Characterization of novel powder and thin film RGB phosphors for field emission display application

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The spectral response, brightness, and outgassing characteristics of new, low-voltage phosphors for application in field emission flat panel displays, are presented. The tested phosphor materials include combustion synthesized powders and thin films prepared by rf diode or magnetron sputtering, laser ablation, and molecular beam epitaxy. These cathodoluminescent materials are tested with e-beam excitation at currents up to 50 μA within the 200–2000 V (e.g., ''low-voltage'') and 3–8 kV (e.g., ''medium-voltage'') ranges. The spectral coordinates are compared to commercial low-voltage phosphors. Phosphor outgassing, as a function of time, is measured with a residual gas analyzer at fixed 50 μA beam current in the low-voltage range. We find that levels of outgassing stabilize to low values after the first few hours of excitation. The desorption rates measured for powder phosphor layers with different thicknesses are compared to desorption from thin films. © *1997 American Vacuum Society.* [S0734-211X(97)01002-0]

I. INTRODUCTION

The choice of phosphor materials is one of the key factors which determines the future success of field emission display (FED) technology. Each phosphor must perform satisfactorily with the voltages accessible in a flat panel display (less than 5000 V) and, at the same time, be compatible with the field-emission array (FEA). Most commercially available cathodoluminescent phosphors have been developed for application in cathode ray tubes which operate in the 10–30 kV range.

Although over the past decade there has been relatively little work done on synthesizing cathodoluminescent materials, new materials are now being developed and tested for low and medium voltage ranges.[1–4] The operating voltage in a field emission display can depend on factors such as (1) the construction of the field emitter array (single- or multiple-gated emitters), (2) focusing technique (proximity focusing, focusing grid, co-planar focusing) and addressing type (addressable pixels in the emitter array or on the screen), (3) the anode-cathode spacing (~0.1–5.0 mm), and (4) the usable excitation energy of the phosphor. Limitations and constraints concerning the applicability of low- and high-voltage phosphors to flat panel displays, including phosphor-cathode interaction issues, electron-stimulated desorbtion from phosphors, cross contamination between phosphor screen and field emission array, phosphor aging effects, and limitations to natural color gamut due to incorrect phosphor color space, were discussed earlier.[5,6]

A. Phosphor materials

In this work, three groups of new candidate phosphors for application in FEDs are examined. A brief description of phosphor samples, including brightness and wavelength data, measured during our experiments, is summarized in Table I.

One group consists of yttrium-based powder phosphors, yttrium aluminum garnet (YAG):Eu, (YAG):Tb, Y_2SiO_5:Ce prepared by combustion synthesis technique which involved an exothermic reaction of a metal nitride and an organic fuel (phosphors were received from J. McKittrick and O. Lopez, AMES Dept., UC San Diego). The as-synthesized foamy, porous powders were heat treated for 1 h at 1600 °C, and electrophoretically deposited onto conductive indium tin oxide (ITO)-coated glass substrates at a constant voltage of 400 V.[4] After deposition, the screens were desiccated at 425 °C for 1 h. Two different regimes were used for electrophoretical deposition producing two different phosphor layer thicknesses. The ''thin'' powder layer was roughly equal to three phosphor particle diameters, i.e., 7–15 μm for different samples; the ''thick'' layer was in the range of 25–40 μm. A specific emphasis was given to determine a difference in brightness and outgassing for different thicknesses of the powder layer as well as to compare performance of the powder phosphors versus thin film phosphors of the similar color and chemical composition.

Another group consists of thin films of Eu and Zn activated tin oxide, zinc oxide and zinc gallate: ZnO:Zn, SnO_2:Eu, $ZnGa_2O_4$:Eu (the thin film phosphors were received from V. Bondar, Lviv State University, Lviv, Ukraine). Thin films are deposited using rf ion-plasma diode deposition or magnetron sputtering on quartz substrates. Thin film phosphors were deposited using different rf techniques and subsequently annealed in the temperature range from 450 to 900 °C, the brightness and the output color of

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TABLE I. Phosphor materials selection.

