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Cambridge University Press
978-1-107-41394-8 - Materials Research Society Symposium Proceedings: Volume 558: Flat-Panel Displays and Sensors—Principles, Materials and Processes
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Part I

Inorganic Low-Voltage Phosphors

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PERFORMING ACCURATE CATHODOLUMINESCENCE MEASUREMENTS OF PHOSPHOR POWDERS AND SCREENS

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ABSTRACT

In the field of display phosphors, the efficiency of the cathodoluminescence process is a characteristic that is often used to assess the potential of a phosphor for use in flat-panel display applications such as field emission displays (FEDs). Cathodoluminescence characterization in a demountable vacuum chamber is important for preliminary evaluation and lifetesting of phosphor powders and screens prior to incorporation into an actual display device. There are many experimental factors that influence accurate measurement and calculation of the cathodoluminescence efficiency. These include electron beam profile (uniform, Gaussian), current density, electron accelerating voltage, secondary electron collection, and optical detection system. This paper will present some methods for achieving improved accuracy of cathodoluminescence measurements in systems at Sandia National Laboratories, using Y_2O_3:Eu as a representative phosphor.

INTRODUCTION

Cathodoluminescence (CL) is the emission of light from a material that is being bombarded by electrons. CL is one of a series of processes that arises when electrons interact with a phosphor material. A portion of the electrons impinging on a phosphor will undergo elastic backscattering from atoms on the surface. Some electrons penetrate deeper into the phosphor, losing their energies by elastic and inelastic collisions with the atoms of the host lattice, generating secondary electrons, Auger electrons, x-rays, phonons, and electron-hole pairs [1]. CL emission is a result of the radiative recombination of migrating e-h pairs at luminescent centers or activator ions.

The CL efficiency of a phosphor is the ratio of the energy output to the energy input. The intrinsic CL efficiency is the efficiency of a powder sample of the phosphor. The screen CL efficiency is the efficiency of a thin layer of phosphor powder deposited onto a substrate. Screen efficiencies may be lower than intrinsic efficiencies, if there is poor adhesion, poor packing density, non-uniformity, and the presence of binders that react chemically with the phosphor material [2]. Certain binders and additives used in screening processes can enhance nonradiative recombination in the phosphor layer and can impair the color purity of the phosphor. In this paper, the techniques described are for accurate measurement of both intrinsic and screen CL efficiencies.

The power deposited by the impinging electron beam must be known in order to calculate the CL efficiency accurately. This power can be estimated as the product of the net accelerating potential and the net beam current. The net accelerating potential is the sum of the electron accelerating voltage and the secondary electron suppression voltage or bias voltage. The accelerating potential of the incident electron beam does not always represent the actual potential of the electrons that penetrate the phosphor, due to variations in the surface potential. Shifts in the phosphor surface potential can be measured by monitoring secondary and Auger electron spectra during electron bombardment [3]. The net beam

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current is the incident electron beam current minus the backscattered and secondary electron currents.

In addition to variations in the surface potential, discrepancies in both measurement and calculation of the CL efficiency typically are a result of the backscattered and secondary electron emission characteristics of the phosphor. A more detailed discussion can be found in a previous paper [4]. Backscattered electron emission characteristics depend primarily on density, average atomic number, and molecular weight of the phosphor. Backscattered electrons typically represent a significant fraction (~25 %) of the primary beam. Consequently, these electrons do not contribute to further phosphor excitation, energy deposition, or charge injection. Since accurate estimates of the losses associated with backscattered electrons are not easily obtained, it may be difficult to ascertain the actual beam current, and hence, the total injected charge and actual CL efficiency.

During electron bombardment, the absorbed primary electrons tend to charge the phosphor negatively. At least an equal number of secondary electrons must be emitted to prevent the phosphor from charging so negatively that the incident electrons are repelled from the surface. The secondary electron emission ratio (η) is the ratio of the number of emitted secondary electrons to the number of absorbed primary electrons. Phosphors are typically operated in the accelerating potential region where η is greater than unity (positive surface potential). Operation of phosphors at accelerating potentials in either of the two less-than-unity regions typically results in negative surface charging.

