CHARACTERIZATION OF NOVEL POWDER AND THIN FILM RGB PHOSPHORS FOR FIELD EMISSION DISPLAY APPLICATION

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ABSTRACT

The spectral response and outgassing characteristics of new, low-voltage phosphors for application in field-emission flat-panel displays, are presented. A variety of tested phosphor materials include combustion synthesized powders and RF diode or magnetron sputtered thin films. These cathodoluminescent materials are tested with e-beam excitation at currents up to 50 μA within the 200-2000V (eg. "low-voltage") and 3-8 kV (eg. "medium voltage") ranges. The spectral coordinates are reasonable compared to industrial low-voltage P22 phosphors. Phosphor outgassing is measured with a residual gas analyzer. 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.

PHOSPHOR MATERIALS

The choice of phosphor materials is one of the key factors which determines the future success of field emission display (FED) technology. The proper phosphor must perform satisfactorily with the voltages accessible in a flat panel display (less than 5,000 V) and, at the same time, be compatible with the field emission array (FEA). Most commercially available phosphors have been developed for application in CRTs which operate in the 10 to 30 kV range.

Although recently there has been relatively little work done on synthesizing cathodoluminescent materials for low and medium voltage ranges, new materials are now being developed and tested [1-3]. In this work, three groups of candidate phosphors for application in FEDs are examined. A brief description of phosphor samples is summarized in Table 1. One group consists of Yttrium-based powder phosphors prepared by combustion synthesis technique [4] and electrophoretically deposited on ITO coated glass substrates. [a)] Two different regimes were used for electrophoretical deposition producing two different phosphor layer thicknesses. The "thin" powder layer was roughly equal to 3 phosphor particle diameters, i.e. 7-15 microns for different samples; the "thick" layer was in the range of 25-40 microns. A specific emphasis is given to determine a difference in brightness and outgassing for different thicknesses of the powder layer. Another group consists of thin films of Eu and Zn activated tin-oxide, zinc oxide and zinc gallate. [b)] Thin films are deposited using RF diode or magnetron sputtering on quartz substrates. The third group includes thin films deposited on ITO-coated substrates preliminary characterized and distributed throughout phosphor synthesis groups sponsored by the Phosphor Technology Center of Excellence (PTCOE). 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 the thin films vary depending on deposition parameters. [c)]

We characterize luminance and chromaticity and the outgassing products and rates of the phosphors as excited in vacuum by an incident electron beam. We characterize the phosphors over two voltage ranges: one defined as "low voltage", spreads from 200 to 2,000 V; the other, designated as "medium voltage", extends from 3 kV to 8 kV. 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 excitation energy of the phosphor. Limitations and constraints concerning the applicability of low- and high-voltage phosphors to flat panel displays were discussed earlier in [5,6].

a - Powder phosphors were received from J.McKittrick and O.Lopez, AMES Dept., UC San Diego;
b - Thin film phosphors were received from V.Bondar, Lviv State University, Lviv, Ukraine;
c - Thin film phosphors were received from B.Wagner, PTCOE/GTRI, Atlanta and G.Hirata, UCSD/AMES

Table 1. Phosphor materials selection

Phosphor, source	Color, peak (nm)	Material	Thickness, μm	Brightness cd/m^2 (at 3 kV)	Brightness, cd/m^2 (at 8 kV)
YAG:Eu , UCSD	Red, 590	powder	12 - thin	78.4	2180
YAG:Eu, UCSD	"	powder	30 - thick	86.0	2940
YAG:Tb, UCSD	Green, 543	powder	15 - thin	58.7	2710
YAG:Tb, UCSD	"	powder	30 - thick	171	4360
Y_2SiO_5:Ce, UCSD	Blue, 419	powder	12 - thin	29.8	1020
Y_2SiO_5:Ce, UCSD	"	powder	30 - thick	49.6	2360
$SrGa_2S_4$:Ce, GTRI	Blue, 443	thin film	0.3	1.05	70.3
YAG:Tb, UCSD	Green, *	thin film	0.5	*	*
Y_2O_3:Eu, UCSD	Pink, 611	thin film	0.5	n/a	357
ZnO:Zn, LSU	Blue, 453	thin film	0.5	0.14	2.12
SnO_2:Eu, LSU	Red, 614	thin film	0.5	<0.1	<0.1
$ZnGa_2O_4$:Eu, LSU	Red, 615	thin film	0.5	1	28
$ZnGa_2O_4$:Eu, LSU	Red, 615	thin film	0.5	3.14	67.8