No.	Phosphor, source	Color, peak (nm)	Material	Thickness, μm	Brightness, cd/m^2 (at 3 kV)	Brightness, cd/m^2 (at 8 kV)
1	YAG:Eu, UCSD	Red, 590	Powder	12 (thin)	78.4	2180
2	YAG:Eu, UCSD	Red, 590	Powder	30 (thick)	86.0	2940
3	YAG:Tb, UCSD	Green, 543	Powder	15 (thin)	58.7	2710
4	YAG:Tb, UCSD	Green, 543	Powder	30 (thick)	171	4360
5	Y_2SiO_5:Ce, UCSD	Blue, 419	Powder	12 (thin)	29.8	1020
6	Y_2SiO_5:Ce, UCSD	Blue, 419	Powder	30 (thick)	49.6	2360
7	$SrGa_2S_4$:Ce, GTRI	Blue, 443	Thin film	0.3	1.05	70.3
8	YAG:Tb, UCSD	Green[a]	Thin film	0.5	a	1.3
9	Y_2O_3:Eu, UCSD	Pink, 611	Thin film	0.5	n/a	357
10	ZnO:Zn, LSU	Blue, 453	Thin film	0.5	0.14	2.12
11	SnO_2:Eu, LSU	Red, 614[a]	Thin film	0.5	<0.1	<0.1
12	$ZnGa_2O_4$:Eu, LSU	Red, 615	Thin film	0.5	1	28
13	$ZnGa_2O_4$:Eu, LSU	Red, 615	Thin film	0.5	3.14	67.8

[a] Insufficient intensity for brightness and spectral measurements.

the thin films vary depending on deposition parameters.[7]

The third group includes $SrGa_2S_4$:Ce:Cl, YAG:Tb, and Y_2O_3:Eu thin film phosphors deposited on standardized ITO-coated substrates distributed to several phosphor synthesis groups sponsored by the DARPA Phosphor Technology Center of Excellence (PTCOE). (Strontium gallate-based samples grown by molecular beam epitaxy were received from B. Wagner, PTCOE/GTRI, Atlanta; and yttrium-based thin films prepared by the laser ablation technique were received from G. Hirata and J. McKittrick, UCSD/AMES.)

II. EXPERIMENTAL TECHNIQUE

In the current work, we characterize luminance and chromaticity and the outgassing products and rates of the phosphors as excited in vacuum by an incident electron beam. We examine the phosphors over two voltage ranges: one defined as ''low voltage,'' spreads from 200 to 2000 V; the other, designated as ''medium voltage,'' extends from 3 to 8 kV.

Two separate ultrahigh vacuum (UHV) systems were used for these experiments. Medium-voltage experiments were performed at a base pressure of 10^{-9} Torr using a system with a quick-access load-lock mechanism and a thermionic electron gun with energies between 3 and 20 kV. We used an unfocused electron beam with current up to 50 μA. A spot diameter of about 3 mm was used for brightness and chromaticity measurements.

Low-voltage and outgassing experiments were performed in an UHV system equipped with a low-energy (between 150 and 1500 V) electron gun and a Balzers residual gas analyzer (RGA).[8] Figure 1 shows a schematic of the UHV system. The recent modifications of the system include addition of a magnetic shield in order to minimize the deflection of low-energy electron beam; also, a set of diaphragms has been added to the RGA chamber to keep electrons emitted by the RGA hot filament from exciting the phosphors and producing unwanted outgassing. The entire system, with the phosphor screen samples loaded, was baked at 150 °C for three days prior to taking desorption measurements. After bakeout, the background system pressure (all electron guns on) was $\sim 5\times 10^{-10}$ Torr. The phosphor samples were loaded in a special carousel allowing the examination of up to eight phosphors under identical vacuum conditions. Two slots in the carousel were assigned for control samples (ITO-coated glass and outgassed Ni foil anode) for background reference measurements. The Ni anode was also used for preliminary outgassing of the electron gun during a 2 h warming-up period.

