

Laser direct writing of phosphor screens for high-definition displays

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A laser-based forward transfer direct writing technique was used to deposit phosphor powder screens for high-resolution display applications. With this technique, called matrix-assisted pulsed-laser evaporation direct write, dense oxide phosphor powders of $Y_2O_3:Eu$ (red) and $Zn_2SiO_4:Mn$ (green) were deposited on alumina and polymer substrates. All processing was performed in air at room temperature. Cathodoluminescent measurements showed that the luminous efficiency of the phosphor powders was not degraded by the deposition process. A 6×6 red and green matrix with pixel sizes of $100 \mu m$ (250 lines per inch) with a $100 \mu m$ spot size is demonstrated; however, with smaller spot sizes this technique is easily scalable to pixel sizes $< 10 \mu m$ (> 2500 lines per inch). © 2000 American Institute of Physics. [S0003-6951(00)00710-5]

Current technologies to fabricate multicolor phosphor screens include multistep electrophoretic deposition, screen printing, and settling techniques.¹⁻⁹ While shadow masks can be used for large pixel sizes, smaller pixel sizes require photolithographic techniques to pattern three colors.¹⁰ Photolithographic techniques require two or more process steps per color and each step can leave organic residue on phosphor particles. Under electron bombardment, it has been shown that organic residues can react and form a thin graphitic layer, which absorbs emitted light and degrades the phosphor performance.¹¹

Over the past decade, many direct write techniques based on laser-induced processes have been developed for depositing materials for a variety of applications. Among these techniques, laser-induced forward transfer (LIFT) has shown the ability to direct write metals for interconnects and mask repair and also simple dielectric materials such as metal oxides.¹² LIFT was first demonstrated using metals such as Cu and Ag over substrates such as silicon and fused silica utilizing excimer or Nd:YAG lasers.^{12,13} It is a simple technique that employs laser radiation to physically vaporize a thin film (≈ 100 nm) from the far side of a laser transparent support into a roughly similar pattern on a substrate placed close ($\leq 100 \mu m$) to it. In order to utilize the process, the laser fluence should be adjusted so that the process is carried out near the energy threshold to remove only the film material and not to damage the support. Target films should not exceed an experimentally determined thickness, generally less than a few 100 nm. Overall, the laser-induced forward transfer process has proven to be a simple technique that can be used on a wide variety of target films of metals, and simple oxides, but not with complex multicomponent materials such as ceramics or phosphors.

A vacuum-deposition technique, known as matrix-assisted pulsed-laser evaporation (MAPLE) has been developed at the Naval Research Laboratory (NRL) for depositing thin, uniform layers of chemoselective polymers¹⁴⁻¹⁶ and fragile organic materials, such as carbohydrates.¹⁷ MAPLE is a variation of the conventional pulsed-laser evaporation process with respect to the laser interactions and the spatial dynamics of the thin-film growth. The “soft” transfer mechanism associated with the matrix-assisted pulsed-laser deposition process enables the deposition of complex and fragile organic molecules into thin films without denaturing. Irreversible structural degradation is typically observed with conventional pulsed-laser deposition even at low fluences.

MAPLE direct write is a process that combines aspects of the transfer mechanism of matrix-assisted pulsed-laser evaporation with the direct write resolution of laser-induced forward transfer allowing the transfer of polymer, metallic, ceramic, and electronic materials without degradation in performance. These materials have been deposited to $10 \mu m$ resolution onto substrates of silicon, fused silica, polyimide, and several types of circuit board materials. MAPLE direct write can be utilized for micromachining, drilling, and trimming applications, by simply removing the transfer material support from the laser path, see Fig. 1(a), and as such it is both an additive as well as subtractive direct write process, see Fig. 1(b). In this letter, we show elements of the MAPLE direct write process, efficiency results of transferred red and green phosphors, and demonstrate the fabrication of a 6×6 array.

The output from a KrF excimer laser ($\lambda = 248$ nm, 25 ns pulse) was directed through a variable circular aperture and then through a $10 \times$ ultraviolet-grade objective lens. By changing the aperture size, beam spots from 10 to $300 \mu m$ could be generated. The laser fluence (0.100 – 2.5 J/cm²) was estimated by averaging the total energy of the incident beam over the irradiated area. Quartz wafers, 5 cm diam \times 2 mm