* - insufficient intensity for brightness and spectral measurements

LUMINANCE AND BRIGHTNESS STUDY

Two separate set-ups were used for the experiments. Medium-voltage experiments (3 to 20 kV) were performed using an unfocused electron beam with current up to 50 μA. A ~3 mm diameter spot was used for brightness and chromaticity measurements. Low-voltage (200 to 2,000 V) experiments were performed in a system equipped with a low-energy electron gun with voltages up to 1,500 V and an additional screen bias up to 500 V.

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 1. 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. Fig. 1a 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. 1b. 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 is clearly proportional to the thickness layer (see plot B1 and B2 in Fig. 1b.). Color space of the tested phosphors was compared with the PTCOE reference. [8] A low-voltage P-22 triplet manufactured by Osram Sylvania was used as a standard. The colors for the tested phosphors are reasonable; however the coordinates, specifically of the green powder sample, were found to be inside the PTCOE reference, indicating the lower spectral range covered by tested phosphors.

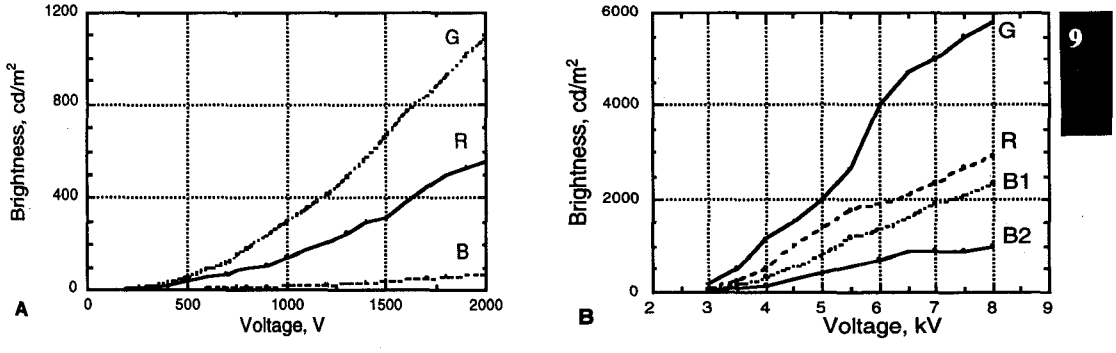

Fig.1. Brightness as a function of beam energy for low (a) and medium (b) acceleration voltages.
R- red (YAG:Eu), G-green (YAG:Tb), B- Blue (Y_2SiO_5:Ce) phosphor; 1-thick layer (30 μm), 2-thin layer (15 μm)

