL green. The efficiency with which the light is produced is also an important metric. For portable displays the efficiency needs to be 2-3 lm/W to compete with LCDs. This requires 1 lm/W blue, 2-3 lm/W red, and 6 lm/W green from the phosphors.

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C. PHOSPHORS IN CATHODE RAY TUBES

The excitation mechanism of phosphors in a CRT is cathodoluminescence, that is, high energy electrons strike the phosphors and excite the activators, which radiatively decay and emit visible light. A color CRT contains three thermionic electron guns. The electrons produced by the guns are rastered across the phosphor screen. The applied voltage is typically 10 to 30 kV. Phosphors in powder form are used in CRTs. The red, green, and blue phosphors are sequentially deposited onto a faceplate. The area for each phosphor is defined by photolithography. A shadow mask in conjunction with a light in the position where each electron gun will be placed in the display are used to expose the photoresist and define the pixels. For CRT phosphors the host lattice is a generally metal sulfide or metal oxysulfide. Sulfides exhibit energy efficiencies in the range 22 to 25%, whereas the maximum for oxides is 10 to 11 %. ZnS doped with various activators is the most extensively investigated phosphor scheme. Phosphors for green light include (Zn,Cd)S:Cu,Al and ZnS:Cu,Au,Al. Phosphors for blue light are ZnS:Ag,Cl and ZnS:Ag,Al. ZnS-based phosphors for red light are no longer used owing to problems with oxidation and poor saturation properties. The standard red phosphor is now $Y_2O_2S:Eu$. Many other lanthanide-doped materials have been developed since the 1950s. These include oxysulfides and oxides, such as, $La_2O_2S:Tb$, $Y_3(Ga,Al)_5O_{12}:Tb$, $Y_2SiO_5:Tb$, $Y_3Al_5O_{12}:Ce$, $Y_2SiO_5:Ce$, $Y_2O_3:Eu$, and $YVO_4:Eu$.

FLAT PANEL EMISSIVE DISPLAYS

A. FIELD EMISSION DISPLAYS (FEDs)

FEDs are analogous to CRTs. Both are vacuum technologies in which the phosphor excitation mechanism is cathodoluminescence. FEDs are operated at lower voltages and higher current densities than CRTs. A schematic of an FED is shown in Figure 1. One version of an FED relies on an addressable array of cold cathode field emitters⁴ to provide electron emission. The cathodes are typically arrays of molybdenum or silicon points⁵ or wedge emitters that are fabricated by the use of integrated circuit technology. A density as high as 10^8 emitters per square centimeter can be achieved. Another version relies on emission of electrons from diamond-like thin films.⁶ Much of the early work on FEDs can be attributed to LETI in France. Prototype FEDs were demonstrated as early as 1991.⁷

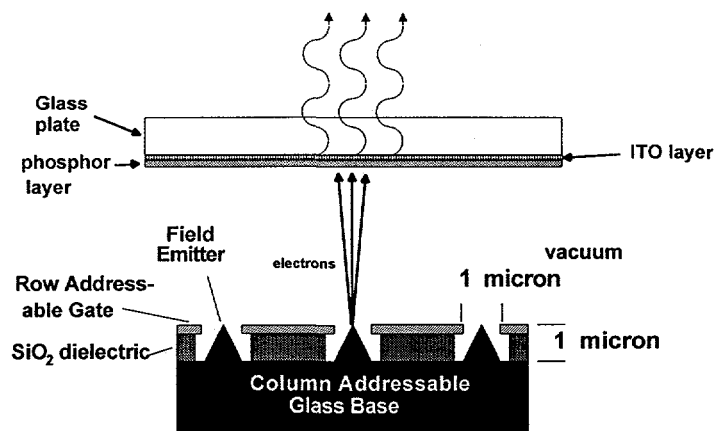


Figure 1. Schematic of a field emission display. Spacers between emitters and faceplate are not shown.

