Cathodoluminescent properties at nanometer resolution through *Z*-contrast scanning transmission electron microscopy

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We report the observation of porous structures in laser-ablation-deposited Y_2O_3:Eu thin films and their correlation with luminescent properties by a combination of transmission electron microscopy and *Z*-contrast scanning transmission electron microscopy (*Z*-STEM). Depending on growth conditions, a large density of voids is incorporated into the films, which leads to a much increased surface area. Cathodoluminescence imaging in the STEM directly reveals a 5 nm ''dead layer'' around each void, which is responsible for the observed reduction in luminescence efficiency. © *2000 American Institute of Physics.* [S0003-6951(00)05229-3]

Rare earth-activated oxide-based phosphor thin films are promising candidates for high-resolution display devices such as cathode ray tubes, graphics, field emission displays (FEDs), and thermomechanical devices.[1–5] However, thin-film phosphors typically have a significantly reduced brightness compared to equivalent powder phosphor materials.[6,7] Several possible explanations have been suggested for the lower brightness including internal reflection or channeling of the emitted light along transverse axes parallel to the surface instead of vertical emission from the surface, and the small interaction volume between the incident beam and the solid. In this letter, we show another factor to be crucial to external radiative efficiency, the porosity of the films. Porosity creates internal surface area, and the associated dead layer decreases the emission efficiency. The dead layer is directly observed by simultaneous cathodoluminescence (CL) imaging and *Z*-contrast imaging in the scanning transmission electron microscope (STEM), and quantitatively accounts for the reduction of luminescent efficiency.

Eu-activated Y_2O_3 thin films with thickness of about 200 nm were deposited on (001) $LaAlO_3$ substrates by laser ablation at different temperatures (735, and 775 °C) and different laser pulse frequencies (5 and 10 Hz).[8,9] A Lambda Physik 305I laser ($\lambda = 248$ nm, $\tau = 25$ ns) is used to irradiate the Eu-doped Y_2O_3 phosphor target (YOE), creating an expanding plume of atomic species. Detailed information about the deposition can be found elsewhere.[10] Cross-sectional slices were obtained by cutting the sample along the [100] or [010] directions of YOE, and then gluing face to face. Both plan-view and cross-section specimens for transmission electron microscopy (TEM) and/or STEM observations were prepared by mechanical grinding, polishing, and dimpling, followed by Ar-ion milling using a E. A. Fichione Ion Polishing System first at a voltage of 3.5 kV and an angle of 12°, and finally at 1.0 kV and 10°. TEM bright field images and the electron diffraction patterns were recorded in a Philips EM-400 electron microscope operated at 100 kV. *Z*-contrast imaging was conducted in VG HB603 STEM at 300 kV,[11,12] while the CL imaging was conducted in a VG HB501 STEM at 100 kV. The CL emission was collected by a lens system and detected by a photomultiplier.[13]

The porous structure of YOE thin films was first demonstrated by TEM images of plan view samples. For comparison, three TEM plan view samples of YOE thin films were prepared at different substrate temperatures and laser pulse rates: (a): 735 °C, 10 Hz, (b) 735 °C, 5 Hz (c) 775 °C, 10 Hz. As shown in Fig. 1(a), the sample prepared at 735 °C, 10 Hz shows a high density of pores at the edge of the sample, with an average size of about 25 nm. When the pulse rate was lowered to 5 Hz, but the substrate temperature was kept at 735 °C, the pore size decreased to 17 nm, as shown in Fig. 1(b). When the substrate temperature was increased to 775 °C with 10 Hz pulse rate, the voids formed were much smaller, ~10 nm, as shown in Fig. 1(c). These observations show that the porosity of the film decreases with higher substrate temperature and with lower laser pulse rate.

In order to check the distribution of the pores through the film thickness, cross-section samples were examined. A *Z*-contrast STEM image of the sample grown at 775 °C, 10 Hz is shown in Fig. 2. Figure 2(a) shows a large area dark field *Z*-contrast STEM image in which both the substrate and the film can be seen. Above the substrate and through the film, some columnar structures and prolonged darker areas are clearly seen extending from the surface to the interface. The brightness in the *Z*-contrast STEM image depends on both the atomic number and the sample thickness. At a specific thickness condition, the brightness will only be determined by Z^2 (where *Z* is the atomic number), but for a constant *Z*, the brightness will reflect the film thickness. So, in our case, the darker regions imply that the pores are columnar in nature. This is confirmed by the following two higher magnification images. In Fig. 2(b), two columnar pores are seen. In the thinnest region (near the top of the image), they both form holes in the specimen. As the sample becomes thicker, a columnar track is seen extending from the left hand