OUTGASSING MEASUREMENTS

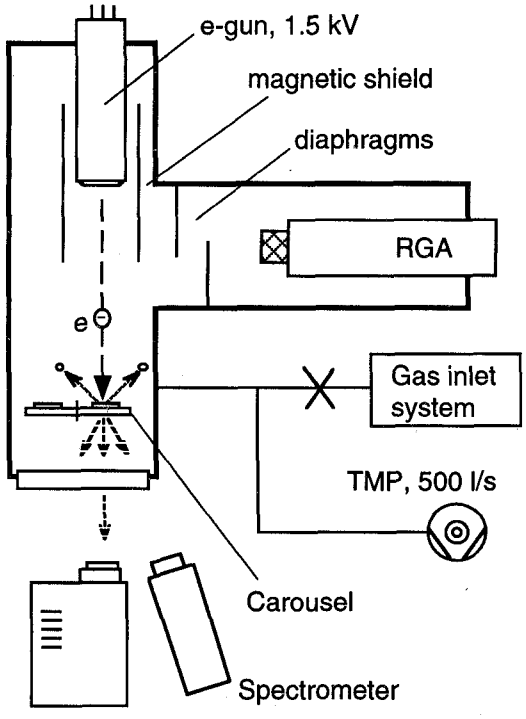

Fig.2. Measurements schematic

Low-voltage and outgassing experiments were performed in a UHV system equipped with a low-energy (up to 1,500 V) electron gun and a Balzers residual gas analyzer (RGA). [7] Fig. 2 shows a schematic of the UHV system. The recent modifications 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 ~ $5x10^{-10}$ Torr. The phosphor samples were loaded in a special carousel allowing the examination of up to 8 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. The Ni anode was also used for preliminary outgassing of the electron gun during a 2-hour warming-up period.

During the gas-desorption measurements, the anode current was maintained at ~ 50 μA for all the phosphor screen samples.

The screens were biased to + 100 V with respect to ground, and the low-voltage electron gun was kept at - 650 volts 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 2,000 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 screen sample. After the background was taken, potential was adjusted such that approximately 50 μA of current was collected on the sample. 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 level (normally, within an hour or two). The beam was then electrostatically deflected by approximately 3-4 mm from its original position. Assuming that 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. We note that outgassing of some phosphor materials at a rate well below our detectability limits may exist and have measurable consequences in an FED.
The estimated minimum detectability for each of the three main gas species are estimated to be ~$4x10^{-9}$ Torr-l/s (corresponds to ~$1x10^{-7}$ Torr-l/s-cm^2 for a 0.004 cm^2 sample) for H_2; and ~$5x10^{-10}$ Torr-l/s (corresponds to ~$1.3x10^{-8}$ Torr-l/s-cm^2 for a 0.004 cm^2 sample) for CO, CO_2. (1Torr-l/s corresponds to ~$3.3x10^{19}$ molecules/s)

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. The background spectrum obtained from an outgassed spot was used as a reference and subtracted from the "fresh" spectrum from a new spot exposed to the deflected electron beam. This procedure characterizes outgassing from the phosphor material alone. A sample spectrum resulting from such subtraction is given in fig. 3.

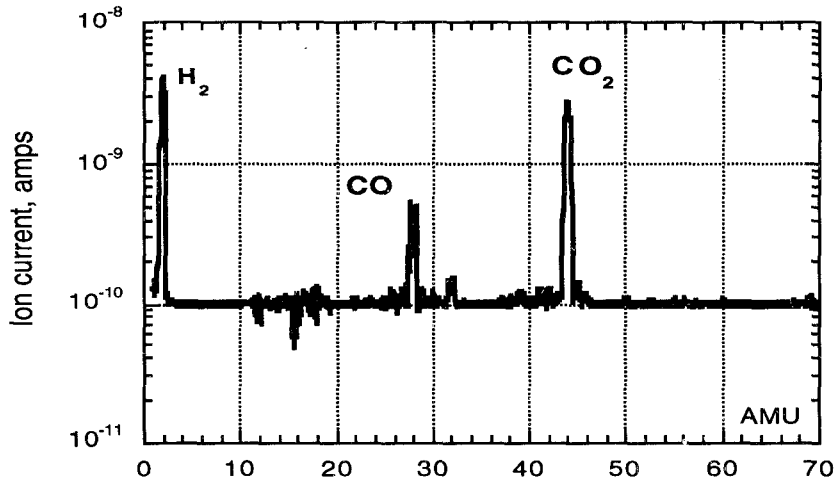

Fig.3. A sample of outgassing spectrum: desorption from YAG:Eu powder phosphor

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 show how much of a gas product is actually desorbed from a certain phosphor, the RGA data was re-calculated to give the outgassing values in Torr-liters per second. The RGA response to a certain gas flow was calibrated by backfilling the vacuum chamber with a standard gas (H_2, CO, or CO_2) through a known leak 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 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.