There are a variety of operational voltages being targeted for use in FEDs. The voltages range from 5 kV to less than 500 V. Each voltage range has distinct advantages and disadvantages. Low-voltage operation is probably more viable, especially if reliable, efficient low voltage phosphors can be developed.

Low-voltage operation, especially at less than 500 V, is attractive from a safety standpoint and less stringent requirements to avoid vacuum breakdown. Low-voltage operation requires higher current densities to maintain the same average power at the phosphor, which can lead to increased degradation and outgassing of the phosphor.⁸ Low-voltage operation also requires phosphors that have low threshold voltages, high thermal conductivity, and requires electrical conductivity of the phosphor/binder matrix to dissipate charge. A conductive layer, such as indium tin oxide, on the faceplate will likely be necessary to help prevent charging of the phosphor layer. Another drawback of low-voltage operation is that phosphor efficiency decreases as voltage decreases at a fixed input power. An efficiency of 2-3 lm/W white is desirable for the device. Many phosphors do not achieve this at 500 V. Also low-voltage, high-current driver development would be required as the final power amplification is provided by the drivers rather than the phosphor screen.

High-voltage operation is attractive to overcome phosphor degradation and charging problems. In this case it will probably be possible to aluminize the phosphor screen as in a CRT and maintain the same efficiency of the phosphors as for low-voltage conditions with no aluminum screen. The aluminum screen provides a physical barrier between the phosphors and emitter tips that can

potentially reduce the concentration of volatile contaminants at the emitters. It also provides electrical conductivity and reflects emitted visible light that radiates toward the aluminum screen back toward the viewer. High voltages introduce several major concerns, these include: increased possibility of vacuum breakdown owing to larger field gradients, increased electrical leakage, potentially more damage to the emitters from an increase in sputtered contaminants from the screen owing to the increased energy of the impinging electrons, the potential for more damage to the device in failure situations, and increased need for aging and testing of the each device prior to shipping. Additionally, high-definition devices would require focused electron beams, which adds cost and complexity to the package.⁹ Phosphors developed for CRTs may be adequate for use in high voltage FEDs (if they do not outgas or decompose).

The inherent challenges of high-voltage operation underscore the importance of low-voltage operation. Many of the problems with low-voltage operation can be overcome with improved phosphors. For low-voltage operation, ZnO:Zn shows the most promise for operation at 500 V or less. Reduced zinc oxide exhibits green-blue fluorescence and can be excited by electrons that have energies as low as 3 eV. It is reported to deliver a luminous efficiency of 13 lm/W at 5 V, and exhibit good operational lifetime under high current densities;¹⁰ however, the green-blue color is a problem in full color applications. Suitable chemical dopants that produce other colors efficiently have not been found.¹¹ Table I^{12,13,14} shows a variety of phosphors examined at 500 V.

Table I. Composition, Color, and Efficiency of Commercial and Experimental Low-Voltage Phosphors

material	color	efficiency at 500 V (lm/W)	ref
ZnS:Ag	blue	0.8	12
ZnGa ₂ O ₄	blue	0.2	12
ZnO:Zn	green	10.7	12
Gd ₂ O ₂ S:Tb	green	7.9	12
(Zn,Cd)S:Cu,Al	green	4.8	12
ZnGa ₂ O ₄ :Mn	green	2.2	12
Y ₃ Al ₅ O ₁₂ :Tb	green	2.0	13
Y ₂ O ₂ S:Eu	red	3.5	12
Y ₂ O ₃ :Eu	red	2.2	12
YVO ₄	red	0.4	14

As indicated in Table I the traditional blue phosphor for CRTs, ZnS:Ag, and one of the more promising oxide phosphors, ZnGa₂O₄, both have efficiencies less than 1 lm/W. There is a report that the blue emitter zinc gallate has a threshold voltage of 8 V and a luminous efficiency of 0.7 lm/W when the display is operated at 30 V DC.¹⁵ Results in Table I do not confirm this luminous efficiency at low voltages. For red phosphors the La₂O₂S:Eu appears to have acceptable efficiency, but long term stability under high current densities is a potential problem. La₂O₃:Eu is an alternative, but the efficiency at 500 V is marginal and the red color saturation is worse than for La₂O₂S:Eu.