Measurement accuracy is further limited by error associated with the type of luminance characterization equipment used. The accuracy of luminance measurements is related to the wavelength of the emitted light and the shape of the spectral energy distribution. Many colorimeters are designed to give best results when measuring broad band emitters, rather than line emitters. Certain colorimeters require that the emitted light from the sample must completely fill or over-fill the instrument aperture. Additional sources of error are typically related to the beam profile (uniform or Gaussian).

EXPERIMENT

Commercially available Y_2O_3:Eu[*] phosphors were characterized in the Phosphor Characterization Facility (PCF) at Sandia National Laboratories in investigations of cathodoluminescent properties.

Cathodoluminescence measurements were performed in a stainless steel demountable vacuum chamber with a hot filament electron gun[$]. Samples were placed inside the vacuum chamber and evacuated to $\leq 10^{-7}$ Torr. The electron beam was deflected through a 90-degree angle to bombard the phosphor normal to the surface. The magnetic deflection of the beam minimizes filament light contamination, avoids filament evaporation products and separates electrons from possible negative ions. To collect secondary electrons, the samples were held at a potential of +50 V relative to ground. An aluminum shield with a 7 mm diameter aperture was placed above the samples to prevent bombardment by secondary electrons originating from the walls of the chamber. Both Gaussian and uniform beam profiles were used for the CL measurements. Beam profile was monitored using a BeamView Analyzer[♣],

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[*] Nichia Chemical Industries, Tokyo, Japan
[$] Kimball Physics, Inc., Wilton, NH 03086
[♣] Big Sky Software Corporation, Bozeman, MT 59772

and solid-state CCD camera[♦]. Photometric data were collected using a spectroradiometer[ϴ]. The emitted light from the phosphor was coupled into an optical fiber bundle leading to the spectroradiometer. The light was dispersed by a 400 line/mm grating and imaged onto a 1024 element linear silicon photodiode array. The resulting spectrum was then weighted by the photopic response of the eye (the relative visual response of the human eye in bright light, as a function of wavelength) and integrated over the range of visible wavelengths. The result of this calculation was the luminous intensity per unit area in cd/m^2. In addition, the chromaticity coordinates were computed by weighting the spectrum with certain color matching functions and similarly integrating. The luminous efficiency (ε) in lumens per watt (lm/W) was calculated using the following formula:

$$\varepsilon = \pi \frac{\mathrm{L} \times \mathrm{A}}{\mathrm{P} \times \mathrm{C}} \qquad (1)$$

where L is the luminance (cd/m^2), A is the area of the emitted light entering the optical fiber bundle (m^2), C is the fraction of the total screen area covered by phosphor, (C = 1 for a powder sample), and P is the power in watts (W), calculated by multiplying the net electron accelerating potential in volts (V) by the net measured current in amperes (A). The net electron accelerating potential is given by the following:

Net electron accelerating potential (V) = (electron accelerating voltage + bias voltage) (2)

The net measured current (I_{net}) can be expressed by the following:

$$I_{net} = I_{in} - I_{bs} - I_{sec} \qquad (3)$$

I_{in} represents the beam current of the incident electrons, I_{bs} is the backscattered electron current, and I_{sec} is the secondary electron current. I_{bs} and I_{sec} were not measured quantities in these experiments. Equation (3) is a qualitative representation.

RESULTS

Figure 1 shows plots of CL efficiency of Y_2O_3:Eu powder as a function of electron accelerating potential (500 V to 5 kV) at 1 µA and beam profile. Irradiating the sample with a uniform beam profile resulted in lower luminance values and subsequently lower values of calculated efficiency than the same sample excited with a Gaussian beam. Since equation (1) for calculating the CL efficiency from luminance data assumes uniform power density, the luminance data obtained from a uniform beam should be more accurate for calculating the true luminous efficiency.