The gas-desorption measurements were performed at the anode current of ~ 50 μA for all the phosphor screen samples. The screens were biased to $+100$ V with respect to the ground, and the low-voltage electron gun was kept at -650 V with respect to the ground (total beam energy 750 eV). During the low-voltage brightness measurements, the combined effective energy of the beam was varied from 200 to 2000 V. Prior to exposing each sample to the electron beam, a background RGA spectrum, from 1 to 101 amu, was recorded with the electron gun turned on but without applying the bias voltage to the sample screen. After the background was taken, potential was adjusted such that approximately 50 μA of current was collected on the sample.

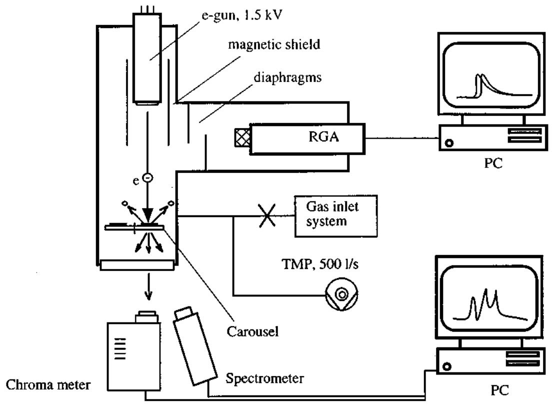

FIG. 1. Schematic of the apparatus used for outgassing, brightness, and luminance measurements.

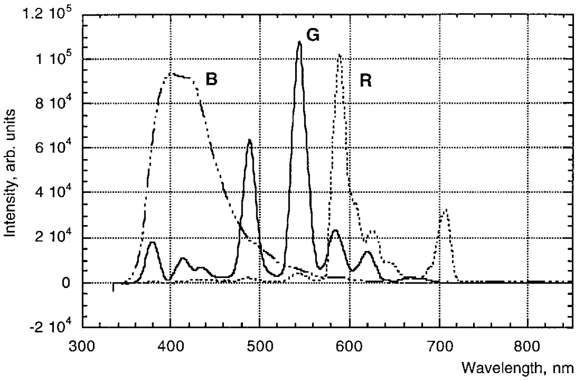

FIG. 2. Sample of luminance spectra: R—red (YAG:Eu), G—green (YAG:Tb), and B—blue (Y_2SiO_5:Ce) powder phosphors.

Additional background outgassing occurred when the beam was transported from the gun to the sample. Electron beam desorption of residual gas (typically hydrogen, carbon monoxide, and carbon dioxide) is a common effect in UHV systems. This outgassing, which was an instrument effect, initially hampered attempts to take meaningful data. In order to circumvent this undesired effect, a different desorption technique was developed. In this technique, the beam was initially undeflected and was kept on one spot of each phosphor screen for a period of time required such that the outgassing rates were stable and unchanging (normally, within an hour or two). The beam was then electrostatically deflected by approximately 3–4 mm from its original position. Assuming the background desorption did not increase during this minor deflection, the new position of the beam would produce a different outgassing rate, an increase of a desorption due to the phosphor alone. This method was effective at detecting prompt outgassing from samples at rates above the detectability limits of the system. The minimum detectability for each of the three main gas species is estimated to be $\sim 4\times 10^{-9}$ Torr ℓ/s (corresponds to $\sim 1\times 10^{-7}$ Torr ℓ/s cm^{-2} for a 0.004 cm^2 sample) for H_2, and $\sim 5\times 10^{-10}$ Torr ℓ/s (corresponds to $\sim 1.3\times 10^{-8}$ Torr ℓ/s cm^2 for a 0.004 cm^2 sample) for CO, CO_2. (1 Torr ℓ/s corresponds to $\sim 3.3\times 10^{19}$ molecules per second.) We note, however, that outgassing of some phosphor materials at a rate well below our detectability limits may exist and have measurable consequences in a FED application.