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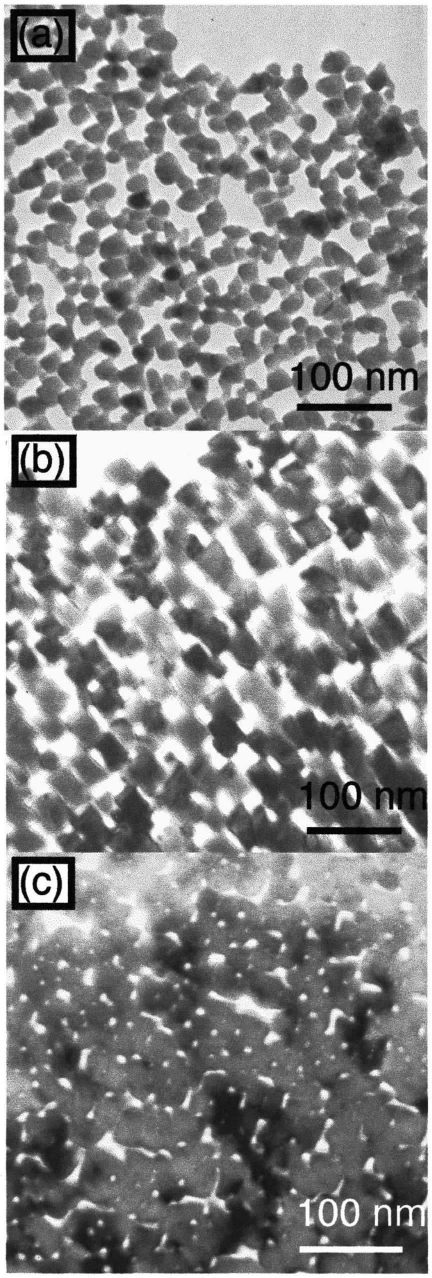

FIG. 1. Three plan-view TEM micrographs of Y_2O_3:Eu thin films prepared at different deposition conditions, showing clearly the variation of void size with substrate temperature and deposition rate, (a), 735 °C, 10 Hz, (b) 735 °C, 5 Hz, (c) 775 °C, 10 Hz.

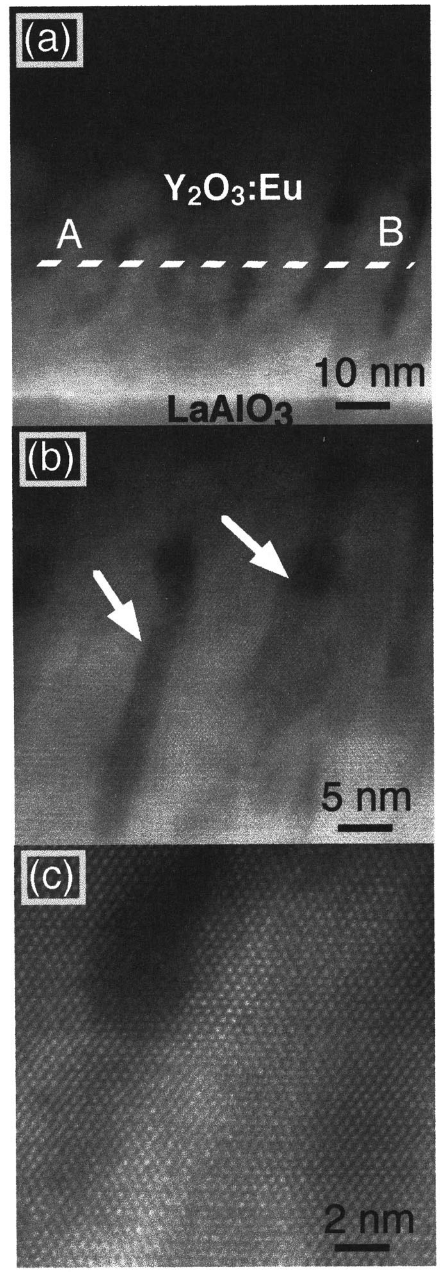

FIG. 2. (a) Dark field *Z*-contrast STEM image of a cross-section Y_2O_3:Eu sample prepared by laser ablation at a substrate temperature of 775 °C and in fast deposition mode (10 Hz), showing the columnar nature of the pores. (b) and (c) are higher magnification images of the region in (a).

pore (arrowed), while the track from the other intersects the sample surface. This contrast shows the pores to be columnar in nature, which is consistent with our previous TEM investigation showing the columnar structure to be formed during the laser ablation film growth.[10] In Fig. 2(c), we can see clearly the well ordered atomic structure around a pore. In agreement with our previous observation,[10] we see that the film is an almost perfect single crystal.