The collection of secondary electrons is an important component of the CL characterization process. Figure 2 shows the net measured current (µA) as a function of sample bias voltage (0 to 100 V) with (curve 1) and without (curve 2) modifications for preventing bombardment from secondary electrons originating from the walls of the stainless

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[♦] Cohu Inc., San Diego, CA 92186
[ϴ] Oriel Corporation, Stratford, CT 06497

steel vacuum chamber. The system modification involved placing an aluminum shield with an aperture of 7 mm in diameter, above the samples and directing the electron beam through the aperture by magnetic deflection. The maximum secondary emission yield of aluminum is 1.0 at a primary electron beam energy of 300 V [5]. When the primary energy is raised beyond this maximum, electrons are excited increasingly deeper into the material so that many are unable to escape to the surface. The characterization energies used in this work fall into this energy regime (>300 V). Secondary emission yields are typically highest for alkali halides

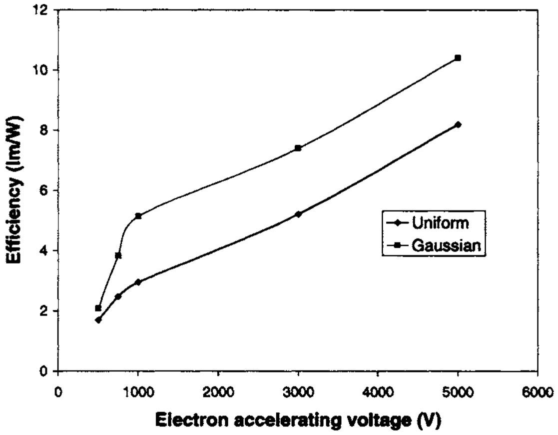

Figure 1 CL efficiency (lm/W) as a function of electron accelerating potential (V) and beam profile. Current was held constant at 1 µA.

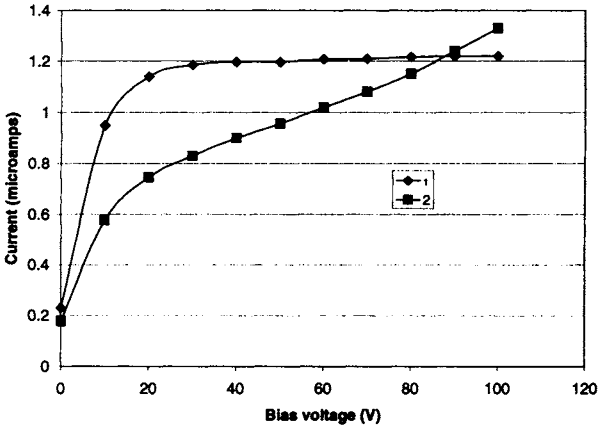

Figure 2 Net measured current (µA) as a function of bias voltage (V) for Y_2O_3:Eu (1) with and (2) without shielding of secondary electrons. Electron accelerating potential ~1 kV.

and oxides such as MgO, with primary beam energy maxima at 1.8 and 1.5 kV, respectively [5].

It should be noted that this procedure and modification was required for the system utilized at Sandia. Other systems may not require such a configuration. However, it is necessary in any system to obtain net measured current vs. bias voltage data to ensure that all secondary electrons are being collected. As shown in Figure 2, proper secondary electron collection should yield a curve similar to (1), with a leveling off of the current at bias voltages of ~30 V.

For this modification to be effective, the distance between the shield and sample surface (D_p) needed to be optimized. The optimal condition for collection of secondary electrons and accuracy of the net measured current, was achieved when $D_p \geq D_a$, where D_a is the aperture diameter. The plots of Figures 3 and 4 illustrate this. Figures 3 (a) and 4 (a) show the equipotential lines between the phosphor surface and the top of the shield, as well as within the aperture, for $D_p < D_a$ and $D_p = D_a$, respectively. As shown in Figure 3 (a), the equipotential lines extend further out through the aperture than in Figure 4 (a). This condition causes secondary electrons from the shield surface and/or the chamber walls to be drawn through the aperture and onto the phosphor surface, leading to erroneous net measured current values. Figure 3 (b) is a plot of the potential (V) as a function of distance from the phosphor, which is biased at +50 V. Figure 3 (c) is a plot of the potential (V) as a function of distance from the center of the aperture to the edge of the shield. Similar plots are shown in Figures 4 (b) and (c) for $D_p = D_a$. These plots were obtained using a program called QuickField[•]