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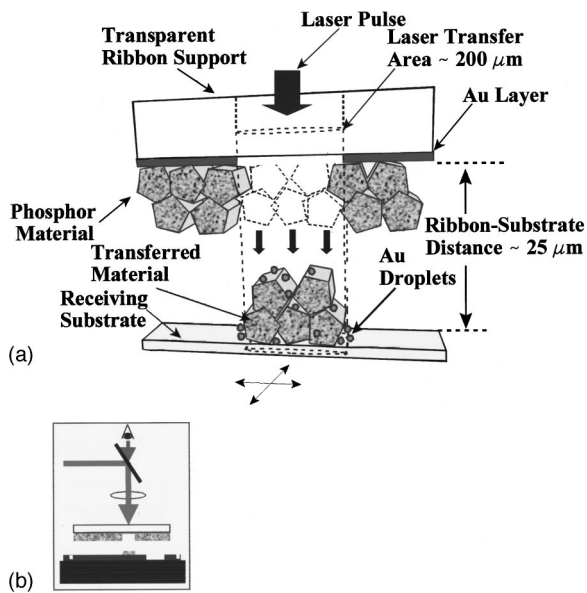


FIG. 1. (a) Schematic diagram of the MAPLE direct write setup used for the transfer of phosphor materials. Inset (b) shows a general schematic of the MAPLE direct write setup used for additive and subtractive processing.

thick, were coated on one side with a thin film and will be referred to as the ribbon, as shown in Fig. 1. The coated side of the ribbon was separated from the receiving substrate by $25\ \mu\text{m}$, see Fig. 1. For the phosphor transfers, $100\ \text{nm}$ of gold was initially sputtered onto a quartz disk. Phosphor powders ($\text{Y}_2\text{O}_3:\text{Eu}$ or $\text{Zn}_2\text{SiO}_4:\text{Mn}$) were suspended in a solution of glycerin, isopropanol, LaNO_2 , and $\text{Mg}_2(\text{NO}_3)_2$ and electrophoretically deposited onto the gold-coated quartz wafer.

Figures 2(a) and 2(b) show a scanning electron microscope (SEM) image of the phosphor ribbon after laser processing with a $200\ \mu\text{m}$ spot size. Figure 2(b) shows that nearly all of the $\sim 10\text{-}\mu\text{m}$ -thick phosphor layer was transferred during each laser pulse. It is important to note that each area or spot received one laser pulse. Figures 2(c) and 2(d) show optical images of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ (green) and

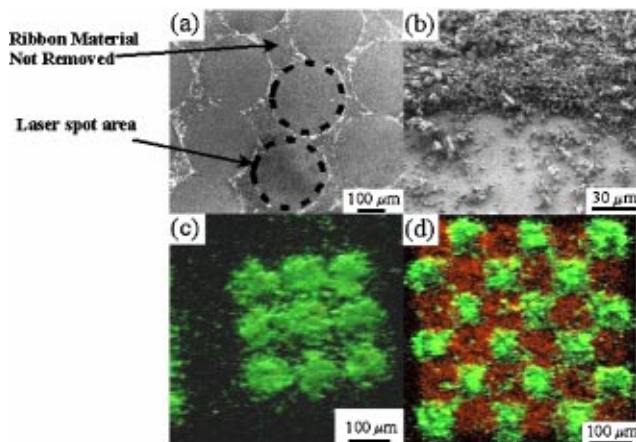


FIG. 2. (Color) Scanning electron micrographs of (a) $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphor ribbon after transfer, circular regions represent the area of laser transfer from the ribbon and; (b) higher magnification of the phosphor ribbon transfer area of (a). (c) shows a 3×3 array of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphor excited at $254\ \text{nm}$, and (d) shows a 6×6 array of alternating $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ transfers excited at $254\ \text{nm}$.

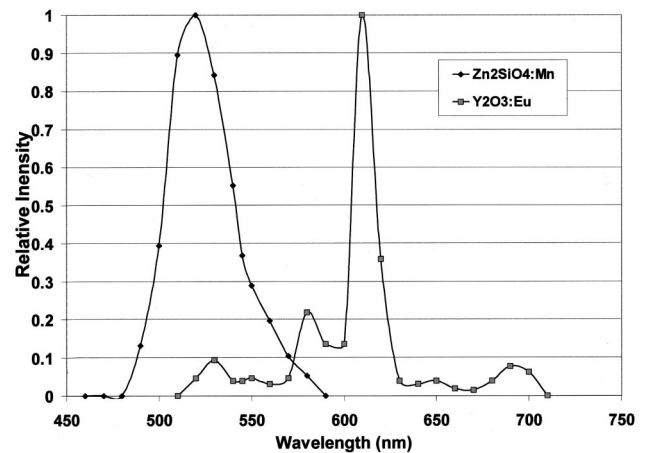


FIG. 3. Cathodoluminescent spectra of the transferred $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ phosphors showing that the spectral properties of each material are not affected by the MAPLE direct write process.