B. ELECTROLUMINESCENT DISPLAYS (ELDs)

In ELDs, high energy electrons from the insulator layer are accelerated into the phosphor layer where they excite the activators; the activators radiatively decay to produce visible light. ELDs are commonly made in thin film form, or TFEL. A schematic of a TFEL display is shown in Figure 2. Typical voltages across the electrodes are 100 to 300 V. Typical AC frequencies employed range from 60 Hz to 1kHz. DC devices can be made in powdered form and rely on a copper sulfide ZnS heterojunction;¹⁶ however, the devices frequently have limited operational lifetimes.

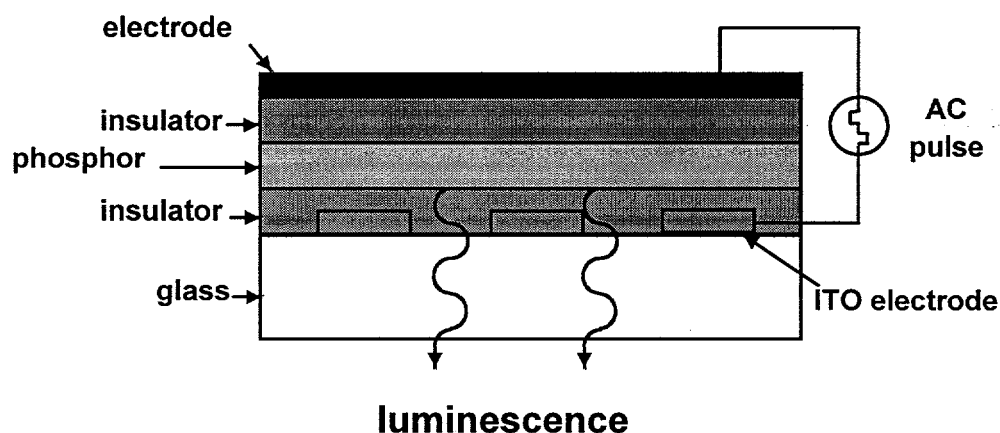


Figure 2. Schematic of an AC thin film electroluminescent display.

Phosphors for TFEL to be used in FPDs must be able to produce desired luminance, have efficiencies of 2-3 lm/W, have threshold voltages well below the operational voltages, be stable in the voltage field, be chemically stable, have low capacitance and resistance, and be amenable to thin film deposition techniques. The brightest and most efficient phosphor material for these devices is ZnS:Mn.¹⁵ A yellow luminescence is produced that provides luminance up to 120 fL with efficiencies of 5 lm/W.¹⁷ Commercial monochrome devices based on ZnS:Mn phosphors have been available for many years. An example is a 17" diagonal monochrome monitor that exhibits 65 fL with VGA resolution is available from Sharp.¹⁸

Red, green, and blue phosphors that have luminances that exceed the desired values stated earlier (25, 65, 10 fL) have not been produced to date, although many studies have been performed in pursuit of improved materials and deposition techniques.^{19,20,21,22,23} Colors other than yellow can be produced by doping ZnS with rare earths.²⁴ Spire along with Planar and Norden have reported several phosphors in which the activator is ion implanted into the thin film.¹⁷ The brightest is ZnS:Tb,²⁵ which emits green light and has a luminance of 10 fL at 180 Hz. The efficiency is less than 1 lm/W. In addition to ZnS, CaGa₂S₄ has promise as a host. It has been doped with Eu to produce green emission (2.5 fL), with Mn and Sm to produce a weak red emission, and with Ce to produce a blue emission (maximum 3 fL).²⁶ SrS:Ce²⁷ provides a greenish-blue output of 20 fL, but is hygroscopic. In all of the ion implanted phosphor films O, F, or S counterions were also implanted for charge balance.¹⁷ Luminance is strongly dependent on counterion type and conditions used to anneal the samples.¹⁷ Currently all of the full color devices fall short of the desired 100 fL luminance.