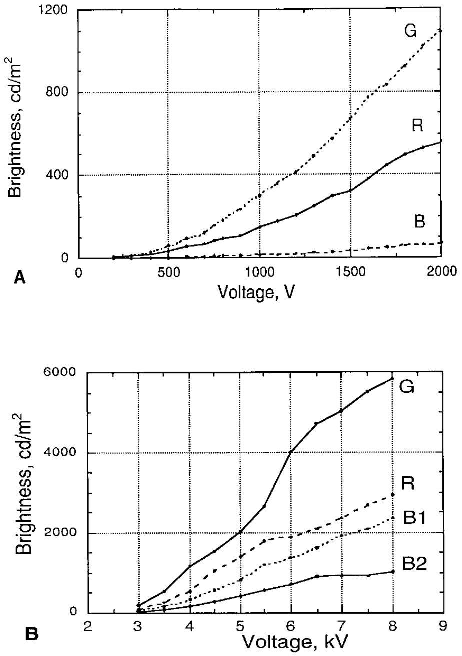

FIG. 3. Brightness as a function of beam energy for low (A) and high (B) acceleration voltages. R—red (YAG:Eu), G—green (YAG:Tb), B—blue (Y_2SiO_5:Ce) powder phosphors; 1—thick layer (30 μm), 2—thin layer (15 μm).

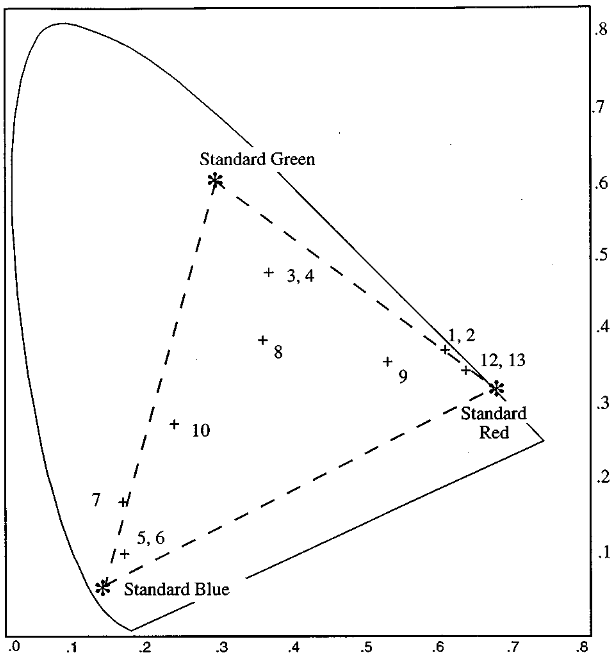

FIG. 4. Color coordinates of the examined phosphors on the 1931 Chromaticity Diagram (shown by + symbols): tested phosphors identified in Table I. The coordinates for the PTCOE standard low-voltage RGB triplet (shown by asterisks), manufactured by Osram Sylvania (see Ref. 9) are given as a reference (SR—Y_2O_2S:Eu, SG—ZnS:Cu, Al, and SB—ZnS:Ag).

III. EXPERIMENTAL RESULTS

A. Luminance spectra

Luminance spectra for the phosphors were measured at an acceleration voltage of 7.5 kV. The wavelengths corresponding to main peaks of spectral output for each phosphor studied are shown in Table I. Figure 2 shows the luminance spectra for some of the phosphors examined: red YAG:Eu, green YAG:Tb, and blue Y_2SiO_5:Ce powders forming a ''RGB triplet,'' This plot demonstrates a possible insufficient color purity of the newly examined phosphors, even if