$\text{Y}_2\text{O}_3:\text{Eu}$ (red) pixels stimulated by a ultraviolet lamp at $254\ \text{nm}$.

Cathodoluminescent (CL) measurements confirm that the laser transfer process does not affect the phosphor performance. The emission spectra were measured from $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ ribbons prior to the transfer and on the transferred substrates (shown in Fig. 3). The emission spectra of the transferred $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ were identical to the CL spectra of the phosphor ribbons. The CL efficiencies before and after the MAPLE direct write process were $1.3\ \text{lm/W}$ for the $\text{Zn}_2\text{SiO}_4:\text{Mn}$ materials and $1.1\ \text{lm/W}$ for the $\text{Y}_2\text{O}_3:\text{Eu}$ materials (measured at $1\ \text{kV}$ and $22.5\ \mu\text{A}/\text{cm}^2$). The consistent CL spectra and efficiencies before and after the laser processing confirm that the MAPLE direct write process did not deleteriously affect the phosphor material.

A laser-based forward transfer technique called MAPLE direct write was used to create high-resolution display pixels. A ribbon consisting of a gold-coated quartz disk was electrophoretically coated with $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ powders and laser transferred onto a receiving substrate. SEM micrographs of the deposited powders and the post-transfer ribbons suggest that the gold layer absorbs the laser radiation and ejects the $\sim 10\text{-}\mu\text{m}$ -thick powder phosphor layer in a controlled fashion. The packing density and the phosphor structure are maintained during the MAPLE direct write process. Initial experiments show that the process does not reduce the CL efficiency or change the emission spectra of the phosphor powders.

¹P. D. Godbole, S. B. Deshpande, H. S. Potdar, and S. K. Date, Mater. Lett. **12**, 97 (1991).

²H. Hu, O. G. Daza, and P. K. Nair, J. Mater. Res. **13**, 2453 (1998).

³D. Ivanov, M. Caron, L. Quillet, S. Blain, N. Hendricks, and J. Currie, J. Appl. Phys. **77**, 2666 (1995).

⁴M. N. Kamalasanan and S. Chandra, Appl. Phys. Lett. **59**, 3547 (1991).

⁵I. Koiwa and H. Sawai, IEEE Trans. Electron Devices **41**, 1523 (1994).

⁶I. Koiwa, T. Kanehara, and J. Mita, J. Electrochem. Soc. **142**, 1396 (1995).

⁷G. Percin, T. S. Lundgren, and B. T. K. Yakub, Appl. Phys. Lett. **73**, 2375 (1998).

⁸U. Selvaraj, A. V. Prasadarao, S. Komarneni, and R. Roy, Mater. Lett. **12**, 311 (1991).

⁹C. Surig, K. A. Hempel, and D. Bonnenberg, Appl. Phys. Lett. **63**, 2836 (1993).

- ¹⁰S. K. Kurinec and E. Sluzky, *J. Soc. Inf. Disp.* **4**, 371 (1996).
- ¹¹C. H. Seager, D. R. Tallant, and W. L. Warren, *J. Appl. Phys.* **82**, 4515 (1997).
- ¹²J. Bohandy, B. F. Kim, and F. J. Adrian, *J. Appl. Phys.* **60**, 1538 (1986).
- ¹³J. Bohandy, B. F. Kim, F. J. Adrian, and A. N. Jette, *J. Appl. Phys.* **63**, 1158 (1988).
- ¹⁴R. A. McGill, R. Chung, D. B. Chrisey, P. C. Dorsey, P. Matthews, A. Piqué, T. E. Mlsna, and J. L. Stepnowski, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **45**, 1370 (1998).
- ¹⁵R. A. McGill, D. B. Chrisey, A. Piqué, and T. E. Mlsna, *Proc. SPIE* **3274**, 255 (1998).
- ¹⁶A. Piqué, R. A. C. Auyeung, R. A. McGill, D. B. Chrisey, J. H. Callahan, and T. E. Mlsna, *Mater. Res. Soc. Symp. Proc.* **526**, 375 (1998).
- ¹⁷A. Piqué, D. B. Chrisey, B. J. Spargo, M. A. Bucaro, R. W. Vachet, J. H. Callahan, R. A. McGill, D. Leonhardt, and T. E. Mlsna, *Mater. Res. Soc. Symp. Proc.* **526**, 421 (1998).