C. PLASMA DISPLAY PANELS

The excitation mechanism of the phosphor in PDPs is photoluminescence. The excitation principal is the same as in the original monochrome neon glow discharge devices. In the case of PDPs a noble gas mixture (typically 93 % He + 5% Kr + 2% Xe) is ionized when sufficient voltage is applied across addressable electrodes adjacent to the gas. The ionized gas molecules emit photons. The high energy photons from the discharge are used to stimulate visible emission from the phosphors. In the display it is necessary to incorporate barriers between each pixel to reduce cross talk between the phosphors. A schematic is shown in Figure 3. The simplest PDPs operate in DC mode. The electrodes are located within the gas container. The phosphors are deposited on or near the anode, which can lead

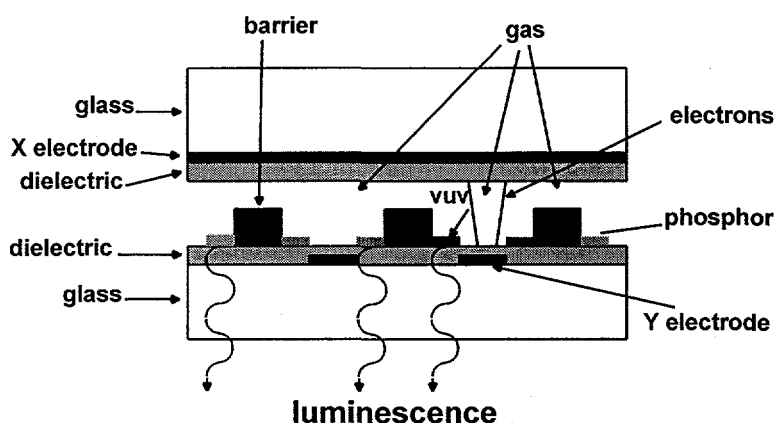


Figure 3. Schematic of a plasma display panel.

to contamination of the electrodes. Problems from contamination of the electrodes can be mitigated by the use of an AC driven design.²⁸ The column and row electrodes can be insulated from the gas discharge. AC PDPs can be driven at frequencies as high as 250 kHz. The high driver frequency helps to increase luminance.

Typical phosphors used in PDP are $Zn_2SiO_4:Mn$ for green, $Y_2O_3:Eu$ for red, and $BaMgAl_{14}O_{23}:Eu$ for blue. The largest issues for the phosphors is their stability in the ionizing conditions in the display and their adherence.²⁹ Efficiency is less of a concern for these displays that run from fixed rather than portable power supplies.

PDPs are a rather mature technology. PDPs were introduced in the 1960s and have been applied in commercial, industrial, and military programs in significant volumes.² The largest area flat panel display of any kind is the 58.6" diagonal AC PDP built by Photonics Systems in 1986. Photonics Imaging demonstrated a 30" full color AC-PDP video monitor in 1987.³⁰ Fujitsu has a commercially available 21" full color AC-PDP that provides 58 fL with full color resolution of 640 x 480 and 256 level gray scale.³¹ Thomson has demonstrated a 13" color AC-PDP with a pixel pitch of 0.4 mm, the highest resolution color reported to date.³² Recently, NHK has announced the fabrication of a 40" DC PDP with a white areal luminescence of about 20 fL and a luminous efficiency of 0.15 lm/W. Trends are toward higher resolution, increased operational lifetime, and lower cost. There do not appear to be any fundamental impediments to fabrication of 50 or 60" diagonal displays.

SUMMARY OF OPPORTUNITIES FOR PHOSPHOR RESEARCH AND DEVELOPMENT

Many opportunities exist to improve phosphors for flat panel emissive displays. For FEDs the major issues are stability under high current densities and efficiency especially of the blue and red phosphors. For ELDs the challenges is to develop red, green, and blue phosphors that are stable and produce requisite luminance for monitor applications. For PDPs issues of adherence and stability must be addressed.

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