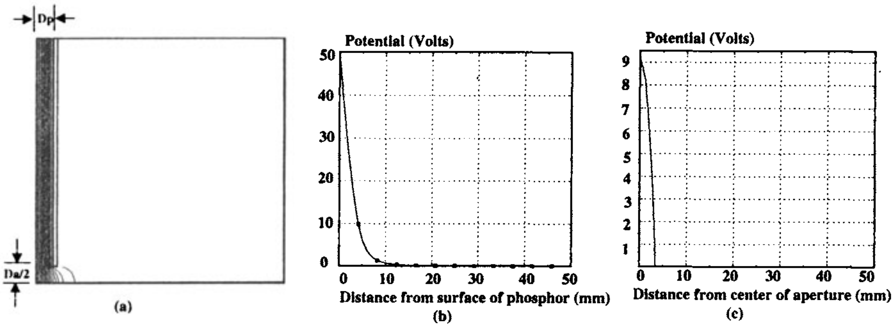

Figure 3 (a) Equipotential lines between phosphor surface and through aperture for $D_p < D_a$. (b) Potential (V) as a function of distance from the surface of the phosphor. (c) Potential (V) as a function of distance from center of the aperture.

[•] Tera Analysis Co., Tarzana, CA 91357

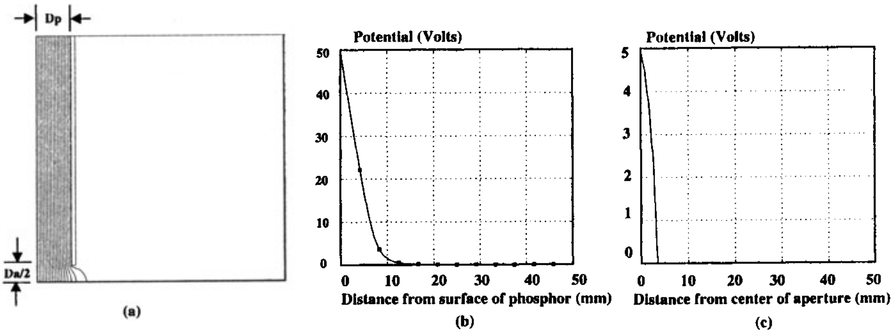

Figure 4 (a) Equipotential lines between phosphor surface and through aperture for $D_p = D_a$. (b) Potential (V) as a function of distance from the surface of the phosphor. (c) Potential (V) as a function of distance from center of the aperture.

CONCLUSIONS

The general procedure for performing cathodoluminescence measurements and efficiency calculations was presented. The collection of secondary electrons and maintaining a uniform beam profile were both found to be important for achieving CL measurement accuracy when using typical stainless steel demountable vacuum systems. The Sandia characterization system was tailored for optimum secondary collection with the use of an aluminum shield containing a circular aperture. The optimum distance between the phosphor surface and the aperture was determined by examining the equipotential lines at given distances and adjusting accordingly to reduce the effects of field penetration. A plot of net measured current versus sample bias voltage is useful for verifying that the secondary electrons are being adequately collected. In general, bias voltages of ~50 V are appropriate. The luminance and CL efficiency of a Y_2O_3:Eu phosphor were found to depend on the beam profile. A lower luminance was obtained when the sample was excited with a uniform beam profile. A Gaussian beam profile resulted in higher luminance values, presumably due to non-uniformity of the power density. To avoid errors in CL efficiency calculations associated with this non-uniformity, a uniform beam profile is required.

ACKNOWLEDGMENTS

The financial support of this work by DARPA under Contract DE-AC04-94AL85000 is gratefully acknowledged. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. Department of Energy.

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FILM PREPARATION CONDITIONS AND CHARACTERIZATION OF CO-DEPOSITED TUNGSTEN DOPED ZINC OXIDE PHOSPHOR

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ABSTRACT

Need for efficient blue light emitting source for optoelectronic device applications such as flat panel displays has made the research in luminescent material ever so important. Tungsten doped zinc oxide (ZnO:W) has been identified as a blue light emitting phosphor exhibiting cathodoluminescence near 490 nm. This paper details work done on ZnO:W phosphor preparation conditions for efficient light emission from the phosphor. Material characterization to identify the possible source of blue light emission will also be discussed.