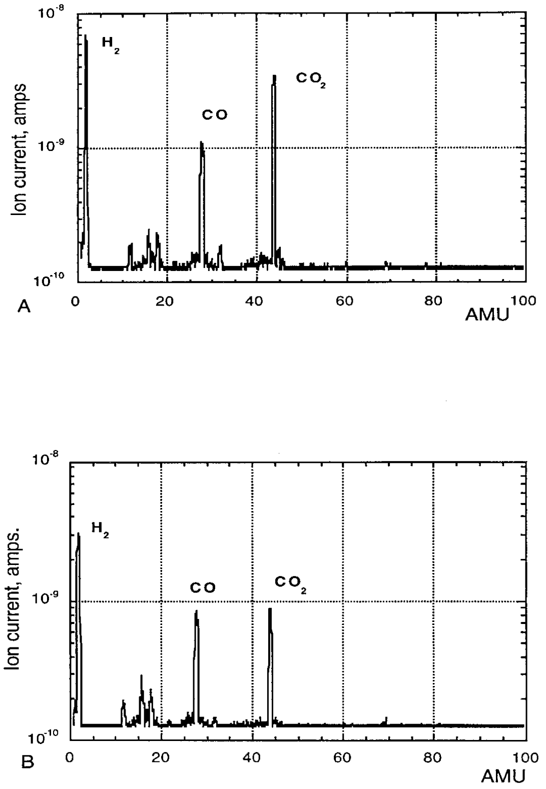

FIG. 5. Sample of outgassing spectrum from the YAG:Eu phosphor: A—fresh spot; B—same spot after 2 h of desorption.

they have a correct main peak wavelength. For example, there are satellite emissions in red and green luminance, and a broadband emission in the blue spectrum.

B. Brightness and chromaticity

Brightness and chromaticity characteristics of the phosphors were measured using a digital chroma meter with a data processor, enabling direct readings of the brightness in candelas per square meter, as well as the color space of the phosphors. The changes in brightness were measured as a function of the acceleration voltage, while keeping the total power of the electron gun constant during the measurements. Figure 3(a) shows the changes in brightness for selected phosphors in the low-voltage range, the same characteristics in the medium-voltage range are shown in Fig. 3(b). Note that the two plots may not be compared directly since they represent similar experimental data taken under slightly different conditions. No brightness saturation was observed in these energy ranges. Some luminance was noticed at 160 V for thin films and 200 V for powder samples. In a medium-voltage range the brightness of all the powder samples was found to be proportional to the thickness layer [see, for example, samples B1 and B2 in Fig. 3(b)].

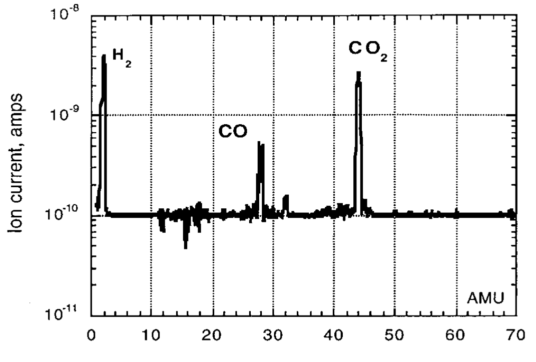

FIG. 6. A sample of ''real'' outgassing from YAG:Eu phosphor: instrument background spectrum is subtracted from the measured desorption spectrum.

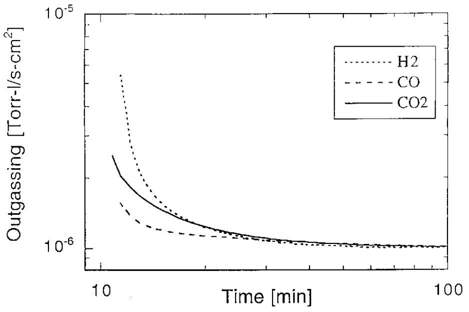

FIG. 7. Outgassing vs time for YAG:Eu powder phosphor (thin layer). E-beam spot size is 9.47 mm^2. The large number of selected data points (more than 15 000) gives the appearance of a smooth characteristic curve.