Fig. 4 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) reading varied from sample to sample due to the thickness of the phosphor layer and to the nature of the phosphor material. The measured intensity of gas desorption from powder phosphors corresponds to the thickness of the electrophoretical coating; the intensity of desorption from thin film samples was significantly smaller than from powder layers. The data for $SrGa_2S_4$:Ce thin film sample is shown in Fig. 5. (For clear comparison the vertical scale in Figs. 4 and 5 is kept the same)

CONCLUSION

The spectral response and peak intensities of powder and thin-film phosphors for application to field-emission flat-panel displays, have been measured. The spectral output and color space for most samples are reasonable. The brightness is linear in the low and medium voltage ranges. Light output intensity as well as the e-beam stimulated outgassing rates are in correspondence to the thickness of the phosphor coating. The outgassing contains none of the phosphor elements and stabilizes at low values within few hours.

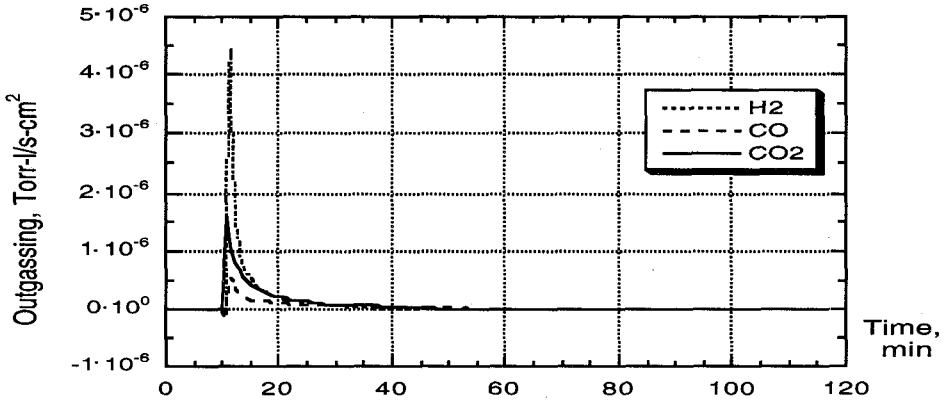

Fig.4. Outgassing versus time for YAG:Eu phosphor (thin layer). E beam spot size is 9.47 mm^2

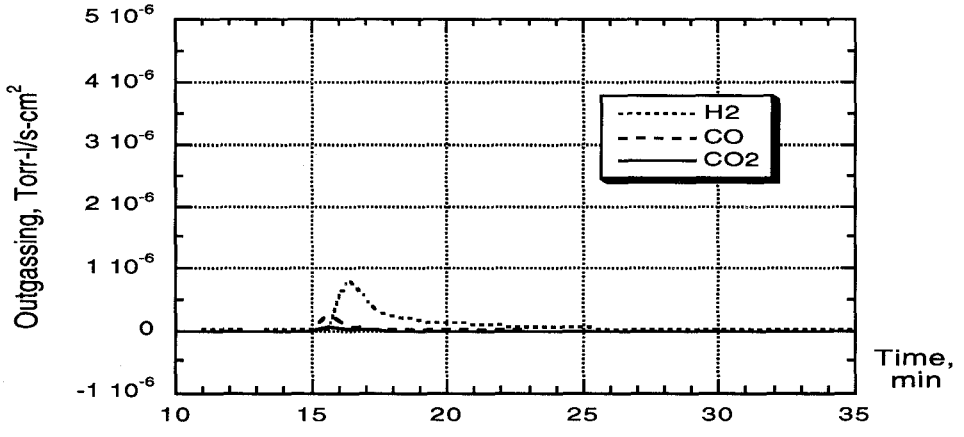

Fig.5. Outgassing versus time for $SrGa_2S_4$:Ce thin film phosphor sample

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