INTRODUCTION

Luminescent materials, in particular compound semiconductors are being studied extensively to produce light in the visible range. For efficient light emission, one is restricted to materials with a bandgap wide enough for visible light emission. In addition to the wide bandgap requirement, efficient luminescence can be expected from materials with direct bandgap. A group of II-VI semiconducting materials, such as ZnS, ZnSe, ZnO etc., have been a focus of luminescence study for many years [1]. Light emission at red and green wavelengths from compound semiconductors has been observed for a number of years and applied in many optoelectronic devices. However, blue light emission has been the most difficult to achieve. Though various types of materials have been investigated to produce blue light, it is the wide and direct band gap materials that are the best candidates for blue light emission such as zinc sulfide.

Zinc oxide, a II-VI compound semiconductor with a direct wide bandgap of 3.2 eV at room temperature, exhibits light emission in the visible range. Various dopants have been introduced in zinc oxide to produce red and yellow luminescence [2][3]. Green luminescence from zinc oxide is believed to be due to a self-activated charge transfer in zinc oxide. Presence of native defects in zinc oxide is believed to be responsible for this self-activated transition [4]. The ability of zinc oxide to luminesce at red, yellow and green wavelengths has made it an attractive candidate as a thin film phosphor for applications such as flat panel displays. Research at Texas A&M University (TAMU) was initiated to find a suitable dopant for zinc oxide to obtain blue luminescence. From this research, it was discovered that blue light emission is observed when tungsten is diffused into zinc oxide [5]. Tantalum has been reported as being responsible for blue luminescence near 400 nm from zinc oxide [6]. Since the discovery of tungsten as a blue light emitting dopant in zinc oxide, the phosphor has been used in the fabrication of a field emission device at TAMU [7]. Following the discovery of tungsten as a blue light emitting dopant in zinc oxide the next logical direction for research after this discovery is to understand the chemical composition of the film and identify the source of luminescence from the phosphor. This required a method of phosphor preparation enabling a quantitative and fundamental analysis of the film.

This paper presents the research conducted to isolate the optimum tungsten concentrations in zinc oxide and annealing conditions to fabricate the most efficient blue light

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emitting phosphor. Results from material characterization to identify the composition of the phosphor and an understanding of mechanism leading to blue light emission will also be reported.

EXPERIMENT

Following the preparation of phosphor samples, study of samples requires various measurements. Characterization of luminescence properties of the samples includes measurement of peak emission wavelength, efficiency of the blue light emitted and the color space coordinates for cathodoluminescence. Material characterization of the samples was carried out using X-ray diffraction analysis. Infrared spectroscopy was also employed to confirm material identification as determined by x-ray diffraction.

Phosphor Preparation

Ion mill sputtering, a well-established technique has been used in preparing the thin films with varying tungsten and zinc oxide concentrations. With this method tungsten and zinc oxide were deposited simultaneously and the deposition rates of tungsten and zinc oxide controlled independently to vary the relative amounts of tungsten and zinc oxide in the films. The films were prepared under high vacuum with a chamber base pressure of $5x10^{-6}$ Torr. Substrates during the deposition were held at room temperature. The substrates are 2-inch silicon wafers with 3000 Å of thermally grown silicon dioxide. The purpose of SiO_2 on the bare silicon wafer is to prevent chemical interaction between the phosphor and Si substrate and to provide electrical isolation.

The factorial experiment for various annealing conditions and tungsten and zinc oxide concentrations to produce an efficient blue light emitting phosphor are as shown in Table1 below.

Table 1. Phosphor preparation conditions

W-to-ZnO volumetric concentrations	50% W	30% W	10% W
Annealing Temperature	850 °C	650 °C	450 °C
Annealing Time	12 hours	8 hours	4 hours
Oxygen-to-Argon concentration	40% O_2	20% O_2	0% O_2

Phosphor Characterization

The study of luminescence properties of these films involves measurements such as the wavelength and irradiance of light emitted and color space coordinates. A luminescence characterization unit built in the TAMU Institute of Solid State Electronics (ISSE) lab was used to collect this data. The characterization unit includes S2000 Ocean Optics, Inc. fiber optic spectrometer for data collection. Excitation is provided by a low energy electron gun (LEED) for cathodoluminescence study and a mercury arc vapor lamp for photoluminescence measurement. The LEED gun has the capability of exciting the phosphor with excitation voltages as low as 300 V and as high as 2000 V with emission current in the microampere range. The characterization unit also contains a cryostat that provides the capability for making luminescence spectroscopic analysis at temperatures varying from liquid nitrogen to room temperature.