The porous structure has a dramatic effect on the external radiative efficiency of the film. This is demonstrated by measuring the efficiency of different samples prepared under different deposition condition, and, therefore, containing different pore sizes.[5,7,14] The photoluminescence efficiency correlates directly with average pore size, as shown in Fig. 3, and we would expect the CL efficiency to be similar. The reason for this correlation is expected to be the existence of a ''dead layer'' near the specimen surface, resulting from nonradiative recombination of electron–hole pairs via surface states.[15–17] Increasing the pore size would create more internal surfaces per unit volume, resulting in lower overall efficiency.

Direct measurement of the dead layer at the surface of a pore has been achieved by comparing the *Z*-contrast image with the CL image obtained simultaneously. Figure 4(a) shows a *Z*-contrast image of a region of film containing some relatively widely spaced pores. The corresponding CL image in Fig. 4(b) shows the variation in CL intensity. It is immediately clear that the edges of the holes in the CL image are much less sharp. Intensity profiles across the hole marked are shown in Figs. 4(c) and 4(d). The width of the pore in the

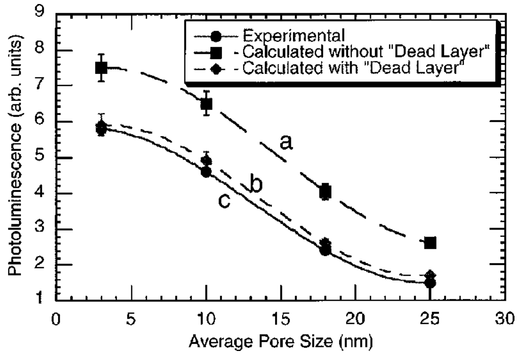

FIG. 3. Relationship between the photoluminescence efficiency and the pore size, showing the decrease in efficiency with increasing pore size. Samples are those shown in Fig. 1, with the addition of a film grown at 775 °C, 5 Hz, which has the highest efficiency. Also shown are theoretical curves with and without the effect of the dead layer.

Z-contrast image is 10 nm, whereas in the CL image is more than doubled to 20 nm. Clearly, if the grain size of a film is comparable to the extent of the dead layer, then the efficiency will be substantially reduced. This explains the order of magnitude reduction in efficiency observed experimentally in Fig. 3. It is clear that because of this dead layer porous structures can lead to greatly reduced emission efficiencies.

The relationship between the decrease of emission efficiency and the pore size can be estimated directly from our plan view images. Assuming the grains to be columnar, extending throughout the film thickness, the relative efficiency can be estimated from the total area of grains observed in the image per unit area of film, giving curve (a) in Fig. 3. Now, if the area of each grain is reduced to take into account the 5 nm dead layer, the relative efficiency is significantly reduced (curve b), resulting in values that agree well with our experimental observations (curve c).

Singh and co-workers[5,7,14,18] have shown that the surface roughness of a film has a close relationship with the luminescent properties, i.e., increased roughness of the film will increase the efficiency. Now, based on our TEM and *Z*-contrast STEM observations, we see that another critical issue is the porosity of the films.

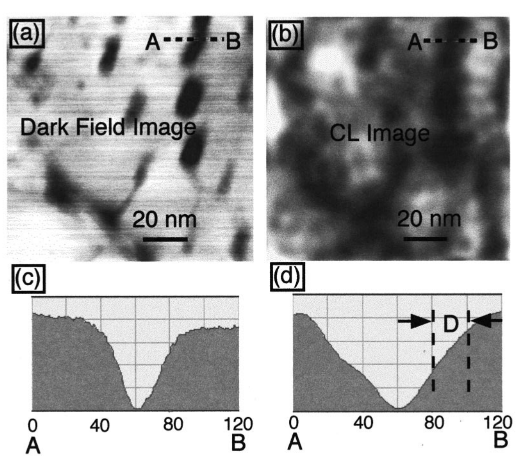

FIG. 4. *Z*-contrast image (a), CL image, (b) and corresponding intensity profiles (c) and (d) across the same hole, showing the ''dead layer'' to be about 5 nm in width (labeled D).

In summary, we have directly correlated the pore structure in laser ablation deposited YOE thin films with luminescent efficiency. A high density of voids creates more internal surface in the films per unit volume. The resulting increase in the surface dead layer reduces external luminescence efficiency. By simultaneous *Z*-contrast and CL imaging, we have shown the extent of the dead layer to be ~5 nm, and obtained quantitative agreement between the measured pore size and luminescent efficiency. We suggest that in the preparation of YOE and related thin films, attention should be paid to avoiding the formation of internal voids in order to increase the radiative efficiency.

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