Figure 4 shows the color space of the tested phosphors compared with the phosphor standard reference provided by the Phosphor Technology Center of Excellence (PTCOE).[9] A low-voltage triplet manufactured by Osram Sylvania was used as a standard. The colors of the tested phosphors are reasonable, however the spectral coordinates of all the samples, specifically of the green powder sample, were found to be inside the PTCOE reference, indicating the lower spectral range covered by tested phosphors.

C. Outgassing

During the electron-beam excitation, a considerable amount of outgassing from the phosphor screens was detected. All powder phosphors showed similar spectra of outgassing, with major detected peaks corresponding to the ions H_2, CO, CO_2 and their fractionation products. No significant peaks above ~60 amu were detected. Figure 5(a) shows the

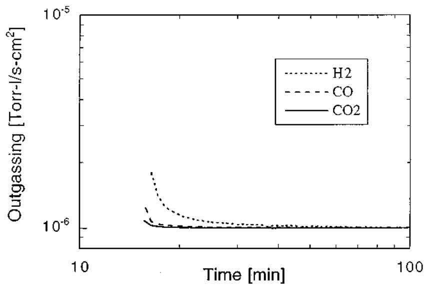

FIG. 8. Outgassing vs time for $SrGa_2S_4$:Ce thin film phosphor sample.

mass spectrum of the outgassing products from one of the phosphors—YAG:Eu. A fresh phosphor surface was exposed to the electron beam having a spot area of 9.47 mm. Figure 5(b) shows the outgassing spectrum for the same spot after 2 h of continuous operation. We used the ''seasoned'' spectrum obtained from an outgassed spot as an instrument background reference and compared it to outgassing from a new, ''fresh'' spot exposed to the deflected electron beam. The background spectra can be subtracted from the fresh spectra giving information on the phosphor material alone. A spectrum resulting from such a subtraction is given in Fig. 6.

The measured RGA spectra show the outgassing rate as an intensity of ion current detected by the quadrupole mass spectrometer corresponding to certain masses of the residual gas ions. In order to determine how much of a gas product was actually desorbed from a certain phosphor, the RGA data were recalculated to give the outgassing values in Torr liters per second. The RGA response to a certain gas flow was calibrated by controlled backfilling the vacuum chamber with a standard gas (H_2, CO, or CO_2) at a series of different pressures. This procedure enabled a conversion ratio between the ion detector current and actual gas flow to be derived, and also determined the system's sensitivity. The actual phosphor area exposed to the electron beam was estimated for each phosphor and for every beam configuration using video frames which showed the exposed area of phosphor samples; known dimensions of the mounting hardware were used to set the scale on the video frame.

Figure 7 shows the amount of gas released by a square millimeter of the phosphor surface versus time for one of the powder phosphor screens. The actual time necessary for the outgassing to reach the initial (background) rate varied from sample to sample due to the thickness of the phosphor layer and to the nature of the phosphor material. We have observed that the intensity of gas desorption from powder phosphors of the same nature has no direct quantitative correspondence to the thickness of the electrophoretical coating; at the same time the intensity of desorption from thin film samples was significantly smaller than from powder layers. The data for the $SrGa_2S_4$:Ce thin film sample are shown in Fig. 8. (For clear comparison the vertical scale in Figs. 7 and 8 is kept the same.)

IV. CONCLUSION

The spectral response and peak intensities of new powder and thin film phosphors for application to field emission flat panel displays have been measured at low and medium operational voltages. The spectral output and major peak wavelengths for most samples are reasonable, however the spectral coordinates of the phosphors are within a color space covered by industrial reference phosphors. Insufficient color purity results from satellite peaks or a broadband emission. The brightness is linear in the low- and medium-voltage ranges, with visibility initiated near 200 V in each case. Light output intensity is in correspondence to the thickness of the phosphor coating. The gas desorption stimulated by electron beam stabilizes at low values within a few hours. The outgassing contains none of the phosphor elements. Outgassing rates for thin film samples are significantly smaller than those for powder phosphor screens.

ACKNOWLEDGMENTS

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